3.3: Research Publications and Awards

EMMANUEL COLLEGE VAZHICHAL

3.3.1.1: Number of research papers in the Journals notified on UGC CARE list year wise during the last five years

3.3.1.1 Number of Research papers in the Journals Notified on UGC CARE List Year wise during the Las five Years

S.No	Title of the paper	Name of the teacher	Department	Name of Journal
2022-2023				
1	Crystallization and Surface Morphology Following Annealing Using ZnO Thin films	C. Rajan	Electronics	Journal of Advances and Scholarly Research in Allied Education
2	A perspective Assessment of the Rubber Boards Contribution to the Promotion of Natural Rubber	Dileep kumar	Commerce	International Journal of Food and Nutritional Sciences
3	A Study on the Impact of Innovative Practices in SIDCO	Vidya. V.J	Commerce	Kanpur Philosophers
4	A Study on artificial intelligence in Indian banking sector	ANU.M	Commerce	Kanpur Philosophers
5	Neuroprotective effect of Morin via TrkB/Akt pathway against diabetes mediated oxidative stress and apoptosis in neuronal cells	Shyma R L	Biochemistry	Toxicology mechanisms and methods
6	Unveiling the Utterances of a Subaltern class	Haripriya R.J	English	IJLMH

7	Shielding Transgender Persons	Haripriya R.J	English	IJPL
2021-2022				
8	Spectroscopic charge transfer interaction and docking studies of gardona insecticide	Anju.LS	Physics	Journal of Molecular Structure
9	A Study on the role of rubber board research department to enhance productivity of natural rubber in India	Dileep kumar	Commerce	Wesleyan Journal of Research
10	Dismantling Double Oppression in Jina Amucha	Haripriya R.J	English	IRJMETS
11	Literary Potential and Reformative Power of Transgender Self Writing from India	Haripriya R.J	English	JRHSSQ
2020-2021				
12	Density functional theory, spectroscopic and hydrogen bonding analysis of fenoxycarbwater complexes	Anju.LS	Physics	Journal of Molecular Structure

13	Spectroscopic, quantum mechanical and docking studies on organochlorine insecticides by density functional theory	Anju.LS	Physics	International Journal of Scientific & Technology Research
14	Strategic for International Finance in Development of Nation	Melbha D	Commerce	International Journal for Innovative Research in Multidisciplinary Field
2018-2019				
15	Spectroscopic, charge transfer interaction and docking studies of gardona insecticide	Anju.LS	Physics	Journal of Molecular Structure
16	DFT and vibrational spectroscopic study on pyrimidine derivative insecticide	Anju.LS	Physics	Journal of advanced scientific research
17	Poyikayil Yohannan and His Attempts in Organizing the Non Caste Christians of Kerala	Beeta John	History	International Journal of Innovative Knowledge Concepts
18	The Role Of Pampady John Joseph In Organizing The Non Caste Christians Of Kerala	Beeta John	History	International Journal of Research and Analytical Reviews

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Crystallization and surface Morphology following annealing using ZnO thin film

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Abstract - The glass substrates had ZnO thin films produced on them using a sol-gel dip coating process. All sorts of temperatures, from 350 to 550 degrees Celsius, were used to anneal the films. The impact of annealing temperature on the films' structural and morphological features was studied using X-ray diffraction (XRD) and atomic force microscopy (AFM). Different processing conditions are used during manufacturing, all of which might alter the final attributes of a device based on amorphous oxides. Although zinc oxide shows promise as a transparent amorphous oxide, its structure is sensitive to temperature changes. Here, we looked at the phenomenon of surface recrystallization in amorphous zinc oxide layers produced by pulsed laser deposition onto fused silica, sapphire, and Si substrates. Extremely out-of-equilibrium phase structures were found in the three-layer preparation. All the developed ZnO films display strongly (0001)-oriented patterns without in-plane rotation, as evidenced by in situ reflection high-energy electron diffraction (RHEED) and ex situ X-ray diffraction (XRD). As evidenced by atomic force microscopy (AFM) pictures, "ridge-like" and "particle-like" surface morphologies are found for the ZnO films formed in a molecular O2 environment with and without an initial deposition of Zn adatoms, respectively, before ZnO development with oxygen plasma. The ultimate surface shape and optical characteristics of the ZnO film are significantly affected by this artificially constructed interfacial layer.

Keywords - ZnO, Surface morphology, Zinc oxide, Thin films, Nanocrystalline

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INTRODUCTION

Cryogenic pulsed laser deposition (PLD) of ZnO thin films is the topic of this review. In order to undergo "real" recrystallization after annealing, amorphous materials are ideal since they provide unique circumstances for this process. The purpose of the study presented was to examine the recrystallization dynamics from amorphous to wurtzite structures as a function of annealing settings, as well as the characteristics of amorphous undoped ZnO films. Due to its high photocatalytic effectiveness and excellent stability, nanostructure ZnO has gained increasing attention as a promising semiconductor photocatalyst. High photocatalytic efficiencies of ZnO nanoparticles, powders, and colloids have been reported in many research. ZnO thin films, however, are favored for use in water purification because they prevent the catalyst from having to be separated once the degrading process is complete. ZnO thin film's photocatalytic characteristics have been studied in a number of published papers. Coatings based on zinc oxide are of great scientific and technological interest because of their many potential uses. Some examples include thermoelectric and gas sensor devices, transparent electrodes, selective surfaces, piezoelectric devices, and so on. ZnO's broad direct bandgap in the near-UV region and its ability to take on a variety of morphologies—nanorods, thin films, nanoflakes, nanowires, nanoplates, etc.—make it useful in a wide range of contexts. ZnO's shape, as well as its bandgap and conductivity, are said to be controlled by the synthesis technique used.

LITERATURE REVIEW

Ewelina Nowak **et.al (2021)** One of the broad-bandgap semiconductors, zinc oxide (ZnO) has potential uses in a wide variety of electrical, optical, piezoelectric, and scintillating devices. Here we take a look at ZnO microfilms made using the sol-gel technique on a sapphire substrate, analyzing their structure and luminescence. Several annealing temperatures were used on the films. The impact of the substrate on the film's structure was analyzed by using XRD and Raman spectroscopy to examine the structures. Film luminescence was studied by using three different techniques: fluorescence at ambient temperature, radioluminescence, and thermoluminescence.

T. Ivanova et.al (2020) Using a spin coating sol-gel method, nitrogen and gallium co-doped ZnO films have been effectively produced. Films of ZnO with various doping levels (N, Ga, and co-doped) are deposited on silicon and quartz. ZnO:N:Ga thin films are characterized by studying their structural, morphological, and optical characteristics as a function of thermal treatments (300-600 °C) and the two dopants, N and Ga. X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Field Emission Scanning Electron Microscope (FESEM), and UVeVISeNIR spectrophotometry have all been used to examine the doped ZnO films. The co-doped (N, Ga) ZnO films were found to form in the wurtzite structure free of impurity phases. Compared to undoped ZnO films, the optical transparency of ZnO:Ga and ZnO:N:Ga films is much higher, at over 80% in the spectral region of 400-800 nm. In ZnO, co-doping with gallium and nitrogen causes the surface morphologies to transform from wrinkle-like (undoped ZnO) to closed-packed grained.

W. Matysiak et.al (2018) In this research, zinc oxide thin films were made utilizing sol-gel and spin coating processes from Zn(COO)2 x 2H2O dissolved in ethanol and acetic acid with ZnO monocrystalline nanoparticles of 0 and 10% (wt.) relative to the final concentration of generated solutions. The impact of calcination procedure on ZnO thin films at 600°C were evaluated using atomic force microscope to analyze the shape of semiconductor coatings, infrared spectroscopy to verify the chemical structure of material. Besides, optical characteristics were assessed on the basis of absorbance in the function of wavelength spectra and the values of energy band gaps were analyzed. The topography examination of ZnO thin films indicated an increase in roughness with the increasing of zinc oxide nanoparticles in the thin film’s material. In addition, the investigation of the optical characteristics of ZnO thin films demonstrated a reduction in absorption level in the region of near-ultraviolet wavelength for the produced layers after annealing. It was observed that ZnO thin films made by spin coating and calcination process are an appropriate material for photoanode in dye-sensitized solar cells, since zinc oxide layers give greater conductivity throughout the photovoltaic cell.

Iping Suhariadi et.al (2018) Using atomic force microscopy, we examine the surface morphology of ZnO thin films formed through the nitrogen assisted crystallization process at varying nitrogen flow rates. At first, the deposited ZnO thin film had a rough surface replete with spiky granules with a skewness and kurtosis of 0.48 and 4.80, respectively. The films' skewness and kurtosis values reduce dramatically with the addition of a little quantity of nitrogen, which is also correlated with a flatter topography. Roughening of the surface is most evident in the increased kurtosis value to 3.30 as a result of increasing the nitrogen flow rate to 16 sccm. These findings suggest that introducing a trace quantity of nitrogen during the deposition process improved the film quality by increasing the grain size and facilitating the mobility of adatoms on the surface. All of the films contain self-affine fractal geometry with total fractal values between 2.14 and above 3.00, as determined by a two-dimensional power spectral density study.

Bakri, A S et.al (2017) The sol-gel dip coating process is used to create thin layers of titanium dioxide (TiO2) on silicon substrates. The film's surface appearance, structure, and electrical characteristics were studied in relation to the annealing temperature. X-ray diffraction, field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and a four-point probe were used to study the crystalline structure, surface morphology, and electrical characteristics. The findings demonstrate that when annealing temperature is raised, the strength of the (101) peak grows while the full-width at half-maximum narrows. Surface roughness and grain size both increase when thin films are deposited at high annealing temperatures. When the annealing temperature is changed from 300 to 900°C, the electrical characteristics of these films reveal that the resistivity changes from 1.40 x 105 to 7.19 x 102.cm, respectively. In comparison to other films, the resistivity of the TiO2 thin films annealed at 900 degrees Celsius was much reduced. Findings indicate that TiO2 thin films' surface morphology, structural, and electrical characteristics are all affected by the annealing temperature.

METHODOLOGY

The glass substrates had ZnO thin films produced on them using a sol-gel dip-coating technique. The raw material was zinc acetate dehydrate [$Zn(CH_3COO)2•2H_2O$], and the solvent and stabilizer were isopropanol and diethanolamine (DEA), respectively. Precursor solution Zn ion concentration was kept constant at 0.3 M by keeping the molar ratio of DEA to [$Zn(CH_3COO)2•2H_2O$] at a constant 1:1. After mixing, the solution was heated to 70 degrees Celsius and agitated for an hour to catalyze the hydrolysis process, yielding a clear and homogenous solution that could be used as a coating solution after it had cooled to room temperature. To get the best results from the dip coating procedure, it is customary practice to let the coating solution sit out for at least 24 hours.

Substrate was withdrawn from the coating solution at a steady rate of 15mm/min while at room temperature. Following coating, the film was preheated in a furnace at 160 °C for 20 minutes to totally eliminate any organic residuals and evaporate the solvent. To get nine layers of film, we repeated the coating and pre-heating procedure nine times.

After that, the ZnO films were annealed at temperatures of 350 C, 450 C, and 550 C.

By using X-ray diffraction (XRD) with Cu K radiation (= 0.15406nm), the films' structures were examined. In order to determine the surface morphology, an atomic force microscope was used (AFM).

Before being inserted into the MBE growth chamber at ultra-high vacuum, the MgO (111) substrates were ultrasonically cleaned in acetone and ethanol, then dried with nitrogen. All the substrates were heated to 490 degrees Celsius for 60 minutes in an oxygen plasma at a power of 250 watts and a partial pressure of 5 x 105 mbar. Different ZnO films were then produced from scratch using the settings described in Table 1 and Additional file 1. An essential step in altering the surface morphology is step (b), which involves growing the initial buffer layer (BLI) without plasma after step (a) heat treatment of the substrate.

RESULT AND DISCUSSION

Effect of annealing temperature on the structural properties of the films

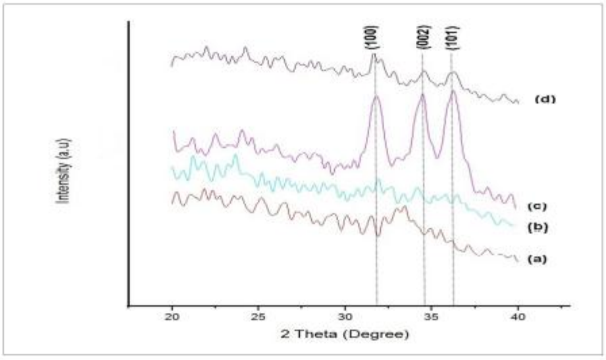


Figure 1: XRD spectrum of ZnO thin films annealed at different temperatures of (a) as grown, (b) 350 °C, (c) 450 °C, (d) 550 °C

The XRD patterns of ZnO films annealed at different temperatures are shown in Fig. 1. Diffraction peaks for the (100), (002), and (101) plane of reflections may be seen in the XRD pattern. Based on these findings, it may be concluded that annealed ZnO films have a polycrystalline, hexagonal wurtzite structure. The XRD pattern for unprocessed, as grown ZnO films is shown in Fig. 1(a). The amorphous-like structure of ZnO films is suggested by the XRD pattern in Fig. 1(a), rather than the polycrystalline structure that would be expected. This might be because of the amorphous nature of the glass substrates utilized, making the lower pre-heating temperature of 160 °C unnecessary for obtaining the desirable orientated ZnO films.

For ZnO films annealed at 450 °C, the reflection intensity is greatest in the (002) plane, which corresponds to the c-axis orientation. It can be seen in Fig. 1 that after annealing at 550 °C, the (002) peak intensity drops and the (100) peak becomes dominants in the film (d). These results suggest that the ZnO film annealed at 550 °C has a crystalline orientation with a preferential a-axis. When the annealing temperature is raised, the zinc ions and oxygen ions on the surface get the necessary energy and mobility to be removed and relocated. Because of this, the (002) peak along the c-axis would be the most successful in terms of growth. Instead of providing enough energy to move onto the stable position, increasing the annealing temperature (>450 °C) may break the bonds within Zn-O, speeding up the rate of re-evaporation.M.Vishwas et al. also reported that Al doped ZnO films annealed at higher temperatures exhibit a preferred (100) a-axis orientation. The current films have crystal lattice constant values of a = 3.2498 angstrom and c = 5.2066 angstrom, which are similar to the a = 3.253 angstrom and c = 5.209 angstrom values of ZnO crystal (JCPDS Card No. 80-00075).

Effect of annealing temperature on the surface morphology the films

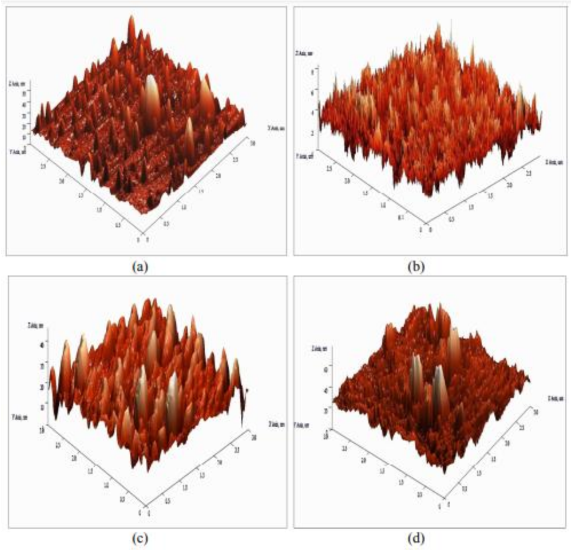


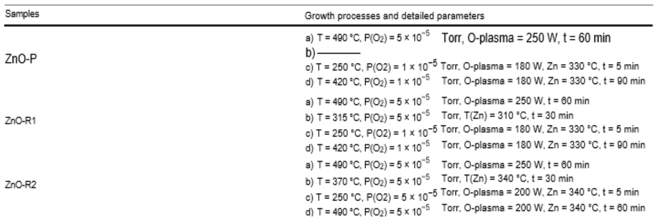
Figure 2: AFM surface morphology images of the ZnO films annealed at the temperature of (a) as grown, (b) 350 °C, (c) 450 °C, (d) 550 °C

Surface morphology photos of annealed ZnO films captured by an atomic force microscope are shown in Fig. 2. ZnO films at 350 °C, 450 °C, and 550 °C had RMS roughness values of 0.897 nm, 5.653 nm, and 7.975 nm, respectively. Similarly, Hwang et al. assert that ZnO films show an increase in RMS roughness with increasing temperature. According to the XRD pattern in Fig. 1, the as developed ZnO films have an amorphous structure rather than a polycrystalline one, as seen in Fig. 2(a) (a). As a result, its surface is relatively rough, with a root-mean-square roughness (RMS) of 5.466 nm. This may be because some leftover organic material was vaporized during the preheating process. ZnO films' RMS roughness rises as their annealing temperature rises over 550 degrees Celsius because their grain distributions become less uniform when the grains agglomerate. This might be because the glass substrate was annealed at a very high temperature, very close to its melting point. ZnO films annealed at

350 °C and 450 °C had larger average grain sizes, at 32.1 nm and 176.0 nm, respectively, whereas those annealed at 550 °C have smaller average grain sizes, at 56.1 nm. The reductions in average grain size for the 550 °C annealed films may be explained by the poorer uniformity in grains size and its distribution, as illustrated in Fig. 2. (d).

In this case, AFM was used to investigate the surface morphologies of ZnO films grown under a variety of circumstances. Surface morphologies of the thin films were significantly affected by the implanted interfacial layer. Figure 3a is an AFM picture of a ZnO-P film, which reveals a distribution of nanoparticles. However, as can be seen in Fig. 3b and c, the ZnO-R1 and ZnO-R2 AFM pictures exhibit more ridge-like characteristics. Zooming in on the square region indicated by the dotted black lines in Figures 3a-c (Figures 1d-f), we see the enlarged photographs. In Fig. 3d, the mean particle diameter of ZnO-P is about 70 nm, and in Fig. 3e, the mean ridge width of ZnO-R1 is about 70 nm, with the presence of numerous apertures between the ridges. The ridges in the modified ZnO-R2 sample are denser and larger (with an average width of 90 nm) compared to the ridges in ZnO-R1, and there are fewer voids in the ZnO-R2 sample. The RMS values of 4.15, 7.51, and 3.10 nm for the ZnO-P, ZnO-R1, and ZnO-R2 films provide additional confirmation of the surface roughnesses. The influence of BLI on the morphology of our samples is significant. It can be shown in Additional file 1 that although all of the BLI samples created at varying substrate temperatures have ridge-like surface morphologies, some of the samples also have surface flaws. Films with and without BLI were compared, and it was discovered that the initial nucleation of ZnO was responsible for dictating the final particular shape. Furthermore, oxygen pressure played a significant role in the nucleation process, exhibiting great sensitivity, since Zn atoms may rapidly desorb without surrounding oxygen owing to their poor stickiness.

Table 1: Detailed growth conditions for the ZnO films



Samples	Growth processes and detailed parameters
ZnO-P	a) T = 490 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, O-plasma = 250 W, t = 60 min b) ——— c) T = 250 °C, P(O2) = 1×10^{-5} Torr, O-plasma = 180 W, Zn = 330 °C, t = 5 min d) T = 420 °C, $P(O_2) = 1 \times 10^{-5}$ Torr, O-plasma = 180 W, Zn = 330 °C, t = 90 min
ZnO-R1	a) T = 490 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, O-plasma = 250 W, t = 60 min b) T = 315 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, T(Zn) = 310 °C, t = 30 min c) T = 250 °C, P(O2) = 1×10^{-5} Torr, O-plasma = 180 W, Zn = 330 °C, t = 5 min d) T = 420 °C, $P(O_2) = 1 \times 10^{-5}$ Torr, O-plasma = 180 W, Zn = 330 °C, t = 90 min
ZnO-R2	a) T = 490 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, O-plasma = 250 W, t = 60 min b) T = 370 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, T(Zn) = 340 °C, t = 30 min c) T = 250 °C, P(O2) = 5×10^{-5} Torr, O-plasma = 200 W, Zn = 340 °C, t = 5 min d) T = 490 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, O-plasma = 200 W, Zn = 340 °C, t = 60 min

T temperature (°C), P oxygen partial pressure (mbar), plasma oxygen plasma power (W), t time (min)

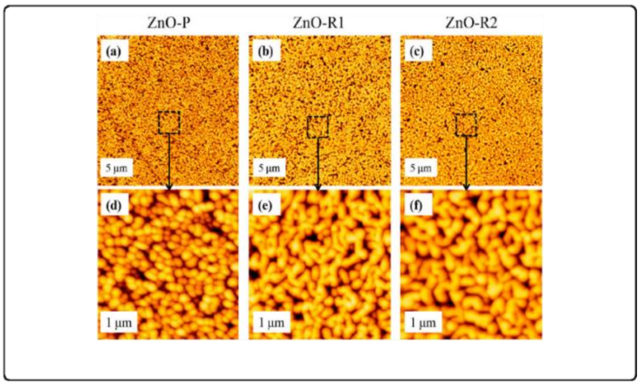


Figure 3: AFM results. a–c AFM images of the ZnO film surface morphologies (5 µm). d–f Magnified images of the square areas (marked by dashed black lines) in a–c

This unique ridge shape is reminiscent of another work in which 3D columnar grains with a particle-like morphology were driven to merge laterally into nanoridges during a 30-minute HT post-annealing. Lateral coalescence, however, is seen here as a normal part of development. Zn atoms, much like the AlN nuclei, preferentially migrate to the substrate's unique step edges, where they combine with O2 to produce ZnO at the edges despite the fact that O2 is not activated by plasma, resulting in the ridge-like morphology. Adatoms migrating to the surface during the first stage of development (when the surface is quite flat) would produce ZnO crystals of superior quality. When O is activated by plasma during deposition of the ZnO film onto the substrate surface in the absence of BLI, the resultant surface morphology is that of typical nanoparticles.

CONCLUSION

The glass substrates had ZnO thin films produced on them using a cheap sol-gel dip-coating method. After being exposed to temperatures between 350 and 550 degrees Celsius, the films were annealed. In contrast to the amorphous structure displayed by as-grown ZnO films, polycrystalline hexagonal wurtize structures were observed in annealed films, with a preference for the (002) c-axis orientation with increasing annealing temperatures. The highest peak intensity was observed in films annealed at 450 °C. ZnO films with ridge-like surface morphologies, which were shown to be sensitive to the initial oxygen pressure, were generated on MgO(111) substrates and compared to a conventional particle-like ZnO film in this study. The elements that affect the morphology were studied using a battery of studies.

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A PERSPECTIVE ASSESSMENT OF THE RUBBER BOARD'S CONTRIBUTION TO THE EXPORT PROMOTION OF NATURAL RUBBER

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Abstract

In terms of export, NR is not a traditional item of Indian export. Despite this, the government has prioritised NR exports since 2001, when quantitative restrictions (QRs) on imports were lifted. The promotion of NR export is being promoted as a counter-strategies to the wild volatility in domestic NR price movements caused by the massive influx of NR imports into the country. The rubber-consuming industry in India has been importing NR in large quantities in recent years, taking advantage of the country's import duty structure. Even though the current demand-supply imbalance and deficit do not call for a robust export promotion strategy for natural resources, the Board will concentrate on export promotion in order to increase the sector's export competitiveness and capabilities so that exports can be made whenever the price environment is favourable. The Board is taking a number of actions to encourage exports and assist Indian exporters in surviving on the international market. The Board's responsibilities include promoting the NR brand, participating in trade shows, and offering training on natural rubber export management, export procedures, and import policy. Therefore, it has become necessary to assess the rubber board's effectiveness from the viewpoint of the rubber farmers in promoting natural rubber exports from India. This article makes an effort to assess the impact of rubber boards on India's exports of natural rubber.

Keywords: Rubber Board, Export, Natural Rubber

Introduction

Under the Rubber Act of 1947, the Government of India established the Rubber Board as a statutory body to promote the overall growth of the nation's rubber industry. The British were responsible for the introduction of natural rubber cultivation on a commercial scale in India, though early attempts to commercially cultivate rubber in India date back to 1873 at the Botanical Gardens in Calcutta. At Thattekadu, commercial plantations were first established in India in 1902.

Generally there are two kinds of agricultural activities existing in India; food crops and cash crops. As we all aware of the meaning of cash crops and food crops. Rubber is one of the most prominent cash crop in India. According to Rubber board of India The total production of Natural Rubber (NR) during 2018-19 is provisionally estimated at 648000 tonnes. The production of NR during April-May 2019 is provisionally estimated at 74000 tonnes. Which reveals the importance of rubber plantation in India. In India, especially in the state of Kerala, a large number of farmers depends rubber farming for their lively hoods. Therefore it is the responsibility of the government to protect the interest of the farmers from the unhealthy competition.

According to (Minstry of Commerce and Industry, n.d.) In recent years, both domestic and foreign markets have seen relatively low prices for natural rubber. The average price for the RSS4 grade in June 2019 was 150.29 per kg. However, rubber prices have started to rise in recent weeks. The prices of natural rubber are determined by market forces and a variety of factors, which include, among other things, economic growth trends in major consuming nations, oil and synthetic rubber price trends, climatic conditions, and market developments. The domestic NR market typically tracks the global market trend, with sporadic deviations brought on by region- and season-specific factors. According to WTO commitments, no quantitative limitations can be placed on the import of NR. The price of domestic NR is affected by NR import. Because of this, the government raised the duty on the import of dry rubber from "20% or Rs. 30 per kg whichever is lower" to "25% or Rs. 30 per kg whichever is lower" as of April 30, 2015, in order to control the import of NR. Additionally, the Government shortened the time frame for using imported dry rubber purchased under an advance licencing scheme in January 2015 from 18 to 6 months. Since January 20, 2016, the Director General of Foreign Trade (DGFT) has restricted the ports of entry for the import of natural rubber to Chennai and Nhava Sheva (Jawaharlal Nehru Port).

Review of Literature

(Uthaman, 2021) The association of planters in Kerala (APK) has expressed concern about the state's declining production shares over the past few decades. The production of natural rubber in the state was 6,68,000 tonnes in the fiscal year 2020 and 7,10,000 tonnes in the fiscal year 2019, according to the annual report of APK. From this, we can see that there has been a small decline of 5.91%. The proportion of Kerala in the national production has decreased from about 92% a decade ago to 69.66% today. The increase in area under cultivation in non-traditional regions like the North Eastern parts and Sindhudurg in Maharashtra was one of the reasons cited by the planters' body. The rubber board and the government decided to create some strategies and tools for the rubber cultivators to combat this, including an awareness campaign, technical assistance, price stability, and financial tools**.**

(M Kannan, 2013) Variables in the production of natural rubber, such as export volume, stock, and domestic price, had a favourable and significant relationship with production. Although natural rubber imports are not significant, they have a detrimental impact on domestic production. The OLS model shows that among the five independent variables affecting natural rubber export, all but production are found to have a significant impact. These variables include stock, global market price, domestic price, and global population. Additionally, he suggests that the government might raise the cost of purchasing natural rubber at a suitable and reasonable rate. The quantity stock has a negative impact on India's natural rubber exports. Therefore, it is suggested and advised that the natural rubber stock be kept below a reasonable and prescribed level in order to increase Indian exports.

(Balasubramani & Swathi Lekshmi, 2001) It was investigated how rubber growers felt about the information technology-enabled Rubber Expert System. The majority of respondents (60.83%) were found to have a high level of perception of contemporary information and communication technologies, followed by 21.67% with a medium level of perception and the remaining 17.50% with a low level of perception. The study's finding that slightly fewer than three-fourths of the respondents said they were most satisfied with the diagnostic path that was sequential and logical in RUBEXS-04 could be used to defend the study's findings. The correct conclusion offered by the RUBEXS-04 satisfied the majority of respondents (81.67%) the most.

(Muthusamy, 2020) The performance of rubber exports from 2010–2011 to 2017–2018 is evaluated in this paper. The Board has been promoting the Indian Rubber export promotion strategy since 2011 with the aim of differentiating Indian rubber in the global market with its discerning quality features. The board is promoting export as a method of market intervention to correct market imbalances brought on by shady imports of rubber. From December 2016 to March 2017, when production is at its highest, exports are at their highest levels. From April to October 2018, India's rubber exports increased to 650 tonnes. Since December 2013, the price of natural rubber (NR) on the Indian market has dominated the prices on the global market.

(Kumar, 2022) According to a report, the Rubber Board wants to increase India's exports of rubber goods from their current level of 25,000 crore over the next 25 years. The Executive Director of the Board, K.N. Raghava, has stated. While opening the Advanced Analysis Laboratory for Rubber Products at the Rubber Research Institute of India, he stated that it was the responsibility of the Board to assist exporters, particularly those in the MSME sector, in any way possible.

Research gap:

Despite the fact that some studies have been conducted in connection with the rubber board's activities, the study that specifies the role of the rubber board in the export of natural rubber is severely lacking, particularly from the perspective of farmers.

Statement of the problem

Rubber board is a statutory body set up by the government of India to promote the rubber industry. Therefore it is essential to assess the performance of rubber board on their various activities for the betterment of their services in the present circumstances. Because there is strong fear among rubber farmers that the rubber board would be shut down or partially privatised. The NITI Aayog had recommended that the board is not essential and its functioning should be discontinued. As a result the board recently convened a gathering of farmers to get their feedback. The central government would make the final decision after weighing the NITI Aayog's observation and the Ministry of Commerce's position. The ministry thinks the board should continue. After the NITI Aayog observation, the ministry asked the board for a thorough report. The board responded to inquiries about, among other things, the services it has provided thus far, import-export information, and farmer welfare (Balagopal, 2022)

Research question

Based on the research gap and statement of the problem, the researcher has identified the following research question:

- What is the perception of farmers on the rubber board about their export promotional activities?

Objectives

- ✓ To assess the perception of farmers on the role of rubber boards on the export of natural rubber in Kerala.

Hypothesis

- ✓ The perception of farmers on the role of rubber board on the promotion for export of the natural rubbers are the same with respect to the type of farmers.

Scope of the study

People who are engaged in the production of natural rubber are the only ones considered for the study. Farmers in Kerala State were polled for information. Farmers engaged in the production of natural rubber were classified into two groups based on the area of cultivation, such as small-scale and plantation farmers. Small-scale farmers are those who planted rubber on less than five acres of land, whereas plantation farmers are those who farm more than five acres of land for rubber cultivation.

Methodology

There are 150 farmers chosen to collect data equally from small scale farmers and plantation farmers. Primary data were collected by using a structured questionnaire, and secondary data were collected from all available sources. Five point Likert scale techniques were used for collecting the data. The researcher opted for a simple random sampling method for selecting the respondent.

According to the Shapiro-Wilk test, the data were normally distributed because the p value was greater than 0.05, so the researcher chose a parametric test to validate the hypothesis.

Data analysis

To compare rubber farmers' perceptions of the rubber board's activities for natural rubber export, data were collected from 150 farmers, 75 from both types of farmers, such as small-scale farmers and plantation farmers. Table 1.1 depicts the farmers' distribution by area of cultivation.

Table 1.1

Type of farmers

Type of farmers	**No of respondent**	**Percent**
Small scale farmers	75	50%
Plantation farmers	75	50%
Total	150	100%

Source: Primary data

According to table 1.1, 75 farmers are small-scale farmers, and the remaining are plantation farmers. There were equal distributions given to both types of farmers to assess their perceptions towards their rubber board.

In order to study the perception of farmers towards the export promotion schemes of the rubber board, the following independent variables are used in statement form:

1. The procedure for issuing a Registration and Membership Certificate (RCMC) is simple.
2. Fees for issuing a Registration-cum-Membership Certificate (RCMC) are moderate.
3. The procedure for issuing a Certificate of Origin (CoO) is simple.
4. The fees for issuing a Certificate of Origin (CoO) are moderate.
5. Participation of rubber board in international trade fairs
6. Rubber board organises and takes part in exhibitions.
7. Gives Indian natural rubber international exposure.
8. Conduct training programmes in export management and procedures.
9. Provide technical assistance for export value-added activities.

10. Financial assistance can be used to protect exporters from competitors.
11. Conducting awareness programmes about the procedure and benefits of exporting natural rubber.

Are farmers' perspectives on the aforementioned independent variables consistent? Or which variable is the most important? To find an answer to this question, one sample t test was used, and the results are shown in table 1.2.

Table 1.2

One sample t test for the farmers' perception on the role of rubber board on the export of natural rubber.

Export promotion support on	**N**	**Mean**	**Std. Deviation**	**Std. Error Mean**	**t value**	**P value**
Procedure for issuing Registration-cum-Membership Certificate (RCMC) is simple.	150	3.72	.547	.0445	87.446	**.000**
Fee for issuing Registration-cum-Membership Certificate (RCMC) are moderate	150	3.61	.654	.053	67.508	**.000**
Procedure for issuing Certificate of Origin (CoO) is simple.	150	3.85	.560	.046	81.258	**.000**
Fee for issuing Certificate of Origin (CoO) are moderate.	150	3.61	.654	.053	67.508	**.000**
Rubber board participating in international trade fairs	150	3.73	.490	.040	93.123	**.000**
Rubber board conduct and participate in exhibitions	150	3.71	.560	.046	81.258	**.000**
Provides international publicity to Indian Natural Rubber.	150	3.81	.460	.038	102.507	**.000**

Conduct training programmes in export management and procedures	150	3.85	.483	.039	96.676	**.000**
Provide technical assistance for the value added activities for exports	150	**3.99**	.331	.017	144.197	**.000**
Support exporters from competitors through financial assistances.	150	**3.91**	.335	.027	142.947	**.000**
Conducting awareness programmes about the procedure and benefits of exporting natural rubber	150	3.71	.538	.044	84.415	**.000**
Perception of farmers	**150**	**3.86**	**.23**	**.020**	**223.18**	**.000**

Source: primary data

A one-sample t test was used to determine farmers' perceptions of the rubber board's export promotional assistance.Based on the mean score, it is evident that farmers have a high perception of statements such as "Procedure for issuing a Certificate of Origin (CoO) is simple," "Conduct training programmes in export management and procedures," "Provide technical assistance for the value-added activities for exports," "Support exporters from competitors through financial assistance," and "Conduct awareness programmes about the procedure and benefits of exporting natural rubber."

Because the mean value of all the independent variables is greater than three, it can be concluded that rubber farmers have a moderate perception of the rubber board's export promotion assistance.

However, one question remains unanswered. Is this the same for both farmers, such as small-scale farmers and plantation farmers? Or is there any difference in any of the independent or dependent variables as a whole with respect to small-scale and plantation farmers? In order to find an answer to this question, the following null hypothesis was developed:

H_0: The perception of farmers on the role of rubber board on the promotion for export of the natural rubbers are the same with respect to the type of farmers.

To check the null hypothesis, the independent sample t test was opted by the researcher and the test results are shown in table 1.3

Table 1.3

Independent sample t test for the perception of rubber farmers

Perception of rubber farmers.	**Type of farmers**	**Mean**	**Std. Deviation**	**t value**	**P value**
Procedure for issuing Registration-cum-Membership Certificate (RCMC) is simple.	Plantation Farmers	3.98	.361	2.293	**.023***
	Small scale farmers	3.78	.621		
Fee for issuing Registration-cum-Membership Certificate (RCMC) are moderate	Plantation Farmers	3.79	.475	2.960	**.004****
	Small scale farmers	3.51	.827		
Procedure for issuing Certificate of Origin (CoO) is simple.	Plantation Farmers	3.75	.389	1.021	.309
	Small scale farmers	3.68	.522		
Fee for issuing Certificate of Origin (CoO) are moderate.	Plantation Farmers	3.72	.508	2.147	**.033***
	Small scale farmers	3.49	.760		
Rubber board participating in international trade fairs	Plantation Farmers	3.83	.381	2.544	**.012***
	Small scale farmers	3.63	.564		
Rubber board conduct and participate in exhibitions	Plantation Farmers	3.85	.392	2.625	**.010****
	Small scale farmers	3.64	.584		

Provides international publicity to Indian Natural Rubber.	Plantation Farmers	3.88	.401	.888	.376
	Small scale farmers	3.81	.512		
Conduct training programmes in export management and procedures	Plantation Farmers	3.81	.512	.808	0.396
	Small scale farmers	3.83	.456		
Provide technical assistance for the value added activities for exports	Plantation Farmers	3.85	.392	-1.487	.139
	Small scale farmers	3.93	.251		
Support exporters from competitors through financial assistances.	Plantation Farmers	3.83	.446	-3.005	**.003****
	Small scale farmers	3.99	.115		
Conducting awareness programmes about the procedure and benefits of exporting natural rubber	Plantation Farmers	3.69	.545	-.303	.763
	Small scale farmers	3.72	.534		
Perception of farmers	Plantation Farmers	**3.99**	**.115**	**3.005**	**.003****
	Small scale farmers	**3.83**	**.446**		

Source: Primary data

**** At 5 percent significance level***

***** At 1 percent significance level***

The independent sample t test was used to check whether there is any significant difference in the perception of farmers towards the schemes of rubber board.The null hypothesis is rejected because the p value is less than 0.01 at the 1% significance level for statements such as "fees for issuing Registration and Membership Certificates (RCMC) are moderate," "Rubber Board conducts and participates in exhibitions," "Supports exporters from competitors through financial assistance," and "overall perception of farmers."This means that there is a significant difference in the perception of the rubber board among plantation and small-scale rubber farmers, such as the "fee for issuing registration/membership certificates (RCMC) is moderate," the "rubber board conducts and participates in exhibitions," the "support exporters from competitors through financial assistance," and the "overall perception of farmers."According to the mean and standard deviation, plantation farmers have more positive perceptions than small-scale farmers based on statements such as "fees for issuing Registration/Membership Certificate (RCMC) are moderate," "Rubber board conducts and participates in exhibitions," and "overall perception of farmers."Small-scale farmers are more optimistic about "protecting exporters from competitors through financial assistance."

Since the p value is less than 0.05 at the 5 percent significance level, the null hypothesis is rejected for statements such as "Procedure for issuing a Registration-Cum-Membership Certificate (RCMC) is simple," "Fees for issuing a Certificate of Origin (CoO) are moderate," and "Rubber board participating in international trade fairs." Based on the mean and standard deviation, it can be inferred that plantation farmers have a more positive perception of the variables "procedure for issuing a registration/membership certificate (RCMC) is simple," "fees for issuing a certificate of origin (CoO) are moderate," and "Rubber board participating in international trade fairs" than small-scale farmers.

Findings

1. Farmers have a positive attitude towards various schemes adopted by the Rubber Board.
2. Farmers have a positive perception of the procedure for issuing a Registration and Membership Certificate (RCMC).
3. Farmers have a positive perception of the procedure for issuing a Certificate of Origin (CoO).
4. The fee for getting a Registration and Commitment Certificate (RCMC) is affordable.
5. The cost of obtaining a Certificate of Origin is reasonable.
6. Plantation farmers have more perceptions about the following aspects of the rubber board than small-scale farmers:

- Fees for issuing registration/membership certificates (RCMC) are moderate
- Rubber boards conduct and participate in exhibitions
- Support exporters from competitors through financial assistance
- Procedure for issuing registration/membership certificates (RCMC) is simple.
- Fees for issuing certificates of origin (CoO) are moderate, and
- Overall perception of farmers".

Conclusion

Rubber Board is one of the statutory bodies of the government of India for protecting the interests of rubber farmers. It should be noted that the Rubber Board helps to stabilise functions related to the rubber industry. But the current situation raises questions about the rubber board and its functions. Recently, the NITI Aayog questioned the activities of rubber boards. According to NITI Aayog, the Rubber Board is now insignificant in the marketing of natural rubber; hence, it should be wound up or partially privatized, even though the Ministry of Commerce is opposed to it. Hence, the study was carried out to address the importance of rubber board, especially in the exporting of natural rubber. The study was conducted from the perspective of farmers. The study concludes that the Rubber Board plays a dominant role in the export of natural rubber by helping and supporting farmers through licensure and providing proper training and development programmes. As a result, it is clear that the rubber board plays an essential role in the operation of the rubber industry, and it must be operational in order to protect the interests of farmers as well as the government.

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A STUDY ON THE IMPACT OF INNOVATIVE PRACTICES IN SIDCO

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BSTRACT

SIDCO, a government owned public sector corporation was established in November 1975 for e development and promotion for small scale industries in Kerala. The main objective of SIDCO is to ulate the growth of industries in the small scale sector. Digital transformation is the integration of gital technology into all areas of business. Technology is important in every business because it helps increase efficiency of systems, products and services. Increased efficiency in operation helps to duce cost as well as enable the business to grow rapidly.

Small business using digitalization successfully generated increased sales that have helped them recover from loses due to the pandemic situation Digital transformation is essential for every siness growth because it can provide better collaboration between organizations, improve customer gagement, bring employee innovation, increase productivity etc.Innovationhas been termed as the st crucial element in todays globalized and competitive environment. Companies focusing on ovation not only competitiveness but also are able to sustain them for a longer period of time

eywords: Government,Organization,SIDCO, Globalization,Technology

NTRODUCTION

SIDCO is fully owned government corporation with its registered office at Trivandrum. It owns d operates production units, raw material depots, industrial estates, mini industrial estates ,industrial rks ,marketing cell, civil construction division, IT&TC division etc. Digital transformation can eatly improve the business operation by allowing the capitalization, production, sale and distribution f goods considerably faster. Technical acceleration and digital transformation both force companies to ove faster. SIDCO rendering assistance to SSI's in the state.

Innovation enables problem solving and provide creative insight that allows to look at things om different perspectives. It helps quickly responding to the external challenges. For a business novation means implementing new ideas, improving services and creating dynamic products. In order drive business growth stay relevant in changing times, and differentiate from the competition siness leaders must be able to think creatively and embrace innovation into their business models. In mple term innovation is an essential element of economic growth and productivity. The main aim of this paper is to examine the impact of innovative approaches in SIDCO.

STATEMENT OF THE PROBLEM

Digital business is the process of applying digital technology to reinvent business models and transform, a company's products and customer experience .Micro, small and medium enterprises are playing a vital role in the economic development of the country.They help to generate more employment and income with lower investment through the utilization of domestically available resources. Digitalization is important for the business sector. Successful business is increasingly based on interactive communication and adapting system of marketing communication analyse the performance of SIDCO in the present innovative world.

OBJECTIVES OF THE STUDY

1. To identify the significance of innovative practices in SIDCO.
2. To measure the satisfaction level of employees towards the modern business strategy of SIDCO.
3. To make suggestion to improve the performance of SIDCO.

RESEARCH METHEDOLOGY

The data used for this study is primary and secondary in nature. Primary are collected directly from 100 respondents through questionnaire. All the respondents selected for the study belongs to Thiruvananthapuram district secondary data has been collected from journal, annual reports etc. The respondents are selected according to convenient sampling method. Correlation and chi-square methods are used to analyze the data.

DATA ANALYSIS

Correlation Showing the comparison between traditional business strategy and modern business strategy.

Table 1

Satisfaction level	Traditional strategy	Modern strategy
Highly satisfied	15	45
Satisfied	40	25
Neutral	15	15
Dissatisfied	10	5
Highly dissatisfied	20	10
Total	100	100

$$r=\frac{n(\sum xy)-(\sum x)(\sum y)}{\sqrt{n\sum x^2-(\sum x)^2 \times n\sum y^2-(\sum y)^2}}$$

Table 2

Satisfaction level	Traditional strategy	Modern strategy	xy	x^2	y^2
Highly satisfied	15	45	675	225	2025
satisfied	40	25	1000	1600	625
Neutral	15	15	225	225	225
Dissatisfied	10	5	50	100	25
Highly dissatisfied	20	10	200	400	100
Total	$\sum x=100$	$\sum y=100$	$\sum xy=2150$	$\sum x^2=2550$	$\sum y^2=3000$

$$r = \frac{n(\sum xy)-(\sum x)(\sum y)}{\sqrt{n}\sum x^2-(\sum x)^2 \times n\sum y^2-(\sum y)^2}$$

$$r = \frac{5\times2150-10000}{\sqrt{}(5\times2550-10000)\times(5\times3000-10000)}$$

$$r = \frac{10750-10000}{\sqrt{12750}-10000\times(15000-10000)}$$

$$r = \frac{750}{\sqrt{2750\times5000}}$$

$$r = \frac{750}{3708}$$

$$r=0.202$$

NTERPRETATION

Since the value of "r" is positive and greater than 0.5, there is a high positive correlation etween attributes.

hi-square between the gender of workers and level of satisfaction of modern business strategy.

HO): There is no significant difference between gender of workers and level of satisfaction.

H1): There is significant difference between gender of workers and level of satisfaction .

TABLE 3 Gender of workers and level of satisfaction

Gender	Highly satisfied	Satisfied	Neutral	Dissatisfied	Highly dissatisfied	Total
Male	25	15	5	5	10	60
Female	15	7	5	8	5	40
Total	40	22	10	13	15	100

The formula for chi- square test(x^2) $(x^2)=\frac{\Sigma(O-E)^2}{E}$

Where O =observed frequency

E = Expected frequency

TABLE 4

O	E	O-E	$(O-E)^2$	$\frac{(O-E)^2}{E}$
25	24	1	1	0.041
15	16	-1	1	0.062
15	13.2	1.8	3.24	0.245
7	8.8	-1.8	3.24	0.368
5	6	-1	1	0.166
5	4	1	1	0.25
5	7.8	-2.8	7.84	1.005
8	5.2	2.8	7.84	1.507
10	9	1	1	0.111
5	6	-1	1	0.166
			Total	3.921

Source: primary data

The calculated value of chi- square =3.921.

Degree of freedom (V)=(C-1) × (R-1)

=(5-1)×(2-1)
=4×1=4

The tabulated value of chi-square at 4 degree of freedom and 5 % level of significance =9.488
The calculated value of chi-square< tabulated value of chi-square.

Ie, 3.921 < 9.488

So accept the null hypothesis (HO). There is no significance difference between the gender of workers and level of satisfaction.

FINDINGS

1. Most of the workers are male, they are highly satisfied with the modern innovative practice of SIDCO.
2. New technologies and tools of the SIDCO are most crucial element in the present globalized world.
3. Digital business work 24/7 and overcome both geographical and timing barriers.
4. Through the innovative business productivity can improved, new markets and opportunities are opened , reduced cost .

SUGGESTIONS

1. Encourage employees to try out new ideas without risking the company main products
2. Provide adequate training and development programs for their better performance.
3. Different risk factors associated with innovation and taking step to mitigate them.

CONCLUSION

The small scale industry has a role in the economic development of India. There are different types of guidelines are followed by SIDCO during the covid-19 situation. Modern and traditional marketing is the medium through which an audience encounters a marketing message. While traditional marketing uses traditional media like magazines and newspapers, digital marketing uses digital media such as social media or websites. Traditional business has restrictions on when and where they function. The innovative and modern strategy of business run 24/7. Innovation can be used to create a positive future for society.

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A STUDY ON ARTIFICIAL INTELLIGENCE IN INDIAN BANKING SECTOR

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ABSTRACT

Artificial Intelligence is rapidly becoming the go-to technology for businesses around the world looking to create a more personalized experience for customers. Artificial Intelligence is predicted to be worth rs 450 billion to banks, and it will make working in the banking business more competitive, productive and efficient. Artificial Intelligence has the potential to be great opportunity for both banks and businesses. This industry is trying to figure out how to bring banking closer to customers. Artificial Intelligence technologies are expected to save banks roughly 450 billion dollars in costs. The banking industry's future will be less manual and more artificial intelligence- based. One of the first adopters of artificial intelligence, the banking sector, is recombining. Banks, like segments, are experimenting with and implementing technology in a variety of ways.

Keywords: *Artificial Intelligence, Technology, Banks.*

INTRODUCTION

Artificial Intelligence is used by payment providers to provide clients with a personalized payment experience. Payment systems can promote the desired payment instrument that best suits a purchase at checkout by using AI and analysis historical payment patterns. For large- ticket purchases, a consumer commonly uses the EMI option. The best EMI choice is then made available to the customer experience, increasing consumer spending and increasing customer loyalty to the product.

According to Accenture's recent Accenture Banking Technology Vision 2020 report, 83% of Indian bankers believe that AI will work alongside humans in the Next Two Years. A higher than the global average of 79%. " 93% of bankers in India said they increasingly use data to drive critical and automated decision making. More partner supplied customer data means a higher degree of responsibility for banks. Yet, 77% of Indian bankers agree that most firms are not prepared to confront impending waves of corrupted insights from falsified data," said the report. AI is not new to India. Research Institutions and universities have been working with various AI technologies for decades, especially in social transformation. With enabling technologies becoming a lot more accessible and inexpensive. AI is now becoming mainstream, with large enterprises and startups looking at different opportunities. The application of AI and Machine Learning (MI) to different functions within the banking industry has enabled them to offer a far more personalised and efficient customer service. By achieving that, banks have also been able to gain better insights into their customer's preferences and

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Unveiling the Utterance of a Subaltern Class: Analysis of Selected Transgender Autobiographies from India

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ABSTRACT

Transgender or people whose gender identity or gender differs from the sex that they were assigned at birth are generally a class of subalterns. They are deprived of even basic and most fundamental rights by different societies. Indian society is also not different. In India people are forced to behave according to the gender constructs which is too narrow and closed. Thus transgender who falls outside the binary classification of gender as male and female are crushed by the cogs of Indian gender norms for years. They are forced to hide their actual gender notions and behave according to the sex they were assigned at birth. This will leads to a traumatic life for the third genders. Gender othering is unbearable when it turns out to be a weapon capable of even taking the lives of transgender. Though many raised their voice against the injustice shown in different realms, the utterance is never fully heard by the society. Thus the research entitled Unveiling the Utterance of a Subaltern Class: Analysis of Selected Transgender Autobiographies from India tries to analyse through the support of selected transgender autobiographies various forms of oppression faced transgender as a subaltern class even today.

Design/ Methodology/ Approach: *The research takes the support of qualitative methods for study. It will be a qualitative analysis including textual analysis, in depth study, close reading as well as interpreting, comparing and contrasting the primary sources chosen for the study. Data for the research will be collected with the help of library resources and online sources. Different articles and books relating to transgender autobiographies from India are carefully read and analysed for the research. Subaltern theory which stands for understanding the society through conditions of subordination of people belonging to the different caste, class, age, gender, race and so on is taken as a effective tool or instrument for analysing the selected autobiographies.*

Findings/Results: *Even now transgender continues to be a subaltern group in India and this is a serious blow on the face of democratic India. Thus a research aiming at addressing the long unheard and silenced voices of transgender and trying to uplift them from their*

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marginal positions to the mainstream is highly essential for India. The research entitled Unveiling the Utterance of a Subaltern Class: Analysis of Selected Transgender Autobiographies from India therefore aims at bringing about a change in subaltern status of transgender in the Indian society. For this, various issues faced by transgender community in India will be addressed with the help of selected autobiographies by transgender themselves and solutions will be offered to wipe out their agonies.

Originality/Value: *Possible solutions for safeguarding the life and dignity of transgender community like institutionalising the category called third gender along with the traditional binary divisions of gender, realising the legal support for trans community, authorising transgender rights, punishing heteronormative assumptions and violence against transgender will be suitably suggested. Changes which can be brought about in socio-economic, political and legal levels within India will be suggested to raise the transgender from their present subordinate positions.*

Paper Type: *Qualitative research paper.*

Keywords: *Gender identity, Gender othering, Indian society, Third gender, Transgender.*

I. INTRODUCTION

India is always hailed for its unity in diversity and secularism but in reality, many groups are given a marginal or subaltern position by the Indian society. A few among them are Scheduled Castes (Dalits), Scheduled Tribes, women and so on. [1] But rarely did anyone addresses transgender as a subaltern group and give space for their expressions in different domains. The utterance of transgender is often unheard or not properly attended by the society. Literature is not different in this aspect. Though many writers tried to express the agonies of transgender community and tried to bring about changes in their marginalized positions, even now something notable is unreached. There are many biographies and other writings about transgender but a search for unveiling the true and most authentic utterance of transgender group will ultimately lead us to transgender autobiographies. They are written from actual experiences and hence are most reliable to recover the grievances of a subaltern class. Thus the research entitled Unveiling the Utterance of a Subaltern Class: Analysis of Selected Transgender Autobiographies from India attempts to address the subaltern sentiments expressed by Indian trans community through their own self-writings. The Truth about Me: A Hijra Life story and A Life in Trans Activism by A Revathi, Me Hijra, Me Laxmi and Red Lipstick: The Men in My Life by Laxminarayan Tripathi, A Gift of Goddess Lakshmi [2] by ManobibBandyopadhyay and I Am Vidya: A Transgender's Journey by Living Smile Vidya are the selected autobiographies for the study. In the course of discussion many sub and related topics like position of transgender in Indian literature [3], potentiality of transgender self-writings, long-term battle of transgender for recognition and acceptance, transgender rights in India will be carefully considered. [4-8]

(A) Objectives

The research basically aims at a study of selected transgender autobiographies from India using subaltern theory. The chief objectives of research are to:

1. Analyze the position of transgender and their autobiographies in Indian literature.

2. Appreciate the literary potential and reformative power of transgender self writings from India.

3. Create awareness among public about the problems faced by transgender and call for a fair and equal treatment of such a community using a subaltern study of selected autobiographies.

4. Discuss the protection offered by Indian government for such a community and how far it is realized.

5. Identify the physical, biological, psychological and sexual difference of transgender from other communities which marks them as a separate class.

6. Discuss whether there is a need for separate category called transgender or third-gender.

7. Provide a subaltern analysis of selected transgender autobiographies and study whether transgender are able to express themselves and their issues without outside agents.

8. Offer some suitable suggestions and solutions for their problems.

II. SUMMARY OF FINDINGS BY SEVERAL WRITERS

Table 1 summarises the contributions of various authors in the discussion of issues and concerns of transgender community in India.

Table 1: Related Works

SN	Author	Date	Findings
1	Raja, Gopika A., &Indu, B. [9]	(2020)	Attempted to study on the traumatic lives of the hijra community and how they encounter the stigma in society with particular reference to LaxminarayanTripathi`s Me Laxmi

			Me Hijra.
2	Cholakkal, Sajeera [10]	(2019)	Focuses on day to day issues and challenges the 'transformed' Vidya came across in her strenuous journey to self-identity, and the predicaments transgender community face when they do not conform to the prevailing expectations about gender in society.
3	Chowdhury,Payel Dutta., &Bhattacharjee, Shreoshi [11]	(2018)	Attempts to throw light on the prejudices and preconceived notions that the society has about the non heterosexuals, particularly the transgender.
4	Lakshmi, Suba P., Mangaiyarkarasi[12]	(2019)	Attempts to show how Manobi faces the struggles and comes out of the crisis to achieve greatness in the society
5	Das, Rajorshi[13]	(2015)	Explores at Laxmi Narayan Tripathi's autobiography Me Hijra Me Laxmi as an important intervention in the debates about what constitutes Indian transgender idendity.
6	Subapriya,K. [14]	(2016)	Focuses on the pathetic state of transgenders in India through the autobiography of an individual Vidya who had a transition from being a man to woman.
7	Baruah, Pallabi [15]	(2016)	Studies how the transgendered identity has been significant to queer theory since the figure of the transgender

			made possible the merging between the gay and the lesbian, giving rise to a different type of homosexuality and thereby broadening its horizon.
8	Dwivedi, Vachaspati [16]	(2016)	Attempts to study the life, culture, desires, trauma and pain of transgender exclusion at the hands of dominant culture.
9	DeBoxi, Chanchal [17]	(2018)	Shows how the transgender people as a distinct category suffer marginalization, oppression as well as colonization in every sphere of their lives at the hand of hetero normative society.
10	T.A, Kavitha [18]	(2019).	Focuses on the identity crisis faced by Indian Hijras.

III. RELATED WORKS

Raja, Gopika A., &Indu, B. (2020) [9] have attempted to study on the traumatic lives of the hijra community and how they encounter the stigma in society with particular reference to LaxminarayanTripathi`s Me Laxmi Me Hijra. A striking feature of Laxmi`s narration is the inherent struggle for making the hijra community visible and audible from the obscurity of vulnerable silence.

Cholakkal, Sajeera.(2019) [10]focuses on day to day issues and challenges the ‘transformed’ Vidya came across in her strenuous journey to self-identity, and the predicaments transgender community face when they do not conform to the prevailing expectations about gender in society.

Chowdhury,Payel Dutta., &Bhattacharjee, Shreoshi. (2018)[11] attempts to throw light on the prejudices and preconceived notions that the society has about the non heterosexuals, particularly the transgender. The transgender or hijra are in a constant battle against the world for their social acceptance and also for their identity crisis. This paper deals with Revathi's autobiography The Truth about Me: A Hijra Life Story from the similar perspective where Revathi struggles to establish her real identity in the society.

Lakshmi, Suba P., Mangaiyarkarasi, (2019) [12] discuss education shapes one's life and gives upliftment. Many transgender persons try to come out of their restricted cage to spread out their wings in flight. Only few transgender people like ManobiBandyopadhyay have come out successfully breaking the shackles of the society. Education and family support alone have helped her to assert her identity and she has become a representative and voice of her community. The paper entitled Voice of a Trans Woman in ManobiBandyopadhyay's A Gift of Goddess Lakshmi is an attempt to show how Manobi faces the struggles and comes out of the crisis to achieve greatness in the society.

Das, Rajorshi.(2015) [13] explores at Laxmi Narayan Tripathi's autobiography Me Hijra Me Laxmi as an important intervention in the debates about what constitutes Indian transgender idendity. Using literary and cinematic works by contemporaries of Laxmi Narayan Tripathi, the writer argues that while the categorisation of the 'third gender' may be necessary to facilitate governmental policies for the community, one has to look beyond law as a legitimizing tool as evident from the uniqueness of Laxmi's 'celebrification' and its impact within Queer activism.

Subapriya,K. (2016) [14] focuses on the pathetic state of transgenders in India through the autobiography of an individual Vidya who had a transition from being a man to woman. The study of autobiography I am Vidya: A Transgender's Journey raises key issues about the status of transgender in India, their identity and the struggle for the survival. The reading of this autobiography expands the role of autobiography. It is not a mere record of the memories and the experience but it is a record of the common plight of several transgender who suffer severe forms of marginalization in the society. The future of autobiographies lies in this sort of text that has a cause and effect. The autobiography of Transgender Vidya is the voice of the voiceless of every transgender in India who constantly faces harassment and atrocities in current scenario despite the awareness and good will spread about them. The very existence in this earth becomes a question mark without the strong support of the family, society and government.

Baruah, Pallabi.(2016) [15] studies the autobiography of a transgender writer from India and attempts to analyse how trans narratives tend to be body narratives, wherein the somatic transitions which hold great significance in trans lives also becomes the central focus in their autobiographies and also how it involves a will to compose a self, literally, a self which they intend to express in the autobiography, out of the many selves and eventually how it becomes political, the will to be heard and accepted, rather than merely being treated as site markers of non-binary gender systems. The paper also studies how the transgendered identity has been significant to queer theory since the figure of the transgender made possible the merging between the gay and the lesbian, giving rise to a different type of homosexuality and thereby broadening its horizon.

IV. NEW RELATED ISSUES

i) Transgender in Public domains: inclusion and exclusion.

ii) Pandemic and the troubles faced by Indian trans community.

iii) Legal status of transgender in India.

iv) Media and gender issues.

v) Relevance and irrelevance of the categorization called ‘third gender’.

V. RESEARCH GAP

It has been identified that though much research is done on identity crisis, trauma, discrimination, social exclusion and otherness faced by transgender with the help of their self-writings, limited study is available on addressing the subaltern sentiments of trangender community in India. Thus the research paper *Unveiling the Utterance of a Subaltern Class: Analysis of Selected Transgender Autobiographies from India* tries to fulfill this gap by discussing about the transgender as a subaltern class in Indian society even today and voicing their utterance silenced and suppressed by our gender norms and rules. [19-35]

VI. RESEARCH AGENDAS

The agenda of the research entitled *Unveiling the Utterance of a Subaltern Class: Analysis of Selected Transgender Autobiographies from India* aims at a qualitative study of selected transgender autobiographies from India for understanding their position as a subaltern class within the society even in these days. Subaltern theory will be used for the dissertation as an efficient tool in unveiling the utterance of transgender who are denied to speak out their agonies even today or are considered as figures to be mocked at in front of the gender ideologies of our society. Thus through such a research, voicing the trauma of a voiceless class, creating awareness among public about the depressed lives of trans people, calling for a revolution in gender ideologies and insistence on the inclusion of third gender along with the existing binary divisions of gender will be the major research agendas.

VII. RESEARCH PROPOSAL

The research entitled *Unveiling the Utterance of a Subaltern Class: Analysis of Selected Transgender Autobiographies from India* addresses the issues of transgender community as a subaltern class in Indian society. The invisibility of transgender in many public domains will be seriously considered for the study. Though many studies have been conducted in the past about transgender, a very few research is available on revealing the subaltern voice of transgender whose journey from margins to centre of Indian society is still unachieved. Thus the main concern of this research is to reveal the true subaltern voice of transgender community as expressed through the autobiographies. The research is hoped to benefit the transgender community by making public aware about their trauma within the gender constructs of Indian society.

VIII. SUGGESTIONS

Transgender will be able to live a peaceful life only when society builds a space for them within the gender constructs which assigns to each individual basic codes of behaviour and if anyone goes against this they are termed outcast. Change in such a prejudiced gender notion will only ensure a secured life for the trans people within India.[36-51]

IX. LIMITATONS

The limitations of present study include:

i)Reliance on translated autobiographies other than on actual writings in regional language of trans writers for the research.

ii)Lack of reliable sources discussing historical and political struggle of transgender in India.

iii)Invisibility of transgender in Indian elite literature of the past.

iv)Unavailability of trustworthy studies on biological, physical, psychological, sexual and mental aspects of transgender.

X. CONCLUSION

Every institution of Indian society be it family, marriage, religion, caste, schools, or colleges need to realize that gender is a socially constructed notion about how each sex should behave in the society and such notion may falls against the actual gender feelings of some class. Transgender are such a category of people whose gender identity or gender expression differs from the sex that they were assigned at birth and thus are considered to be outcast in front of the established gender norms proposed by the society. But we must realize transgender as people with their own whims and fancies which need to be respected and accepted like that of other's in a society. Transgender autobiographies vehemently oppose myriad forms of discrimination in the name of gender. A reading of them will make us realize the level of oppression they faces from different realms of Indian society which curtail their freedom to fly. Thus a research about them is truly necessary for people to realize the suppressed lives of trans community and call for a revolution to up bring them from their subaltern or subordinate levels.

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Shielding Transgender Persons: An Analysis of Transgender Rights in India

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Shielding Transgender Persons: An Analysis of Transgender Rights in India

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ABSTRACT

Purpose: *Indian society is undoubtedly known for its lawfulness and strict observance of legal principles. But socially constructed norms about gender in India displaces many sections outside the gender binaries as outcaste and such a placement of gender fluidity outside the mainstream can damage the legality of India. Only a genuine awareness and recognition of laws and rights of each section can ensure proper functioning of government. But the stark reality in India, as in many other parts is that people are unaware of or fail to observe the basic rights of different sections. Transgender community is one of the important sections facing extreme level of legal discrimination from public. Traditionally believed and followed notions about transgender community hinder people from considering them as normal. They are always positioned as the other in terms of the gender. This kind of otherness felt by transgender from their own society often turns into a weapon capable of destroying their very existence. Thus there is a growing necessity to educate the masses about the basic rights and legal protection offered by Indian constitution for such a community. An earnest attempt to accommodate such a class as normal and not as the other should come from every citizen who are part of a democratic country like India. Thus the paper entitled 'Shielding Transgender Persons: An Analysis of Transgender Rights in India 'attempts to highlight the legal rights of gender minorities thereby creating proper attention to the same.*

Design: *The article is prepared by collecting information from secondary sources such as peer-reviewed journals, National and International Publications. Internet sources, and research sources like Google Scholar, Research Gate, SSRN, Elsevier, Academia, and Shodhganga are used for identifying the research gap. To highlight the key aspects of the research ABCD analysis is used. Data is acquired from research journals, doctoral theses, scholarly articles, and websites to carry out the research that has been proposed. Concentrating on the keywords Transgender, Transgender in India, Transgender Rights, Legality, and Lawfulness, Gender fluidity, Gender Binaries, of the chosen topic, the methodology used depends mostly on collecting, analyzing, and interpreting previous knowledge. The textual analysis and comparative method will be used in the methodology. There will be a close reading of the select works of Transgender writers followed by discussions on related issues. Writing research papers and participating in conferences on the subject are also aimed at. While conducting the analyses of the study, APA Manual has been followed to adhere to its requirements.*

Findings: *It has been found out that limited study is available regarding the real rights of transgender population in India, thus a paper discussing the legal protection offered for such a minority in India is very essential for educating public about the need to provide humane treatment for such a class within the gender divisions.*

Originality: *The proposed study focuses primarily on the constitutional rights offered to the transgender community in India and the measure of its realization by different gender sections. An awareness created through this paper which manages to be an original one about the rights* *for such a community is primarily intended to ensure safe and secure survival of Indian transgender. Equal treatment of different gender categories is a must for any society aiming to be democratic in its principles and procedures.*

Paper Type: *Research Article*

Key Words: Transgender, Transgender in India, Transgender Rights, Legality, and Lawfulness, Gender fluidity, Indian Gender Binaries, ABCD Listing

1. INTRODUCTION :

Indian society regarded transgender highly during ancient times. They were believed to have many divine powers and their presence for auspicious occasions was approved wholeheartedly. Indian mythology, religious textbooks, legal writings, epics, and scriptures placed the third gender at the topmost positions and honored them with all due respect. But the current situations reveal a series of agonies faced by them from the heterosexual gender regulations of Indian society. Though there are laws in support for such a community, even transgender are themselves unaware of their fundamental rights. Many fail to treat them even as human beings and they are subjected to harsh discrimination and injustice [1][2][3].

2. RELATED WORKS :

The keywords used to search the literature are Transgender, Transgender in India, Transgender Rights, Legality, and Lawfulness, Gender fluidity and Indian Gender Binaries ranging from the years 2005-2022. The search engines used for the search are Google Scholar, Research Gate, SSRN and Academia.edu.

Table 1: Related works on Transgender, Transgender in India, Transgender Rights, Legality, and Lawfulness, Gender fluidity and Indian Gender Binaries

S.No	Focus	Outcome	Reference
1.	Transgender	Talks about transgender theory, which was a model developed to acknowledge the existence of transgender community or accept gender fluidity.	Sullivan, K. M. [4].
2.	Transgender in India	Discusses in detail the bisexual, gay, lesbian, transgender human rights for developing an international strategy.	Swiebel, J. [5].
3.	Transgender Rights	Gives a detailed analysis of transgender history, politics and identity and suggests changes that are needed for such a community.	Reis, E. [6].
4.	Legality	Discusses the steps to ensure the welfare of transgender community in India.	Jain, A. K., & Rhoten, K. M. [7].
5.	Lawfulness	Provides an understanding about third gender category in India with particular focus the lawfulness of Indian constitution.	Prakash, L. O., & Karunanithi, G. [8].
6.	Gender Fluidity	Gender identity and the underlying causes for gender fluidity is analysed in detail using many evidences and explanations from psychiatry and medical science.	Sawant, N. S. [9].
7.	Indian gender binaries	Discusses the complexities associated with gender norms and regulations in India.	Kannabiran, K. [10].

3. RESEARCH GAP :

According to the literature review many studies have been conducted about the transgender community in India, but very few works talk about the actual legal rights for the transgender community and the extent to which it has been realized.

4. OBJECTIVES OF THE STUDY :

The chief objectives of the paper are as follows:

(1) Analyze the legal protection offered in India for transgender community.

(2) Evaluate how far the rights are realized for such a community.
(3) Suggest ways to improve the status of transgender in India
(4) Educate people about the atrocities faced by transgender community in India.
(5) ABCD Analysis to analyze the individual characteristics and check the effectiveness of a concept or idea.

5. METHODOLOGY :

The paper entitled 'Shielding Transgender Persons: An Analysis of Transgender rights in India ' is an explorative research article trying to explore the question of discrimination faced by third gender in spite of legal protection offered to them in India. Though many talked about the laws for such a section, very few researches reveals the disparity between the existence of laws and exploitation of transgender. Thus, the article is an explorative study using search engines like Google Scholar, Research Gate, SSRN and Academia.edu to search authentic records to reveal such an irony between what is believed to be about the transgender in the light of laws but what is actually felt by them in society.

6. ANALYSIS OF LEGAL PROTECTION OFFERED IN INDIA FOR TRANSGENDER COMMUNITY :

The section titled 'Analysis of legal protection offered in India for transgender community' focuses on an intensive analysis of the place of transgender communities in India across different timeframes.

6.1 Ancient India

Indian society recognized and accepted the third gender from ancient times in one way or the other. Ardhnareeshwara sangalpa of Lord Shiva and Mohini avatar of Lord Vishnu in Indian mythology highlight the importance of equality of genders. Similarly Ramayana places them as loyal servants who were granted the power to bless others by Lord Rama himself. Mahabharata on the other hand is noted for characters like Shikandi and Brihanalla. There is also a mentioning about transgender monks called 'Vinaya Pataka' in Buddhist Pali texts whereas Shaun Marmon's book *Eunuchs and sacred boundaries in Islamic society* talks about eunuchs guarding the tomb of Prophet Muhammad. Thus ancient India always regards third genders highly and respects them or praises them for their loyalty, cleverness, trustworthiness and other qualities [11][12][13][14].

6.2 Mughal period

The Hijras played a pivotal role in the royal courts of the Islamic world. They were also having prominent positions during the Ottoman empires and the Mughal periods. Third genders equally adorned titles like political advisors, administrators, generals and guardians of the harems. But in spite of such things, during the Mughal Empire, a set of punishments were enforced for zina (unlawful intercourse) which included homosexuality. These could include 50 lashes for a slave, 100 for a free infidel or death by stoning for a Muslim. With the end of Mughal Empire and arrival of the British East India Company the third gender in India experienced worst level of humiliation and discrimination [15][16].

6.3 British Raj

British totally marginalized sexual and gender minorities. They expressed serious opposition and criticism towards the gender expressions of hijras. In the 1864, the British applied the British Buggery Act of 1533 to India to criminalize non-procreative sexuality, which mainly targeted the hijras. Criminalization of homosexual activity was enacted by Section 377 of Indian Penal Code by the British in 1860 which stood for more than 70 years after Independence. In 1871, British labeled hijra population as a criminal tribe. They were declared an ex-criminal tribe and were not allowed to hold jobs, were prohibited from dressing as women or performing in public places. Basic agenda was obviously to exterminate them [17][18].

6.4 Post Independence

From the 20th century onwards some hijra activists and NGOs called for official recognition of the hijra as third gender or third sex and voting rights. All India Hijra Kalyan Sabha fought for over a decade to get voting rights which they got in 1994.Shabnam Mausi is the first transgender Indian to be elected to public offices. She was the elected member of Madhya Pradesh State Legislative Assembly from 1998-2003. In 2003, hijras in Madhya Pradesh announced establishment of their own political party called Jeeti Jitayi Politics (JJP). The Delhi High Court decision of 2009 found Section 377 of IPC & other legal prohibitions against private, adult, consensual & non-commercial same-sex conduct to be in direct violation of fundamental rights provided by Indian Constitution. In 2014, the Supreme Court of India recognized hijras, transgender, eunuchs and intersex people as third gender in law. Justice K S Radhakrishnan said that transgender should be treated consistently with other minorities under the law, enabling them to access jobs, healthcare and education. In 2015, Manobi Bandopadhyay became India's first transgender college Principal (Krishnanagar Women's College, West Bengal)Real Estate Act 2016 outlawed discrimination in housing on the basis of religion, caste, gender, sexual orientation, marital status & dietary preference. Discrimination, ragging, bullying at a student on the basis of sexual orientation or gender identity is prohibited under UGC Regulation on Curbing Ragging in Higher Educational Institutions (3rd Amendment) 2016. In 2018, in the landmark decision of Navtej Singh Johar versus Union of India, the Supreme court of India decriminalized consensual homosexual intercourse by reading down Section 377 of the Indian Penal Code & excluding consensual homosexual sex between adult from its ambit. Transgender Persons Act 2019 bans discrimination against transgender people in educational establishment & services, employment, healthcare services & access to goods & services, right to movement, purchase, reside, rent or occupy property. On 4 February 2021 Allahabad High Court ruled that firing & discriminating a person on the basis of sexual orientation is a violation of Supreme court judgement. Tamil Nadu & Kerala were the first Indian states to introduce a transgender welfare policy according to which they can access free sex reassignment surgery in government hospitals, free housing, admission in government colleges with scholarship for higher studies, etc. Article 15 of Indian Constitution prohibits discrimination on the ground of religion, race, caste, sex or place of birth. In case of physical attacks against LGBT people Section 307 (attempt to murder) and Section 323 (voluntarily causing hurt) of Indian Penal Code and in case of hate speech Section 153 A (Hate Speech Law) of IPC has been used. Current Situation [19].

7. EVALUATING HOW FAR THE RIGHTS ARE REALIZED FOR SUCH A COMMUNITY:

An analysis of the crimes committed against the transgender community reveals the stark reality that in spite of the existence of many laws to protect and safeguard gender minorities, nothing of notable relevance is acquired to ensure the secured lives of gender divisions. Even today the number of transgender registering for studies in educational institutions, applying for the allocation of safe sex reassignment surgery at government hospitals, appearing for reputed jobs are too low. We find them still wandering in the streets at night as sex workers or during day time as beggars or thieves or censured as criminals by the public. Though there are many reputed transgender persons in different realms like film, makeup industry, politics and social work, the number is not equal to those who are suffering from gender norms. Thus a sea change is needed to uplift them to the central focus of various arenas [20].

8. SUGGESTING WAYS TO IMPROVE THE STATUS OF TRANSGENDER IN INDIA :

(1) Practicing what is preached in democratic ideals of each society for gender minorities.
(2) Authorizing lawfulness of constitution.
(3) Analyzing and eradicating heinous crimes against gender categories.
(4) Punishing gender discrimination and methods of unequal treatment of people based on man made divisions like class, caste, religion, gender, language, region or economy.
(5) Providing reservations for minorities who are given limited chances by heteronormative societies. [21]

9. EDUCATING PEOPLE ABOUT THE ATROCITIES FACED BY TRANSGENDER COMMUNITY IN INDIA :

- 2003- a hijra was gang raped in Bangalore and then gang raped by the Police.
- 2007- a gay man was abducted by Delhi Police & raped by police officials for several days.
- 2011- in Haryana a lesbian couple was murdered by their nephews.
- 2018- a lesbian couple committed suicide saying "the world did not allow us to stay together".
- 2020- a young transgender woman Alka, was killed by two men who felt so angry that they decided to punish Alka by mutilating her genitalia and then killing her.

- September 2021- A 17-year-old transgender girl was murdered in Tamil Nadu's Salem district by her brother who did not approve of his sibling's gender identity.
- December 2021- A 31-year-old transgender was attacked and found dead in Cuddalore district of Tamil Nadu.
- LGBT are still banned from openly serving in Indian Armed forces [22][23][24][25].

10.ABCD ANALYSIS :

In qualitative company analysis, after choosing various issues to be analysed in a company, one can list important advantages, benefits, constraints, and disadvantages of every identified determinant issues. This will also give the basic idea and can be considered as the predefined condition for ABCD analysis and is named as ABCD listing. The variation in ABCD analysis called ABCD listing is a **qualitative discussion method.** ABCD listing consists of a listing of advantages, benefits, constraints, and disadvantages of the usage of the system/model. The purpose of this study is to analyze these five indices using a novel method of qualitative analysis of a system or notion known as ABCD analysis/listing. Analyzing the planned study with the ABCD Analysis framework is a good concept that needs some serious thought [26].

In this paper, a qualitative analysis of a system or concept termed ABCD analysis framework/listing to investigate these five indices developed by, Aithal, P.S. is used to find out the advantages, Benefits, Constraints, and Disadvantages of the research. Below is a qualitative analysis of the proposed research using ABCD Analysis [27].

Table 2: List of References for ABCD Analysis used in the paper [26][27]

S.NO	FIELD OF RESEARCH	FOCUS	OUTCOME	REFERNCE
1.	Use of ABCD framework	Analyzing, evaluating a business model, concept, product, strategy, or system can be accomplished with the use of the ABCD framework. It is made use of to evaluate the results of their research projects, in a wide variety of academic subjects	Online services advantages and significance of the company.	Frederick, D.P., & Bhat, G., (2022). [26]
2.	ABCD analysis and listing	Several new research indices, such as the ARP-index (Annual Research Publication Index), RE-Index (Research Expansion Index), RCIndex (Research Continuation Index), cost index, and Project Productivity Index are used to measure the research productivity of both individuals and teams within an organization. We have attempted to analyse these five indices in this study using our unique approach of qualitative analysis of a system or notion known as ABCD analysis/listing	Understanding the use of several research indices.	Aithal, P. S. (2017). [27]

Advantages: The paper is aimed to be advantageous to the transgender community in particular to know about the rights from legal system and protect it for betterment and the public in general to be aware of the status of gender minorities before law.

Benefits: The paper aims to be beneficial as a true portrayal of agonies of transgender community and authentic representation of lawfulness of Indian constitution before different minority sections.

Constraints: Lack of reliable and plentiful sources about legal rights of gender minorities for better learning and analysis formed as a main barrier for the research.
Disadvantages: Though there are many researches discussing about the rights of transgender in India, still something highly valuable is unachieved as far the current situation of transgender is taken into consideration. Still many violence is faced by transgender community in and outside their own gender [28].

11. FINDINGS :

The paper reveals the discrepancy between legal system and societal system in terms of transgender. When the former supports them through laws, the latter oppresses them through various restrictions. A proper analysis of transgender laws and rights and clear uncovering of the exploitation shows this disparity clear to the public and teach them how far they are removed from justice and equality as such a section is crushed seriously based on the gender rules formulated by Indian society [29][30].

12. CONCLUSION :

It is clearly evident that despite the existence of many laws and rules in support of gender or sexual minorities, many are suffering under the harsh forms of oppression. Crimes committed against them reveal the range of discrimination and violence that they faced. Thus there is a high disparity between what is proposed by the law and what is observed in reality.

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Spectroscopic, charge transfer interaction and docking studies of gardona insecticide

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ABSTRACT

The aim of this study is to provide deeper knowledge of structural activity, spectroscopic analysis, chemical reactivity and insecticidal activity of gardona and its related compounds by combining experimental and computational methods. The natures of the hydrogen bonds were characterized by NBO analysis. Hirshfeld surfaces display all of the intermolecular interactions within the molecule. The ^{1}H and ^{13}C NMR spectra were recorded. The evaluated HOMO and LUMO energies indicate the chemical stability of the molecules. The molecular docking was made on the compounds to study the hydrogen bond interaction and the minimum binding energy. Insecticidal activities of extracts were determined against larvae of Corcyra *cephalonica.*

1. Introduction

Gardona is an organophosphate insecticide which is an effective foliar insecticide for a wide range of crops and particularly active against adult and larvial forms of lepidopterous pests [1]. It was used for external parasite of livestock and poultry for pests of fruits, vegetable on agricultural equipments. It is also added to soil before crop cultivation and is useful for control of flies in livestock manure. It is moderately toxic, affecting the respiratory system and is quickly incorporated into the body through the skin. Exposure to this organophosphate causes acetylcolinsterase inhibition and it is also responsible for carcinogenic problems, liver damage and damage to thyroid cells [2].

The structural features of organophosphate includes a terminal oxygen connected to phosphorous by a double bond, two lipophilic groups bonded to the phosphorous and a leaving group bonded to the phosphorous often a halide [3]. The word organophosphate refers to a group of insecticides or nerve agents acting on the enzyme acetylcholinsterase responsible for facility neurotransmission in many organisms. The present study is to understand the spectroscopic feature of gardona (TCVP) using experimental and theoretical studies. The related compounds such as 2–chloro-1-(2,4,5-trichloro phenyl)ethenyl) methyl hydrogen phosphate(TCHP) and 2–chloro-1-(2,4,5-trichloro phenyl) ethenyl dihydrogen phosphate (TCDP) have been selected to compare the structure activity study and bioactivity with TCVP by computational methods. To the best our knowledge no detailed spectroscopic studies of these compounds were performed.

2. Experimental methods

Gardona was purchased from Sigma-Aldrich (St. Louis, MO, USA) company with 99% purity and used without further purification. The FT-IR Spectrum of the sample was recorded using the Perkin Elmer Spectrometer in the range 4000–400 cm^{-1}. The FT-Raman spectrum in the range 3500–50 cm^{-1} was also recorded using a powdered sample. The ultra violet absorption spectra of gardona were examined in the range 800–200 nm using CARY 100 BIO UV visible - Spectrophotometer in acetone and dichloromethane solvents. Insecticidal activity of extracts were determined against larvae of Corcyra *cephalonica***.** The TCVP sample was prepared by dissolving different concentrations of extracts in acetone (6.25 mg,12.5 mg, 25 mg, 50 mgand 100 mg/ml) and loaded in a Petri dishes covered with the filter papers. After 24 hours, 10 test insects were placed in each plate and incubated at 27 °C for 24 hours with 50% relative humidity in growth chamber.

3. Computational methods

Gaussian 09 software package was used for theoretical calculation. The quantum chemical calculations were performed by

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applying DFT method with Becke3-Lee-Yang-Parr (B3LYP) supplemented with the standard 6–311G(d,p) basis set. The optimized geometry answering to the merest on the potential energy surface has been obtained by solving self consistent field equation iteratively. The computed wavenumbers are scaled by an empirical scaling factor of 0.9682 [4] to fit with the experimental wavenumbers. Chemical shifts were reported in ppm relative to tetramethylsilane for 1H and 13C NMR spectra [5]. Additionally the calculated vibration frequencies are clarified by means of potential energy distribution analysis of all fundamental vibrational modes by using VEDA 4 program [6].The natural bonding orbital (NBO) calculations were performed using NBO 3.1 [7] program. The TD-DFT method was used to calculate CAM-B3LYP/6–311 g (d,p) basis set. The frontier molecular orbitals and the HOMO-LUMO energy gap were computed and analysed. Hirshfeld surface map and the finger print plots were generated using the crystal explorer 3.1 program [8]. The hyperconjugative interaction energy was deduced from the second order perturbation approach [9]. The docking studies were performed using the molecular docking software, Auto Dock 4.2 [10].

4. Results and discussion

4.1. Structural analysis

The optimized geometry with atomic numbering scheme for TCVP and its related compounds were given in Fig.1. The experimental bond lengths bond angles and dihedral angles are shown in Table 1. It is observed that most of the optimized bond lengths are significantly larger than the experimental values, since the theoretical calculations belong to isolated gaseous molecules in gaseous phase and the experimental results belong to molecules in solid state [11].

The changes in frequency or bond length of C–H bond on substitution due to the change in charge distribution on the carbon atom of benzene ring. The substitution may be either of electron withdrawing or electron donating group. The carbon atoms are bounded to the hydrogen atom with σ bond in benzene and the substitution of a halogen for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atom resulting in an increase in C–H force constant and a deviation in the corresponding bondlength. The actual change in the C–H bond length would be influenced by the combined effect of the inductive mesomeric interaction and the electronic dipole field of polar substituent, In this study C–H bond length were calculated as 1.080 Å and 1.091 Å for ring and methyl group respectively. The C–Cl bondlength shows a considerable increase when substituted in the place of C–H. This has been observed even in benzene derivatives [12].

The central phosphorous atom is surrounded by four oxygen atoms in coordination geometry closely resembling a regular tetrahedron with P-O distance and O-P-O angle in the 1.532–1.534 Å and 109.7–119.7° respectively. In TCVP the C_{16}-P_{17} bond was lengthened was due to the attachment of vinyl and methoxy groups. Comparing TCVP and TCHP, the $P_{17}–O_{24}$ bondlength decreased due to the substitution of methyl group. In TCDP, the $P_{17}–O_{19}$ bond increased due to the presence of hydrogen atom. The bond $C_3–C_{11}$ in TCVP, TCHP and TCDP are 1.489, 1.485 and 1.484 Å respectively. The slight variation is due to the substitution of dimethyl phosphate, methyl hydrogen phosphate and dihydrogen phosphate groups.

In TCVP $C_{11}–O_{16}$ is (1.382 Å) shortened compared with other C–O bond, because of the substitution of trichlorophenyl ring. Due to the substitution of heavy atom (Cl) the ring angles are deviated from 120°. Bond angle $C_2–C_3–C_4$ is deviated from 120° because of the substitution of vinyl group. Comparing bond angle $O_{19}–C_{20}–H_{21}$ in TCVP and TCHP with TCDP the increase is due to C–H…O hyperconjugative interaction. In trichlorophenyl region, the TCVP and related compounds show that the bond angles $C_1–C_2–C_3$ (121.3°) and $C_3–C_4–C_5$ (121.4°) are slightly increased and the bond angle $C_2–C_3–C_4$ (118.0°) was slightly decreased. These deviations are occurred due to the influence of distortion in the aromatic character. In TCVP and its related compounds the dihedral angles $C_2–C_3–C_{11}–O_{16}$ (72.9°), $C_2–C_3–C_{11}–C_{12}$ (−104.2°), $C_4–C_3–C_{11}–O_{16}$ (−106.6°) and $C_4–C_3–C_{11}–C_{12}$ (76.3°) show non planar nature of phenyl ring with the dimethyl phosphate region.

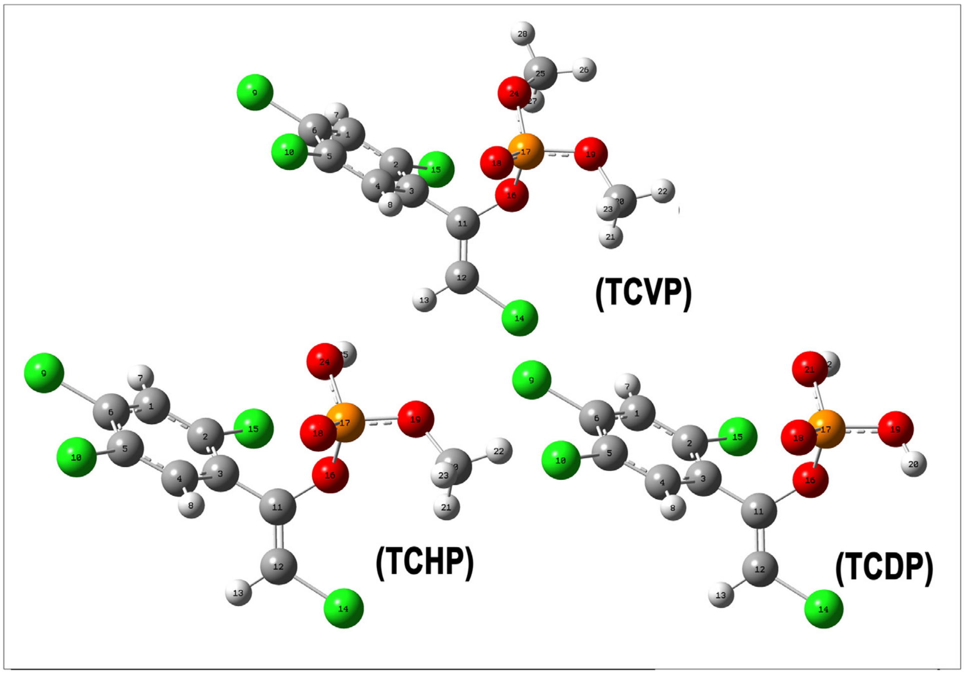


Fig. 1. Optimized geometry with atomic numbering scheme for TCVP and its related compounds.

Table 1
Optimized geometrical parameters of TCVP and its related compounds.

Bond Length	Experimental value (Å)	Calculated value (Å)		
		TCVP	TCHP	TCDP
C_1-C_2	1.380	1.387	1.387	1.387
C_1-C_6	1.381	1.393	1.393	1.393
C_1-H_7	0.930	1.081	1.081	1.081
C_2-C_3	1.376	1.401	1.402	1.403
C_2-Cl_{15}	1.729	1.753	1.754	1.754
C_3-C_4	1.389	1.396	1.397	1.397
C_3-C_{11}	1.485	1.489	1.485	1.484
C_4-C_5	1.376	1.391	1.391	1.391
C_4-H_8	0.930	1.081	1.081	1.081
C_5-C_6	1.182	1.397	1.397	1.397
C_5-Cl_{10}	1.736	1.743	1.743	1.742
C_6-C_{19}	1.726	1.743	1.742	1.742
$C_{11}-C_{12}$	1.310	1.331	1.333	1.333
$C_{11}-O_{16}$	1.392	1.382	1.380	1.383
$C_{12}-H_{13}$	0.930	1.0789	1.079	1.079
$C_{12}-Cl_{14}$	1.713	1.739	1.737	1.737
$O_{16}-P_{17}$	1.598	1.648	1.643	1.639
$P_{17}-O_{18}$	1.449	1.469	1.467	1.465
$P_{17}-O_{19}$	1.560	1.594	1.592	1.602
$P_{17}-O_{24}$	1.545	1.585	1.596	–
$O_{19}-C_{20}$	1.430	1.446	1.448	0.965
$C_{20}-H_{21}$	0.960	1.091	1.091	–
$C_{20}-H_{22}$	0.960	1.088	1.087	–
$C_{20}-H_{23}$	0.960	1.091	1.091	–
$O_{24}-C_{25}$	1.449	1.445	–	–
$C_{25}-H_{26}$	0.960	1.090	–	–
$C_{25}-H_{27}$	0.960	1.091	–	–
$C_{25}-H_{28}$	0.960	1.088	–	–

Bond angle	Experimental value (º)	Calculated value (º)		
		TCVP	TCHP	TCDP
$C_2-C_1-C_6$	120.4	119.9	120.0	120.0
$C_2-C_1-H_7$	119.7	120.4	120.3	120.3
$C_6-C_1-H_7$	119.8	119.8	119.7	119.7
$C_1-C_2-C_3$	120.8	121.3	121.3	121.2
$C_1-C_2-Cl_{15}$	118.6	118.3	117.9	117.9
$C_3-C_2-Cl_{15}$	120.6	120.5	120.8	120.8
$C_2-C_3-C_4$	117.8	118.0	117.8	117.8
$C_2-C_3-C_{11}$	122.1	122.3	122.9	122.9
$C_4-C_3-C_{11}$	120.1	119.6	119.3	119.2
$C_3-C_4-C_5$	121.3	121.4	121.6	121.6
$C_3-C_4-H_8$	119.3	119.1	119.1	119.1
$C_5-C_4-H_8$	119.4	119.5	119.3	119.3
$C_4-C_5-C_6$	120.3	119.5	119.5	119.5
$C_4-C_5-Cl_{10}$	119.6	118.9	118.9	118.9
$C_6-C_5-Cl_{10}$	119.4	121.6	121.6	121.6
$C_1-C_6-C_5$	119.3	119.9	119.8	119.8
$C_1-C_6-Cl_9$	118.1	118.4	118.5	118.5
$C_5-C_6-Cl_9$	122.6	121.7	121.7	121.7
$C_3-C_{11}-C_{12}$	123.5	121.2	121.4	121.9
$C_3-C_{11}-O_{16}$	116.6	117.8	118.2	118.1
$C_{12}-C_{11}-O_{16}$	119.9	120.9	120.3	119.9
$C_{11}-C_{12}-H_{13}$	118.9	121.9	121.9	122.1
$C_{11}-C_{12}-Cl_{14}$	122.0	123.9	123.8	123.5
$H_{13}-C_{12}-Cl_{14}$	119.0	114.2	114.3	114.4
$C_{11}-O_{16}-P_{17}$	122.3	121.6	122.6	122.5
$O_{16}-P_{17}-O_{18}$	113.8	113.3	113.9	114.3
$O_{16}-P_{17}-O_{19}$	100.9	100.3	99.8	99.6
$O_{16}-P_{17}-O_{24}$	105.9	105.4	105.4	–
$O_{18}-P_{17}-O_{19}$	118.4	119.2	119.8	119.6
$O_{18}-P_{17}-O_{24}$	112.9	114.7	114.2	–
$O_{19}-P_{17}-O_{24}$	103.4	102.1	101.5	–
$P_{17}-O_{19}-C_{20}$	120.9	121.1	120.9	113.7
$O_{19}-C_{20}-H_{21}$	109.4	109.9	109.9	–
$O_{19}-C_{20}-H_{22}$	109.5	105.9	105.9	–
$O_{19}-C_{20}-H_{23}$	109.5	110.1	110.1	–
$H_{21}-C_{20}-H_{22}$	109.5	110.2	110.2	–
$H_{21}-C_{20}-H_{23}$	109.5	110.4	110.4	–
$H_{22}-C_{20}-H_{23}$	109.5	110.1	110.1	–
$P_{17}-O_{24}-C_{25}$	123.5	123.2		–
$O_{24}-C_{25}-H_{26}$	109.4	109.9	–	–
$O_{24}-C_{25}-H_{27}$	109.5	110.3	–	–
$O_{24}-C_{25}-H_{28}$	109.5	105.8	–	–
$H_{26}-C_{25}-H_{27}$	109.5	110.4	–	–

Table 1
Continued.

Dihedral angle	Experimental value (º)	Calculated value (º)		
		TCVP	TCHP	TCDP
$C_6-C_1-C_2-C_3$	1.4	0.2	0.04	0.0
$C_6-C_1-C_2-Cl_{15}$	176.8	178.8	178.2	178.2
$H_7-C_1-C_2-C_3$	178.5	−179.3	−179.3	−179.3
$H_7-C_1-C_2-Cl_{15}$	−3.4	−0.6	−1.1	−1.2
$C_2-C_1-C_6-C_5$	−1.6	0.0	0.1	0.1
$C_2-C_1-C_6-Cl_9$	176.9	−179.9	−179.9	−179.8
$H_7-C_1-C_6-C_5$	178.6	179.5	179.5	179.5
$H_7-C_1-C_6-Cl_9$	−2.9	−0.4	−0.5	−0.5
$C_1-C_2-C_3-C_4$	2.7	−0.6	0.6	−0.6
$C_1-C_2-C_3-C_{11}$	177.3	179.9	179.7	179.9
$Cl_{15}-C_2-C_3-C_4$	−175.4	−179.2	−178.7	−178.7
$Cl_{15}-C_2-C_3-C_{11}$	4.6	1.3	1.5	1.8
$C_2-C_3-C_4-C_5$	−1.2	0.8	1.0	1.06
$C_2-C_3-C_4-H_8$	178.7	−177.3	−177.3	−177.2
$C_{11}-C_3-C_4-C_5$	178.8	−179.7	−179.2	−179.4
$C_{11}-C_3-C_4-H_8$	−1.3	2.3	2.5	2.4
$C_2-C_3-C_{11}-C_{12}$	−120.8	−104.2	−116.8	−118.9
$C_2-C_3-C_{11}-O_{16}$	56.9	72.9	60.7	58.7
$C_4-C_3-C_{11}-C_{12}$	59.2	76.3	63.5	61.5
$C_4-C_3-C_{11}-O_{16}$	−123.1	−106.6	−119.1	−120.8
$C_3-C_4-C_5-C_6$	−1.7	−0.6	−0.9	−0.9
$C_3-C_4-C_5-Cl_{10}$	179.5	179.8	179.8	179.8
$H_8-C_4-C_5-C_6$	178.4	177.5	177.4	177.3
$H_8-C_4-C_5-Cl_{10}$	−0.44	−2.2	−1.9	−1.9
$C_4-C_5-C_6-C_1$	3.1	0.2	0.3	0.3
$C_4-C_5-C_6-Cl_9$	−175.3	−179.9	−179.7	−179.7
$Cl_{10}-C_5-C_6-C_1$	−178.1	179.8	179.7	179.6
$Cl_{10}-C_5-C_6-Cl_9$	3.6	−0.3	−0.4	−0.4
$C_3-C_{11}-C_{12}-H_{13}$	2.3	1.8	2.8	3.3
$C_3-C_{11}-C_{12}-Cl_{14}$	−177.6	−179.4	−178.3	−177.7
$O_{16}-C_{11}-C_{12}-H_{13}$	−175.3	−175.3	−174.5	−174.4
$O_{16}-C_{11}-C_{12}-Cl_{14}$	4.7	3.6	4.3	4.7
$C_3-C_{11}-O_{16}-P_{17}$	73.6	60.8	56.1	59.5
$C_{12}-C_{11}-O_{16}-P_{17}$	−108.6	−122	−126.4	−122.8
$C_{11}-O_{16}-P_{17}-O_{18}$	24.9	25.9	31.6	28.4
$C_{11}-O_{16}-P_{17}-O_{19}$	152.9	154.1	160.6	157.1
$C_{11}-O_{16}-P_{17}-O_{24}$	−99.6	−100.2	−94.4	–
$O_{16}-P_{17}-O_{19}-C_{20}$	−84.9	−72.5	−71.7	–
$O_{18}-P_{17}-O_{19}-C_{20}$	39.97	51.7	53.4	–
$O_{24}-P_{17}-O_{19}-C_{20}$	165.6	179.1	−179.8	–
$O_{16}-P_{17}-O-_{24}-C_{25}$	−58.3	−56.9	–	–
$O_{18}-P_{17}-O_{24}-C_{25}$	176.6	177.8	–	–
$O_{19}-P_{17}-O_{24}-C_{25}$	47.5	47.5	–	
$P_{17}-O_{19}-C_{20}-H_{21}$	−140.8	64.9	67.8	–
$P_{17}-O_{19}-C_{20}-H_{22}$	−20.7	−176	−173.1	–
$P_{17}-O_{19}-C_{20}-H_{23}$	99.3	−56.9	–	–
$P_{17}-O_{24}-C_{25}-H_{26}$	43.3	−63.9	–	–
$P_{17}-O_{24}-C_{25}-H_{27}$	163.3	57.9	–	–
$P_{17}-O_{24}-C_{25}-H_{28}$	−76.7	176.9	–	–

4.2. Vibrational analysis

The vibrational spectral analysis has been performed on the basis of the characteristic group vibrations of phenyl ring, dimethyl phosphate group vinyl group and C–Cl vibration. The experimental (TCVP) and calculated (TCHP and TCDP) wavenumber along with their respective dominant normal modes and the corresponding Potential Energy Distribution (PED) [13] are presented in Supplementary Table S1. The observed and simulated FT-IR and Raman spectra of TCVP are shown in Figs. 2 and 3 respectively.

4.2.1. Ring vibration

In TCVP heavy atom chlorine is substituted at the positions 2, 5 and 6 and vinyl group is substituted at the positions 3. Vibrations of these heavily substituted groups have been extensively studied by adopting Wilson's scheme [14]. The selection rules allow five normal modes 12,8a, 8b, 14 and 19a for the tangential C–C stretching in benzene derivatives. It is well established that the wavenumber of mode 8b is more substituent sensitive and it

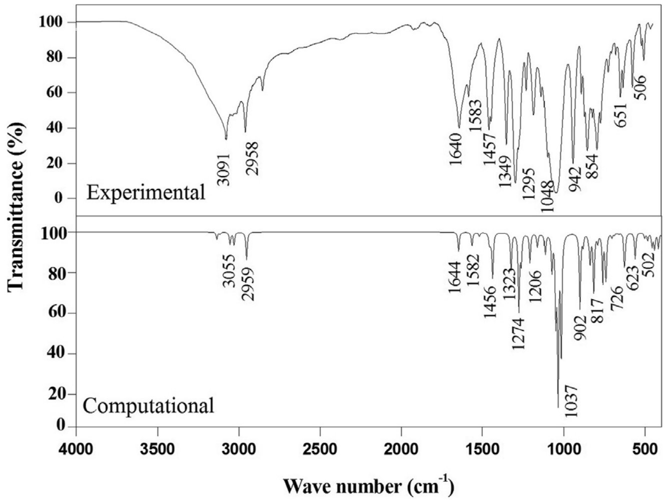
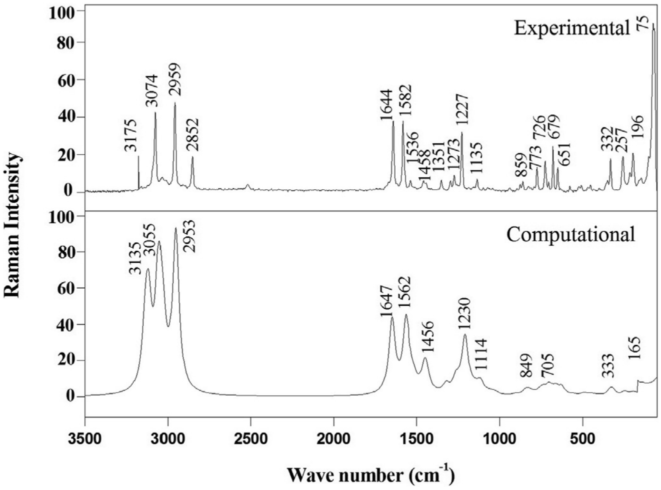


Fig. 2. Combined FT-IR spectrum of TCVP.



Fig, 3. Combined FT-Raman spectrum of TCVP.

is higher than that of 8a. The mode 8b manifests as strong band in Raman at 1552 cm^{-1} and mode 8a is observed as a weak band at 1582 cm^{-1} in Raman. Corresponding IR bands are observed at 1583 cm^{-1} as weak band. The intensity of this mode independent on the algebraic difference of the electronic effects of the substituent, which is justified by the large intensity difference observed between 8a and 8b modes in the IR spectrum. In addition, the experimental wavenumber of the 8b and 8a modes are higher than the computed result, which indicates the strengthening of C–C bonds of phenyl ring in the crystalline state [15].

Mode 19a is identified as a very intense band at 1349 cm^{-1} in IR and weak band at 1351cm^{-1} in Raman. Computation result shows that 19a modes have a strong coupling with the vibration of the substituent. The simultaneous IR and Raman activation of the phenyl ring modes of 8 and 19a also provide evidences for the charge transfer interaction between the donor and the acceptor group through the π system [16]. In chlorine substituted polysubstituents, vibrational mode 14 appears in the region from 1260 to 1200 cm^{-1}. Observed intense band at 1227 cm^{-1} in Raman is attributed to mode 14. In-plane bending skeletal vibration mode 12 is expected to occur in the regions 1070–1000 cm^{-1} [14]. The mode 12 vibration is observed as a strong band at 1048 cm^{-1} in IR. The theoretically predicted value is found to be at 1050 cm^{-1}. Mode 13 is observed in the region 3110–3060 cm^{-1} and the corresponding calculated value was obtained at 3115 cm^{-1}. CH out-of-plane deformation vibration is expected in the region 850–790 cm^{-1}. A strong band is observed at 795 cm^{-1} in IR and the corresponding calculated value is obtained at 793 cm^{-1}.

4.2.2. *C–Cl vibration*

The vibrations belonging to the bond between the ring and halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of molecular symmetry and the presence of heavy atom of the molecule. Mooney assigned vibrations of C-X group in the frequency range of 1129–480 cm^{-1} [17]. The C–Cl vibrations give generally strong bands in the regions 710–505 cm^{-1}. Compounds with more than one Cl atom exhibit very strong band due to the asymmetric and symmetric stretching modes [18]. Vibrational coupling with other group may result in a shift in the absorption as high as 840 cm^{-1}. For simple organic chlorine compounds C–Cl absorption is in the region 750–700cm^{-1}. In the present study the C–Cl vibrations are observed at 773,577 cm^{-1} in FT IR and 773,578 cm^{-1} in Raman. The corresponding calculated values are obtained at 762 and 560 cm^{-1}.

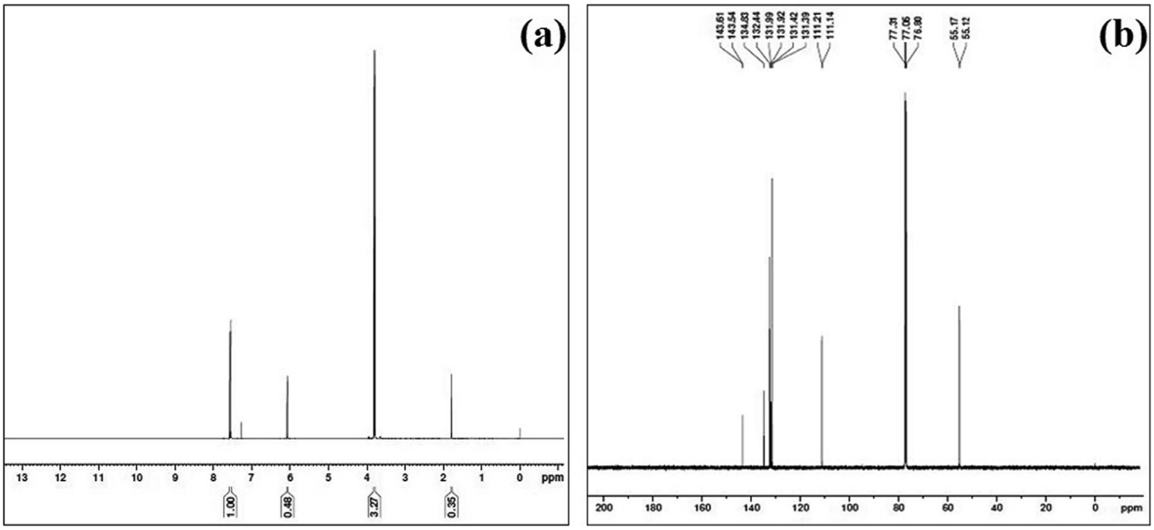


Fig. 4. Experimental (a) 1H and (b) 13C NMR spectra.

Some C–Cl inplane deformation modes are higher than the corresponding out-of-plane deformation modes [19].

4.2.3. Dimethyl phosphate group vibration

The asymmetric C–H stretching mode was expected at 3026–2993 cm^{-1} and the symmetric stretching is expected at 2956–2844 cm^{-1} in dimethyl phosphate group [20]. In TCVP, the asymmetric stretching is observed as medium band in IR at 3091 cm^{-1} and a strong band at 3074 cm^{-1} in Raman. The corresponding calculated value is obtained at 3055 cm^{-1}. The blue shifting in methyl C–H stretching vibration was due to $C_{20}–H_{21}...O_{19}$ ($O_{19}...H_{21}$= 2.087 Å) hyprconjugative interaction. The C–H deformation mode of methyl group was expected at 1462–1454 cm^{-1} and 1450–1439 cm^{-1} in asymmetric and symmetric deformations respectively. In TCVP the asymmetric deformation mode was observed as very intense band in IR at 1457 cm^{-1} and medium band at 1458 cm^{-1} in Raman. The asymmetric deformation mode is observed as a weak band at 1444 cm^{-1} in IR and 1448 cm^{-1} in Raman. Compounds containing P-O-R group give rise to bands currently within the region 1088–920cm^{-1}. There bands are usually very strong in IR and medium-weak in Raman spectrum. They involve out of phase P-O-C stretching with greater participation of the O–C stretching than P-O stretching. P-O-CH_3 group have band in the region 1088–1015 cm^{-1} and weaker at 845–725 cm^{-1} thought to involve in-phase P-O-C stretching or mainly due to P-O stretching [21]. In TCVP, P-O stretching is observed as a medium band at 823 cm^{-1} in IR and weak band at 808cm^{-1} in Raman. Methyl rocking is observed as week band at 1137 cm^{-1}in IR and medium band at 1135 in Raman. The corresponding calculated value is obtained at 1136 cm^{-1}. The P=O band appears in the region 1420–1310 cm^{-1}. A very strong band observed at 1295 cm^{-1} in IR and Raman spectra and corresponding calculated values observed at 1274, 1288, 1297 cm^{-1} in TCVP and its related compounds respectively. The exact position of bands varies with sum of the electro negativities of attached groups [22].

4.2.4. Vinyl group vibration

The C–H stretching vibration in the vinyl group was expected in the region 3040–3010 cm^{-1} [23]. In TCVP the stretching vibration was observed a medium band at 3110 cm^{-1} in IR and corresponding calculated value at 3135 cm^{-1}. There is a blue shifting in C–H stretching vibration due to $C_{12}–H_{13}...Cl_{14}$ hyprconjugative interaction. The vibration of alkene band stretching vibration in conjugated systems without a center of symmetry interact to produce C=C stretching band near 1650 and 1600 cm^{-1}. Conjugation of an alkene double bond with an aromatic ring produces enhanced alkene absorption near 1625 cm^{-1}. The $C_{11}–C_{12}$ stretching bands were identified as strong band at 1640 cm^{-1} in IR and 1644 cm^{-1} in Raman. The corresponding calculated values are 1647, 1640, 1639 cm^{-1} in TCVP, TCHP and TCDP respectively.

4.3. Natural charge analysis

Natural charge analysis is used to describe electron distribution of each atom by using B3LYP/6-311G(d,p) basis set for TCVP, TCHP and TCDP. The charge distributions on the molecule have significant influence in vibrational spectra. The net atomic charges of TCVP and its related compounds obtained by means of natural charge analysis are listed in Table 2. The calculated results show that the negative charge is localized between carbon and oxygen atoms. In TCVP, the O_{19} atom has more negative charge (0.829e) than other oxygen atoms due to the possibility of $C_{20}–H_{21}...O_{19}$ hyperconjugative interactions. H_{13} atom shows (0.250e) more positive charge than other hydrogen atoms due to the possibility of $C_{12}–H_{13}...Cl_{14}$ hyperconjugative interaction as supported by vibrational analysis. This result clearly reveals the insecticidal activity of the compound. In TCVP, C_{11} atom has more positive than other carbons which shows the conjugation between phenyl ring and electronegative oxygen O_{16}. The carbon atoms C_1, C_3, C_4, C_5, C_{12}, C_{20} and C_{25} have negative charges. The chlorine atoms Cl_9, Cl_{10}, Cl_{14}, Cl_{15} posses low electropositive charge which shows the electron withdrawing nature of the electronegative carbon atoms. Comparing TCVP with TCHP and TCDP, the charge of P_{17} was increased due to the attachment of two methoxy groups.

Table 2
Natural charges of TCVP and its related compounds.

Atom	TCVP (e)	TCHP (e)	TCDP (e)
C_1	−0.239	−0.235	−0.241
C_2	0.012	0.015	0.008
C_3	−0.122	−0.123	−0.125
C_4	−0.163	−0.164	−0.164
C_5	−0.055	−0.054	−0.057
C_6	−0.032	−0.033	−0.032
H_7	0.239	0.239	0.239
H_8	0.216	0.216	0.218
Cl_9	0.038	0.04	0.037
Cl_{10}	0.037	0.038	0.039
C_{11}	0.283	0.283	0.283
C_{12}	−0.212	−0.214	−0.208
H_{13}	0.250	0.242	0.261
Cl_{14}	0.001	0.005	0.005
Cl_{15}	0.016	0.013	0.017
O_{16}	−0.81	−0.808	−0.818
P_{17}	2.516	2.494	2.497
O_{18}	−1.04	−1.033	−1.031
O_{19}	−0.829	−0.828	−0.992
C_{20}/ H_{20}^{TCDP}	−0.189	−0.19	0.528
H_{21}/ O_{21}^{TCDP}	0.182	0.182	−0.972
H_{22}	0.184	0.186	0.508
H_{23}	0.182	0.182	–
O_{24}	−0.82	−0.957	–
C_{25}	−0.188	0.504	–
H_{26}	0.18	–	–
H_{27}	0.179	–	–
H_{28}	0.186	–	–

4.4. NBO analysis

NBO analysis give information about inter and intramolecular hydrogen bonding interaction with neighbouring bonds and hyperconjugative interactions in molecular system [24]. The NBO calculations of TCVP and related compounds are performed using NBO 3.1 program. The possible hydrogen bonding and hyperconjugative interactions are listed in Table 3. The hyperconjugative interaction energy was deduced from the second order perturbaton approach [7], the large $E^{(2)}$ value shows the more intensive in interaction. Hyperconjugation may be given as a stability effect that arises from overlap between an occupied orbital with another neighbouring electron deficient orbital when these orbitals are properly oriented. The intramolecular interactions are formed by the orbital overlap between C–C bonding and C–C antibonding obital that causes stabilization of the system. These interactions are observed as an increase in electron density in C–C, P-O antibonding orbitals that weaken the respective bonds.

The second order perturbation theory analysis was presented in supplementary table S2. In TCVP, TCHP and TCDP the most intramolecular energy at $C_3–C_{11}$, $C_{11}–C_{12}$ leads the stabilization energy 18.9, 19.6 and 19.9 kJ/mol respectively. The low stabilization energy contribution occurred in TCVP is due to the attachment of dimethyl phosphate substitution at C_{11} atom. The charge transfer from lone pair Cl_{14}, O_{19} and O_{24} the hydrogen bonded oxygen atom to antibonding $C_{12}–H_{13}$,$O_{20}–H_{21}$/$O_{25}–H_{26}$ and $C_{25}–H_{26}$/$C_{25}–H_{27}$ was sufficiently providing definite evidence regarding intramolecular interactions. There occurs an intramolecular

Table 3
Possible hyperconjugative interactions of TCVP and its related compounds.

Compound	Donor	ED (e)	Acceptor	ED (e)	$E^{(2)}$ (kJ/mol)	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
TCVP	$\sigma(Cl_{14})$	1.994 −0.915	$\sigma^*(C_{12}-H_{13})$	0.021 0.417	25.081	1.079	2.392	1.739	150.3
	$\sigma(O_{19})$	1.949 −0.593	$\sigma^*(C_{20}-H_{21})$	0.014 0.382	22.578	1.091	2.087	1.446	40.6
	$\sigma(O_{19})$	1.949 −0.593	$\sigma^*(C_{20}-H_{23})$	0.013 0.381	2.889	1.091	2.090	1.091	40.5
	$\sigma(O_{24})$	1.949 −0.580	$\sigma^*(C_{25}-H_{26})$	0.014 0.381	23.252	1.090	2.086	1.445	40.6
	$\sigma(O_{24})$	1.949 −0.58	$\sigma^*(C_{25}-H_{27})$	0.014 0.381	3.322	1.091	2.091	1.091	40.4
TCHP	$\sigma(Cl_{14})$	1.995 −0.917	$\sigma^*(C_{12}-H_{13})$	0.02 0.415	25.177	1.079	2.392	1.737	−79.6
	$\sigma(O_{19})$	1.950 −0.599	$\sigma^*(C_{20}-H_{21})$	0.013 0.379	23.396	1.091	2.087	1.448	40.7
	$\sigma(O_{19})$	1.950 −0.599	$\sigma^*(C_{20}-H_{23})$	0.013 0.378	3.274	1.091	2.090	1.091	40.5
TCDP	$\sigma\ (Cl_{14})$	1.995 −0.917	$\sigma^*(C_{12}-H_{13})$	0.022 0.413	25.707	1.079	2.393	1.737	41.4

interaction of $C_{20}-H_{21}$ from O_{19} which increases electron density (1.949e) that weakens the respective bonds $C_{20}-C_{21}$ to stabilization energy 22.578 kJ/mol.

4.5. ^{1}H and ^{13}C NMR spectral analysis

The experimental ^{13}C and ^{1}H NMR spectrum are shown in Fig. 3. The calculated ^{13}C NMR and ^{1}H NMR chemical shifts for the TCVP together with the corresponding experimental values and the assignments are listed in supplementary Table S3 as values relative to TMS. The isotropic shielding values are used to calculate the isotropic chemical shift with respect to tetramethylsilane.

In aromatic ring a large chemical shift was usually observed near 7 ppm. They are deshielded by anisotropic field generated by the electrons in the ring π system. In the present study the experimental isotropic shift values for proton are 7.58 and 7.55 ppm respectively. This greater deshielding is attributed to electro negative effect of adjacent oxygen atom. In the present investigation, H_{21}(6.07 ppm) and H_{26}(6.08 ppm) shows intermolecular interaction. The hydrogen atom attached to the same carbon as a halide atom will increase the chemical shift. i.e., H_{13} (1.79 ppm). This shielding effect is due to the electro negativity of attached chlorine atom. The hydrogen of aromatic ring exhibits signals between 8 and 6.5 ppm. The peaks with δ_H of 7.58 and 7.55 ppm are assigned to the proton bonded to C_1 and C_4 respectively. The corresponding computed values lie at 7.73 and 7.84 ppm.

Normally, the carbons on phenyl ring are supposed to give NMR signals in the region of 175–110 ppm [25]. In the present study, the carbon atoms C_1, C_2, C_3, C_4, C_5 and C_6 show the peak in the expected range. The peak of carbons of vinyl group generally occurs at 80–35 ppm. In the present investigation the experimental values of carbon atoms in the vinyl group is 77.31 ppm. The chemical shift for carbon atoms in the methyl phosphate region is generally observed 52 ppm. There is down shielding effect at C_{20}, C_{25} atom, which occurs due to the influence of electro negative O_{19} and O_{24} atoms. In C_{20}, C_{25} atoms the experimental value is observed at 55.17, 55.12 ppm and corresponding calculated peak is observed at 54.48, 56.14 ppm respectively [26].

4.6. UV visible spectral analysis

UV-Visible spectral analysis of TCVP has been carried out on acetone and dichloromethane solvents. TD-DFT calculation was used to determine the excited states of TCVP. The theoretical absorption wavelengths, excitation energy, C.I. expansion coefficient, oscillator strength and dipole moments are tabulated in Table 4. The calculated wavelengths are found to be 229 nm for gas phase, 218 nm in acetone and 246 nm in dichloromethane by CAM B3LYP/6–311G(d,p) method. The experimental UV-Visible spectrum shows the wavelength position in acetone solvent at 212 nm and in dichloromethane 254 nm respectively. The excited states H →L is assigned to n →π^* transition [27]. The experimental electronic spectra showed also little variations due to solvent effects. The experimental UV-visible spectrum for acetone and dichloromethane solvent are shown in supplementary Figure 1.

4.7. Hirshfeld surface analysis

The interactions present in the molecule and corresponding area of the surface of each interaction were studied by generating two dimensional fingerprint plots through the combination of di and de. The fingerprint plot, a simplified 2D chart of the internal and external distances of atoms from the surface is an ideal tool to compare structures directly to distinguish changes in the packaging. Furthermore, analyzing the fingerprint plot enables a very quick overview of all intermolecular interactions without simply focusing on specific interactions (such as H-bonds) that are perceived as important. Through observing the changes in the fingerprint plots for the variety of structures in the data set, features that frequently observed [28].

The frequency of each combination of di and de are indicated. 2D fingerprint plots of important contacts were (H...H, H...Cl, O...H, C...Cl, Cl...Cl, C...C) are shown in Fig. 5. The percentage area

Table 4
Experimental and calculated absorption wavelength, energies and Oscillator strengths of TCVP using the TD-DFT method in acetone and dichloromethane solvents.

Solvent	Transition Feature	Oscillator Strength (f)	C.I Expansion Coefficient	Excitation Energy (Ev)	Calculated value (nm)	Experimental value(nm)	Dipole Moment (D)	Assignment
Acetone	H→L	0.124	−0.139	5.690	218	212	4.35	n → π^*
Dichloromethane	H→L	0.023	−0.379	5.044	246	254	4.24	n → π^*
Gas	H→L	0.113	0.513	5.419	229		3.42	

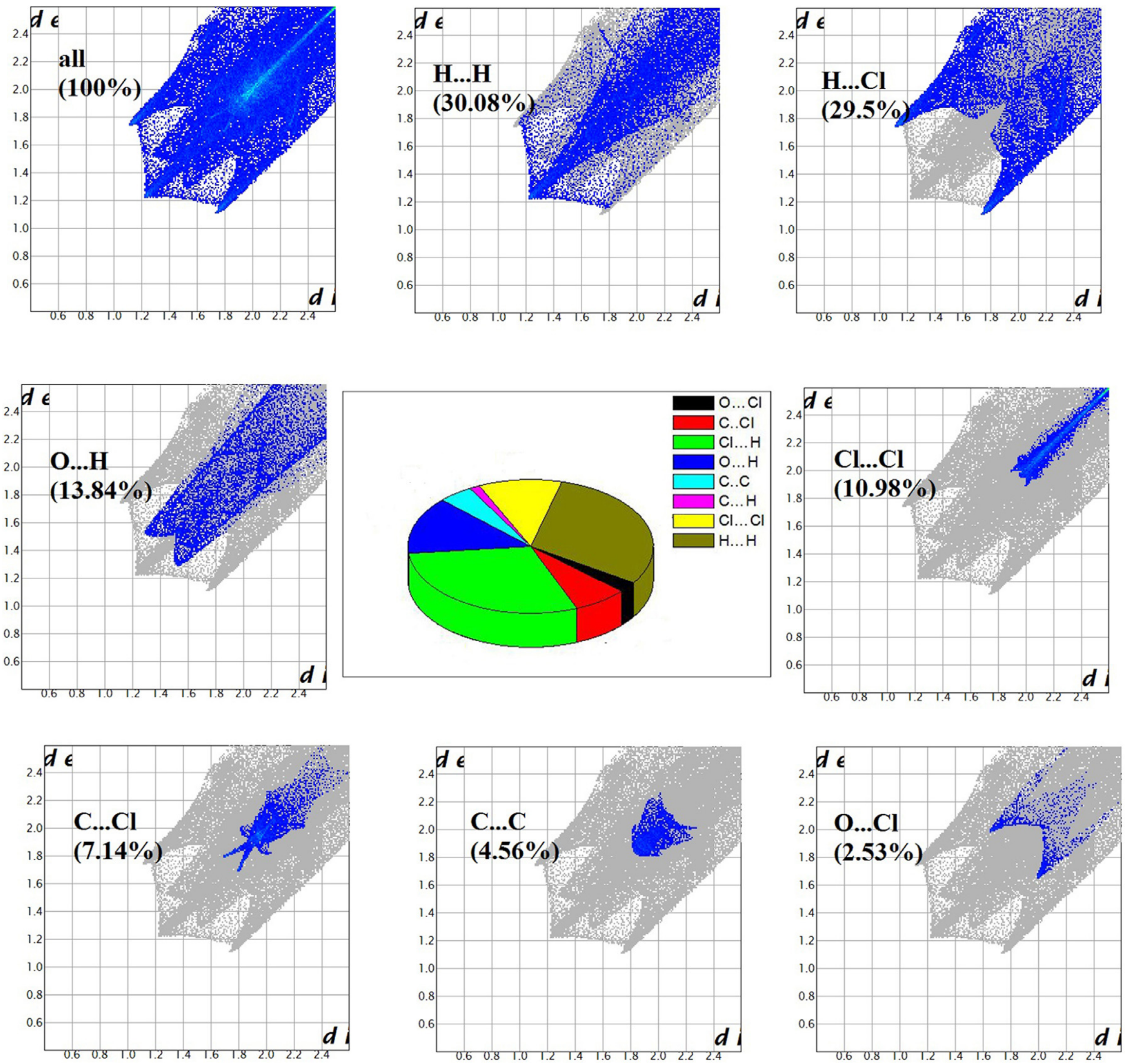


Fig. 5. 2D fingerprint plots of TCVP.

of H…H contacts including reciprocal contacts was 30.08% of total Hirshfeld surface area. This large percentage is a strong outcome for compounds with high percentage of hydrogen atom in the structure, even though it does not contribute to a directional role of H…H contacts. The second share of entire surface is related to H…Cl contact (29.5%) that are observed as to distinct spikes. The proportion of H…H, H…Cl, O…H, C…Cl, Cl…Cl and C…C were 30.08%, 29.5%, 13.84%, 7.14%, 10.98% and 4.56% respectively (H…H>H…Cl>O…H>C…Cl>Cl…Cl >C…C). The H…H contact show a spike in Fig. 3a and the sum of di and de is 2.4 Å. It should be mentioned that these contavt distances are longer than twice the vander Walls radii calculated for hydrogen atoms. These interactions are represented as "wings" which are identified as a result of C_{12}–H_{13}…Cl_{14} hyperconjugative interaction [29,30].

4.8. HOMO LUMO analysis

The wave function shows that electron absorption corresponds to the transition from the ground to the first excited state and is represented mainly by one electron excitation from the highest molecular orbital to the lowest molecular orbital. The HOMO LUMO energy gap of TCVP reveals that the chemical activity of the molecule. The HOMO energy characterises the electron giving ability and LUMO characterises the electron accepting ability. The orbital frontier gap helps to describe the molecule's chemical reactivity and kinetic stability. Surfaces for the frontier orbitals were drawn to understand the bonding scheme of present compounds. The positive phase is red and green are negative. It is clear from the figure that, the HOMOs are mainly located on the ring and that the LUMOs are located on the ring and vinyl group. The electron density groups to the efficient electron acceptor group through π conjugation path. The strong charge transfer interaction through π conjugated bridge results in substantial ground state donor acceptor mixing and the appearance of charge transfer band in the electron absorption spectrum. The molecular orbital of HOMO-LUMO diagram of TCVP and its related compounds are shown in Fig. 6. Global reactive desctiptors are calculate using Koopman's theorem for the molecules [31].

$$\text{Hardness of the molecule } \eta = \frac{1}{2}(E_{LUMO} - E_{HOMO})$$

$$\text{Hardness of the molecule } \eta = \frac{1}{2}(E_{LUMO} - E_{HOMO})$$

$$\text{Chemical potential of the molecule } \mu = -\chi = \frac{1}{2}(E_{LUMO} + E_{HOMO})$$

$$\text{Softnessofthemolecule}\, S = 1/\eta$$

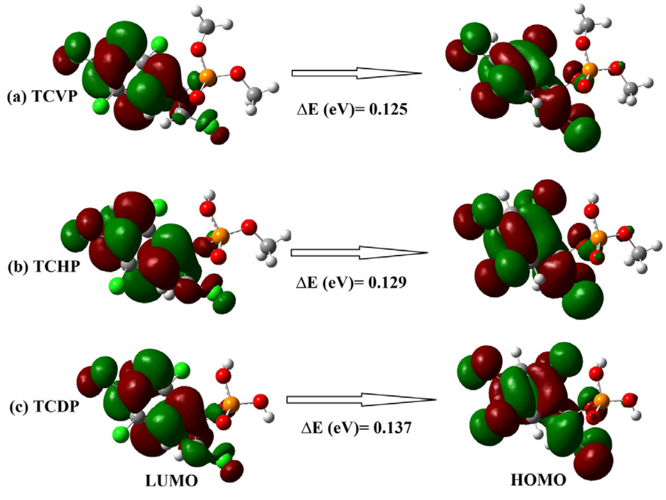


Fig. 6. HOMO-LUMO plot of TCVP and its related compounds.

Table 5
Global descriptive parameters of TCVP and its related compounds.

	TCVP	TCHP	TCDP
HOMO	−0.313	−0.315	−0.313
LUMO	−0.188	−0.186	−0.176
ΔE(eV)	0.125	0.129	0.137
Ionization Potential	0.313	0.315	0.313
Electron Affinity	0.188	0.186	0.176
Electronegativity	−0.250	−0.251	−0.244
Chemical potential	0.250	0.251	0.244
Hardness	0.063	0.065	0.069
Softness	7.995	7.722	7.280
Electrophilicity index	0.502	0.486	0.436

$$\text{Electro negativity of the molecule} \quad \chi = -\frac{1}{2}(E_{LUMO} + E_{HOMO})$$

$$\text{Electrophilicity index of the molecule}\, \omega = \frac{\mu^2}{2\eta}$$

The values of global reactive descriptors are listed in Table 5. The Ionization potential E_{HOMO} and electron affinity E_{LUMO} of TCVP are 0.313 eV and 0.188 eV respectively. The calculated values of the hardness and softness of TCVP molecule are $\eta = 0.063$ eV and $S = 7.995$ eV. The chemical softness and hardness of a molecule is related to band gap energy of a molecule. If the molecule has large energy gap then the molecule can be called as hard molecule and the presence of small energy gap makes the molecule as soft. The soft molecules are more polarizable than the hard ones because they need small energy for excitation. Comparing TCVP with its related compounds, the electrophilicity index $\omega = 0.502$ eV for TCVP is high which describe the biological activity of TCVP molecule [32]. More over lower in the HOMO and LUMO energy gap explains the eventual charge transfer interaction taking place within the molecule and also evident for the stability.

4.9. *Biological activity studies*

4.9.1. *Molecular docking*

Docking studies have been carried out for TCVP and its related compounds with the help of Autodock 4.2 software. Protein-ligand interactions in biological systems and processes play a critical role in the distribution metabolism and transport of small molecules. It is also an important tool for understanding the interactions between ligand and protein that can substantiate the experimental results [33,34]. Using docking approach, the docking of the molecule to the target is done without a prior knowledge of the location of the binding site of the system [35]. Figures were drawn using the BIO-VIA discovery studio. The ligand structures have been built and energy minimized using the program Gaussian 09.Visual analysis of TCVP molecule showed that the whole ligand was focused on the groove of the protein. For the identification of TCVP molecule insecticidal activity in which 3 pdbs of acetylcholinesterase (AChE) were selected. Docking was performed for the different receptors of (PDB ID: 1GQR, 5EHN and 5EIE) and the ligand acetylcholinesterase (AChE). The protein pdb has been downloaded from the protein data bank.

The best docked conformation were those with the lowest binding energy. High energy describes the quick binding characters of both the protein and ligand. Least energy has the highest value of RMSD. Autodock binding energies, inhibition constants (μM) and reference RMSD were obtained. From (Table 6) the observed results, 1GQR target protein has the lowest binding energy and highest reference RMSD value for TCVP. Thus 1GQR therefore possesses the highest possible binding affinity to the binding site of the molecule. In TCVP, 1GQR target protein creates hydrogen bonding interaction (−31 kJ/mol) corresponding to the bond distance 1.586 Å. Thus the lowest value of protein ligand interaction leads to the insecticidal activity of TCVP. The data corresponding to other target proteins 1GQR and 5EHN for TCVP, TCHP and TCDP are shown in Fig. 7.

4.9.2. *Insecticidal activity study*

Insecticidal activity of TCVP was determined against larvae of Corcyra *cephalonica* [36]. The results were analysed as percentage mortality. The percentage of mortality is listed in supplementary Table S4 and shown in Fig. 8. From this it is clear that after 4 h the TCVP sample with concentration 50 mg in acetone show 100% of mortality. The inhibitory activity of TCVP on the organism shows high concentration level, which indicates that concentration of the title compound increases. When concentration increases mortality also increases. It indicates that the presence of dimethyl phosphate in TCVP is responsible for the insecticidal activity.

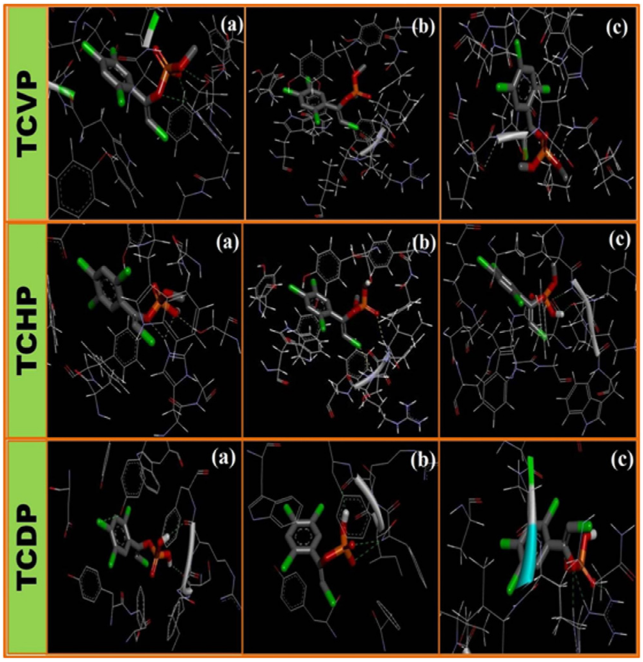


Fig. 7. Molecular Docking of TCVP, TCHP and TCDP with pdb ids: (a) 1GQR (b) 5EHN and (c) 5EIE.

Table 6
Molecular docking results of TCVP and its related compounds with different protein targets.

Compound	PDB ID	Binding energy (kJ/mol)	Estimated inhibition constant (μM)	Reference RMSD (Å)	Bond distance (Å)	H-bond energy (kJ/mol)
TCVP	1GQR	−31.045	3.62	91.08	1.586	−17.297
	5EHN	−28.075	12.14	41.33	2.024	−21.150
	5EIE	−23.849	66.71	29.67	2.127	−22.426
TCHP	1GQR	−22.552	112.3	92.88	1.954	−2.276
	5EHN	−21.464	173.4	41.45	2.040	−9.083
	5EIE	−18.451	187.7	52.68	2.241	−7.477
TCDP	1GQR	−22.384	183.4	92.53	2.023	−8.339
	5EHN	−21.966	142.6	41.91	2.440	−7.627
	5EIE	−20.962	119.7	21.47	2.083	−18.711

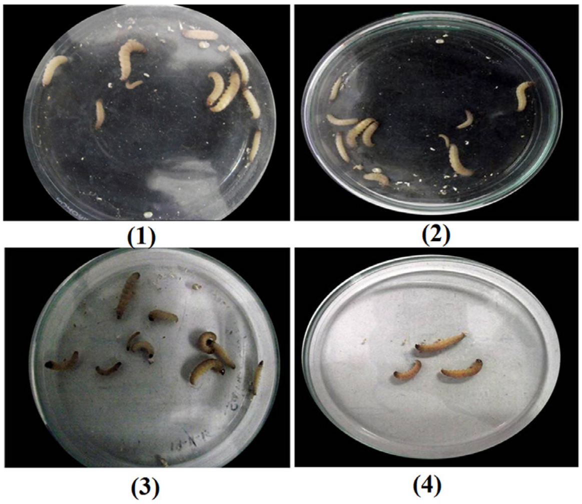

(1) (2) (3) (4)

Fig. 8. Insecticidal activity of TCVP against larvae of *Corcyra cephalonica*.

5. Conclusion

In the present work, the optimized geometric parameters were theoretically determined for gardona and it's related compounds were compared with the experimental data. Comparing O_{19}–C_{20}–H_{21} bond angle in TCVP and its related compounds, the increase is due to C–H...O hyperconjugative interaction, this leads a blue shifting in methyl C–H stretching vibration. All the vibrational bands, which are observed in the FT-IR and FT-Raman spectra of the title compound, were completely assigned with the help of PED analysis. H_{13} atom shows (0.250e) more positive charge than other hydrogen atoms due to the possibility of C_{12}–H_{13}...Cl_{14} intramolecular interaction as supported by vibrational analysis. The NBO analysis has been made with the stability and intramolecular interactions have been interpreted and the stabilization to the structure has been identified by second order perturbation energy calculations. The natural charge analysis of the molecules have been calculated and are also plotted. The experimental UV-visible spectrum shows an absorption maxima at 212 nm ($n \rightarrow \pi^*$) in the acetone and 259 nm in dichloromethane environment. In NMR spectral analysis down shielding effect at C_{20} and C_{25} atoms are due to the influence of electro negative O_{19} and O_{24} atoms. The intermolecular interactions have been studied by Hirshfeld surface and its associate fingerprint plots. The HOMO and LUMO orbital analysis have been visualized and the gap (3.390 eV) has been calculated. Molecular docking study reveals that the title compound possesses more insecticidal activity. TCVP exhibits high insecticidal activity due to the influence of dimethyl phosphate bioactive region. Docking study reveals that the protein receptor 1GQR possesses the highest possible binding affinity to the binding site of the molecule. In insecticidal activity test, considerable activity was observed against larvae of Corcyra *cephalonica*.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129557.

CRediT authorship contribution statement

L.S. Anju: Data curation, Writing - original draft, Formal analysis. **D. Aruldhas:** Conceptualization, Methodology, Supervision, Writing - review & editing. **I. Hubert Joe:** Software, Visualization.

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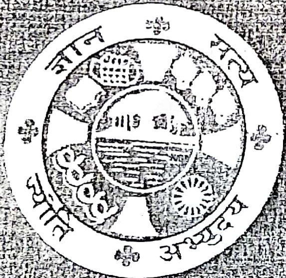

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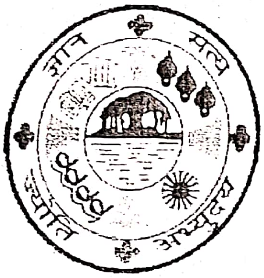

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February. 2021

A STUDY ON THE ROLE OF RUBBER BOARD RESEARCH DEPARTMENT TO ENHANCE THE PRODUCTIVITY OF NATURAL RUBBER IN INDIA

Dileep Kumar.S 1

Dr.J. Vijin Shaji Kumar 2

Abstract

The research department under Rubber board plays a crucial role for the productivity of natural Rubber. The major research divisions are agronomy/soils, biotechnology, botany, plant pathology plant physiology climate change and eco-system, latex harvest technology, rubber technology and economics. All these area focused on improving the productivity of natural rubber. The study focused on the role of research divisions and its functions.

Introduction

The rubber research institute of India was established in 1955. The thrust area of research of agronomy /soils divisions are investigations of the nutritional requirement of rubber, irrigation, intercropping, cover crop management ,weed control and the study of rubber growing soils, development of tissues and proper culture systems for propagation and crop improvement ,the important field of research of the botany division are breeding, evaluation and selection of new clones ,propagation techniques, planting methods ,anatomical studies and cytogenetical investigation .The plant pathology division is engaged in investigation on the disease and pests of rubber and associated cover crops and their control. The plant physiology Division conducts studies on both fundamental and applied aspects of Hevea tree physiology, Climate Change and Ecosystem studies concentrate on impact analysis and resilient technology development for climate change ,carbon sequestration, water and biodiversity conversation and natural resource management .The Exploitation Technology Division is concentrates on all applied aspects of crop harvesting in rubber.

The Rubber technology division concentrates on improvement in primary processing of rubber manufacture and quality control of processed rubber .The Economics Division undertakes studies on economic aspects related to rubber plantations. The research supporting sections includes library and Documentation ,instrumentation

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DISMANTLING DOUBLE OPPRESSION IN JINAAMUCHA

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ABSTRACT

Feminism in India conceived the term "woman" as a metonymy for all Indian women oppressed for their womanhood and gender. Issues of class, caste, race, and ethnicity which were severe weapons against women were excluded from the general concerns of feminist studies in India for many years. Gender was considered the basic tool which oppressed all women in India. But this essentialization or sisterhood based on the shared experience of gender discrimination ignored many sections of women and their problems from sources other than gender. Dalit feminists from the 1970s argued against such a generalization by stating that they never found their issues taken fully in the existing realm of Indian feminism. Thus Dalit feminism needs to stand as a separate bough in Indian feminism as its concerns, aims, and issues are exclusively related to Dalit women. This research paper attempts to examine how double oppression, used to suppress Dalit women is criticized by Kamble using her Dalit feminist voice in the autobiography and also earnestly studies using Kamble's work as a piece of evidence, the general issues of Dalit women and concerns of Dalit feminist studies in India. Patriarchy and caste rupture the very existence of Dalit women and such to double oppression they faced is different from what their men faced from caste or other Indian women suffered from patriarchy. For them, both the oppressive forces operate hand in hand even today though not as before and thus their suffering needs special footage. This is the basic drive behind and concern of the paper.

Keywords: Dalit, Caste, Patriarchy, Double oppression, Dalit Feminism.

I. INTRODUCTION

While Indian literature was for centuries been the most noted one, the literature of India, for many years failed to recognize the agonies of untouchables or Dalits whose subaltern voice remained feeble in the Indian social system due to the caste-based oppression in myriad forms [1,2]. The literature of elites never succeeded in addressing authentically the real torments faced by low caste. Rarely did a writer take up an untouchable character or discusses his problems sympathetically. Thus, the untouchables were invisible in Indian literature as in Hindu society or their issues were unheard of in the great literary texts of India framed by the upper class. Dalit women took even more years than their menfolk to appear in the literature. They remained 'downtrodden among the downtrodden' of literature [3, 4].

II. OBJECTIVES OF THE STUDY

The paper tries to present in detail the oppression faced by Dalit women from the perspectives of caste and patriarchy which is problematized in Kamble's work using Dalit feminist theory. The present study also includes,

1) An etymological study of the term "Dalit"
2) Analysis of varied forms of oppression against Dalits

3) A historical survey of Dalit movements, and parallel movements from Dalit women leading to Dalit feminist writings as vehicles of expression like Kamble's autobiography.
4) Assertion of the relevance of Dalit autobiographies.
5) Identification of Baby Kamble's work in the field of the Dalit feminist school of criticism as a vibrant voice dismantling the hidden demonic face of casteist Indian society crushing Dalit women under caste, patriarchy, and gender is successfully stated [5].

III. DALITS AND OPPRESSION FACED BY THEM

The term 'Dalit' meaning 'ground broken' or 'reduced to pieces generally' stands for a group of suppressed beings who are denied even the most fundamental rights by the Indian caste system [6, 7]. 'Untouchables' or 'Dalits' were not given access to public facilities like schools, rivers, wells, roads, and markets. In addition to this, Indian society granted them the status of animals or was treated as a bad omen. Thus they were asked to live a life of aliens in their homeland.

IV. EMERGENCE OF DALIT LITERATURE

A Dalit community for many years was silenced from revealing their haunting life story. Elite literature of the time never tried to sympathize with them or allowed them to travel from margins and furnish their sufferings in the form of literary texts. Moreover, the lack of education and awareness of basic rights prevented them from opposing the traumatic condition to which they are tied down by the upper class. It is only after Independence with the help of political movements headed by B .R. Ambedkar, Dalit Panthers, and other activists that the Dalit community started to realize their true rights and began to fight for it. Thus reformist current from politics slowly traveled to literature and an increased number of Dalit writings began to appear [8-10].

V. RISE OF DALIT WOMEN

Indian women were and even now victims of serious oppression from patriarchy and when it comes to Dalit women, they are victims of both caste and patriarchy, thus are struggling under the cogs of crushing double oppression. The resistance against casteism voiced through social reformers like Phule, Ambedkar, and Periyar and, so on inspired Dalit women to fight against varied forms of oppression. They began to take part in political movements and social activities and organized various conferences to fight against oppressive social institutions like child marriage, enforced widowhood, and dowry system, and so on. Soon women from the Dalit community realized the power of literature and started to record the untold agonies of their life. Poems, stories, novels, memoirs, and autobiographies were taken by them as a suitable medium for revealing their pathetic life condition [11, 12].

VI. DALIT WOMEN AUTOBIOGRAPHIES

Among various literary forms, the autobiography was selected by many women from the Dalit community to write about their stories. Due to lack of English education, mostly these women chose to write in their regional languages which were then translated by many others and thus made available for vast readership. Dalit women autobiographies by Urmila Pawar, Baby Tai Kamble, Bama, Santabai, and so on voiced the long unheard cries of the subaltern group called Dalit women [13,32].

VII. JINA AMUCHA

Baby Kamble's autobiography, JinaAmucha or The Prisons We Broke offers itself as a fine specimen for us to study the double oppression faced by Dalit women right from the time of birth from the caste system and patriarchy. These women need special footage as they are victims of twin-fold oppression while other subaltern classes like women, Dalit men, and so on are only victims of either caste or patriarchy. But in the life of a Dalit woman, both the oppressive systems operate hand in hand like in the case of black women were racism and patriarchy suppresses their existence. This difference in the form or nature of oppression faced by Dalit women is captured by Kamble through her autobiography [14].

VIII. CASTE AND DALIT WOMEN IN THE PRISONS WE BROKE

Caste is not just religious and social, but also an economical factor in India. Indian caste system formulates rules and regulations for every group which ultimately decides their privileges and restrictions. Social, religious, and economical rights and restrictions are devised based on the caste. Such an uncivilized division of society neglected many sections placed outside such a structure called the untouchables or Dalits or denied them even their fundamental rights. Ruthless classification will never prove good for any society. It will only make a socially unjust and undemocratic. Though the victims of oppression from the Indian caste system are many, the most suppressed ones were the Dalit women itself. They are forced to live a life without self-respect or self-love. They are made to submit themself for the benefit of the upper class who are very oppressors for them. "Standing in the courtyard, keeping a distance from the shopkeeper, she would pull her pallav over her face and then, using the most reverential and polite terms of address, she would beg him with utmost humility to sell her the things she wanted.'Appasab, could you please give this despicable Mahar woman some shikakai for one paisa and half a shell of dry coconut with black skin?" [15-16].

The diseased notions of caste hierarchy and untouchability are passed down to the coming generations also. Kamble clearly shows this through the attitude of shopkeepers, "Chabu, hay you, can't you see the dirty Mahar woman standing there? Now don't you touch her? Keep your distance"[(17]. Due to ignorance and lack of education, Dalits unquestioningly followed senseless notions like the concept of "Vaghya or Potraj", child marriage, and possessions of god. They were living under the sky of many superstitious beliefs. The writer regretfully quotes this through the following lines. "The entire community had sunk deep in the mire of such dreadful superstitions. The upper castes had never allowed this lowly caste of ours to acquire knowledge. Generations after generations, our people rotted and perished by following such a superstitious way of life. Yet, we kept believing in your Hindu religion and serving you faithfully." She vehemently opposes the ruthless nature of the upper caste whose uncivilized notions are threats to the simple and innocent lives of low caste people. She says, "We were the people who lived in your house, yet we dared not drink even a drop of water there. We never dared to cross your path. We dedicated ourselves to the service of the civilization and culture that was so precious to you, even though it was always unkind and unjust to us. Why we would ever spread out our hands like spittoons for you if you want to spit! Then why did you treat us with so much contempt? "Kamble also brings to light the animal-like existence of her people who were reduced to a condition that of the bullocks in the courtyard of high castes [18].

"Such was the condition of our people. We were just like animals, but without tails. We could be called human only because we had two legs instead of four. Otherwise, there was no difference between us and the animals. But how had we been reduced to this bestial state? Who was responsible? Who else, but people of the high caste! They destroyed our reasoning, our ability to think. We were reduced to a condition far worse than that of the bullocks kept in the courtyard of the high castes."Dalit women are the most vulnerable victims of the caste structure. Just like their male members they too suffer from poverty, slavery, humiliation, and so on but more than that they are also victims of sexual harassment and brutal treatment. They are made to meekly follow other people. The woman who opposes will either have her nose chopped off or killed or abused terribly. The following lines show the gravity of caste oppression Dalit women faced". They were not allowed to use the regular road that was used by the higher castes. When somebody from these castes walked from the opposite direction, the Mahars had to leave the road, climb down into the shrubbery and walk through the thorny bushes on the roadside [19, 20]. They had to cover themselves fully if they saw any man from the higher castes coming down the road, and when he came close, they had to say, ' The humble Mahar women fall at your feet master.' This was like a chant, which they had to repeat innumerable times, even to a small child if it belonged to a higher caste".

There are even certain codes of dressing predetermined for the Dalit women that they must follow without any protest no matter whether they are covered in rags or tattered ones. Kamble points out that"There were caste rules even for how one tucked the pleats. Mahar women had to tuck them in such a way that the borders remained hidden. Only high caste women had the privilege of wearing their saris in such a way that the borders could be seen. A Mahar woman was supposed to hide the borders under the pleats; otherwise, it was considered an offense to the high castes."Kamble portrays the caste notions in the mind of upper-class women who fail to realize the troubles and tragedies of their gender. Though they are also women, a sense of sisterhood is lacking among them for the tragic Dalit women

"The Brahmin kaki, sitting in the cool shade and supervising this operation, would keep shouting instruction after instruction, 'Listen carefully, you dumb Mahar women, check the sticks well. If you overlook any of the threads sticking to the wood, there will be a lot of trouble. But what's that to you? Your carelessness will cost us heavily. Our house will get polluted. Then we will have to polish the floor with cow dung and wash all our clothes, even the rags in the house! Such trouble we'll have to undergo for your foolishness! And how will the gods tolerate this, tell me? They too will be polluted, won't they?... 'These idiotic Mahar women! Hey, you, why do you bring these brats along? They'll touch things and pollute everything. Tell them to sit quietly'...Finally, the kaki would throw from above, to avoid any contact, a couple of coins on each palm. The same process was followed while selling grass as well. The kaki would get the women to carefully check each blade of grass!" Due to ignorance of their community "One in every ten lost their lives during childbirth. Infants died as well.". They are also made victims of cruel practices like Sati. Thus women in Kamble's community are doubly oppressed or are the 'downtrodden among the downtrodden'. The Dalit feminist standpoint of Kamble faithfully brings to the forefront varied facets of oppression faced by Mahar women from higher castes other than being victims of suppressive patriarchal dominance of their men [21-23].

IX. PATRIARCHAL OPPRESSION AGAINST DALIT WOMEN IN THE PRISONS WE BROKE

Dalit feminist writings are authentic attempts to expose the twin fold oppression that the Dalit women had to undergo right from her birth to her death bed. She is caught in the cages of malevolent caste structure and patriarchy which offer her predetermined roles and codes of conduct regarded proper. Baby Kamble and her autobiography are undoubtedly voicing the pathetic living conditions of Dalit women oppressed by caste and patriarchy. She offers a strong protest against the man-made notions meant to suppress fellow human beings without any reason [24-26]. Patriarchy which crushes the state of every woman is a true repressive apparatus in the case of Dalit women, as their already suppressed state under caste is further widened by patriarchy. Baby Kamble clearly shows through the following lines the very patriarchal notion that honor of each family lies with the range of restrictions put on their women, which again is a bait to trap poor women. "In those days, it was the custom to keep women at home, behind the threshold. The honor enjoyed by a family was in proportion to the restrictions imposed on the women of the house. When no one could see even a nail of the woman thus confined within the four walls of the house, then this 'honor' became the talk of the town – a byword among the relatives and friends in the surrounding villages. Then people would tell each other, how one Pandharinath Mistry kept his wife completely hidden in the house and how even the rays of the sun did not know her" [31, 33].

Kamble through her works says, "My father had locked up my aai in his house, like a bird in a cage"[11]. Her mother too faced the typical fate of a Maharwada woman that is to have a caged life at home as well as in the society. The following line shows the importance Mahars give for marriage in a girl's life no matter whether she is happy or not in it "Yesterday, I had gone to leave my daughter at her in-law's place. She is most lucky, you know, to get into such a house, what a prestigious house"[9]... They consider the luxury of in-law's house as probable to a girl's happiness even when she is a slave there. It's not the life of a daughter that is valued but it's the honor and prestige. For instance, Kamble says the humiliation a newlywed girl should pass through if she happens to fails the custom of bowing before the masters or failed to chant the lines of submission before them. She says"Sometimes there would be a young, newlywed girl in the group and she would fail to join the chant out of sheer ignorance or awkwardness. All hell would break loose then. The master would simply explode in rage. He would march straight to the Mahar chawdi, summon all the Mahars there and kick up a big fuss. 'Who, just tell me, who the hell is that new girl? Doesn't she know that she has to bow down to the master? Shameless bitch! How dare she pass me without showing due respect? ". Young Mahar women were brutally punished in their in-law's house. "In those days, at least one woman in a hundred would have her nose chopped off. You may well ask why. It's because of the sasu, who would poison her son's mind [26-28]. These sasus ruined the lives of innocent women forever. Every day the Maharwada would resound with the cries of hapless women in some house or the other. Husbands, flogging their wives as if they were beasts, would do so until the sticks broke with the effort. The heads of these women would break open, their backbones would be crushed, and some would collapse unconscious. But there was nobody to care for them. They had no food to eat, no proper clothing to cover their bodies; their hair would remain uncombed and tangled, dry from lack of oil. Women-led the most miserable existence" [29, 35].

In those days, it was considered manly for a husband to beat his wife and even his whole family and community would render support for such actions. "You are a man. You must behave like one! You must be proud and firm. You must walk tall. Twirl your mustache and show us that you are a man...Never mind if you have to go to prison for six months! You must chop off your wife's nose and present it to her brother and father. They mustn't have any respect left to sit with the members of the panch."(100-01)Kamble thus speaks through a Dalit feminist's voice by clearly analyzing how poor Dalit women despite the chain of agonies they face from poverty, hunger, epidemics and so are crushed to the floor by the so-called two institutions in society called caste and patriarchy which are purely man-made creations to bring unwanted divisions and stratification in the society. Women of lower caste are and always the victims of dual oppression from such systems. Kamble through her book emerges as an important advocate of Dalit feminist notions seeking to bring some attention to doubly suppressed womenfolk and suitable reformation to raise them from the wheels of suppression [11].

X. CONCLUSION

As a Dalit writer Baby Tai Kamble remains faithful to her people by turning her works as efficient tools against the dominant Hindu society acting against the whims and fancies of her community. She gives an unbiased account of the atrocities done against Dalits and thus drives the reader to strongly oppose the infected ideologies of caste and patriarchy [11].

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Research Paper

Literary Potential and Reformative Power of Transgender Self Writings From India

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ABSTRACT
Transgender, an umbrella term used for persons whose gender identity, gender expression or behaviour does not conform to that typically associated with the sex to which they are assigned at birth are marginalized in different countries in the name of gender. India also places transgender in the margins of different human realms. Literature also confers them a subordinate position though our epics, Vedas, Puranas, different ancient literary texts, religious writings, and Indian mythology provided them a place equal or close to god. They are given large amount of money and great gifts by people as well as their blessings on auspicious occasions like child birth or marriage is regarded highly once by the Indians. Shikandi in "Mahabharata", Ardhanarishivara figure of Lord Shiva, Mohini avatar of Lord Vishnu, disguised figure of Arjuna as Brihannala, story of King Ila, shows the extent to which Indian mythology respected and recognised gender fluidity. But today we could see transgender writing about their subaltern agonies through their works. They are denied prominent positions in our elite literature. Even if they are provided a space it is one of a minor relevance. Thus transgender started to voice their feelings through their own self writings. They seek for a reformation in the gender norms and are highly noted for their literary relevance. Thus the research article entitled" Literary Potential and Reformative Power of Transgender Self Writing" earnestly tries to appreciate Indian transgender autobiographies and their importance. The Truth about Me: A Hijra Life story and A Life in Trans Activism by A Revathi, Me Hijra, Me Laxmi and Red Lipstick: The Men in My Life by Laxminarayan Tripathi, A Gift of Goddess Lakshmi by Manobi Bandyopadhyay and I Am Vidya: A Transgender's Journey by Living Smile Vidya are the selected autobiographies for the study.

KEYWORDS: *Transgender, gender fluidity, Indian literature, subaltern, transgender autobiographies.*

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I. INTRODUCTION

Autobiographies are first person account of a person's life written by that person itself. Writers use autobiography as a suitable form to express themselves more clearly and deeply. Autobiographies provide a platform for the readers to understand and evaluate the writers more intensely. Many suppressed classes like women, untouchables, and transgender make use of autobiographies to reveal their trauma to the public and thereby calling for a change in their discriminated status. Among this transgender self writings are specially noted as they truly picture the long term suppression and discrimination experienced by them from the gender constructs of society. Though many biographies tried to address their issues, it is not completely reliable or accurate as they are not written by transgender themselves. Autobiographies thus stand out as trustworthy records of real trans life.

II. OBJECTIVES OF STUDY

The research basically aims at a study of selected transgender autobiographies from India using subaltern theory. The chief objectives of research are to:
i. Analyze the position of transgender and their autobiographies in Indian literature.
ii. Appreciate the literary potential and reformative power of transgender self writings from India.
iii. Create awareness among public about the problems faced by transgender and call for a fair and equal treatment of such a community.

III. METHODOLOGY

The research takes the support of qualitative methods for study. It will be a qualitative analysis including textual analysis, in depth study, close reading as well as interpreting, comparing and contrasting the primary sources chosen for the study. Data for the research will be collected with the help of library resources and online sources. Different articles and books relating to transgender autobiographies from India are carefully read and analysed for the research.

IV. LITERARY GENIUS OF TRANGENDER AUTOBIOGRAPHIES

Transgender self-writings are noted for their power of language. The potential of chosen words marks them most memorable and touching among different self-writings as the words are nothing but actual bitter experiences in the life of writer. Literary figures, puns, comparisons, irony, choice of words, sarcasm, and monologue indicate an outflow of strong impressions from a swollen and wounded heart. At times language even fails to truly draw the picture of intense feelings from the life of a transgender. Among many works, *The Truth about Me: A Hijra Life stor*y and *A Life in Trans Activism* by A Revathi, *Me Hijra, Me Laxmi* and *Red Lipstick: The Men in My Life* by Laxminarayan Tripathi, *A Gift of Goddess Lakshmi* by Manobi Bandyopadhyay and *I Am Vidya: A Transgender's Journey* by Living Smile Vidya are fine pieces to unearth the literary and reformative potentials of transgender autobiographies.

I Am Vidya: A Transgender's Journey by Living Smile Vidya pictures the trauma faced by a tirunangai, a transgender in the society which defines the rights and limits of men and women in terms of biology alone. Vidya's narrative clearly suggests the agonies undergone by a woman trapped within a man's body. We could see the linguistic mastery of her words through the following lines where she can through a few sentences draw herself very vividly in front of the readers.

I was girl. Unfortunately, the world saw me as a boy. Inwardly I wanted to be a girl, but I made every effort possible to hide my feminity from the outside world. I took particular trouble to remain inconspicuous at college, the unpleasant memories of my bitter experience at school still fresh in my mind. I lead a false life of strenuous attempts to swagger like a man and speak like one; (Vidya 40)

The inner turmoil of a transgender could be understood and related by only a transgender since there is a huge difference between a victim and a witness. Vidya's ardent wish to be admitted as a woman is penned most touchingly through the following lines where we could find her spirit earning for a complete realization of her true gender identity. Here the language is loaded with intense emotions.

Amma, Amma, I have become a woman. I am not Saravanan anymore. I am Vidya. A complete Vidya. A whole woman. Where are you, Amma? Can't you come to me by some miracle, at least for a moment? Please hold my hand, Amma. My heart seems to be breaking into smithereens. Radha, please Radha, I am no longer your brother, Radha. I am your sister now, your sister. Come to me, Radha. Chithi, Manju, Prabha, Appa….(Vidya 17)

Similarly in *The Truth about Me: A Hijra Life stor*y and *A Life in Trans Activism* we could find the cry of a person suffering from gender fluidity or queerness when Revathi says,

Why did I love men? Was I mad? Was I the only one who felt this way? Or were there others like me, elsewhere in the world? Would I find them, if indeed they were there? (Revathi, 14)

Revathi's narration portrays her earnest wish for acceptance in a world of gender norms neglecting and discriminating the trans people as other. When she says the following lines, it is evident that she is deeply affected by the queerness in her gender identity and her words suggest her dilemma and sorrow to the fullest.

A woman trapped in a man's body was how I thought of myself. But how could that be? Would the world accept me thus? I longed to be known as a woman and felt shamed by this feeling. I wondered why God has chosen to inflict this peculiar torture on me, and why he could not have created me wholly male or wholly female. (Revathi, 15)

Me Hijra, Me Laxmi and *Red Lipstick: The Men in My Life* by Laxminarayan Tripathi, also offers before the readers a painful saga of torture and humiliation experienced by a transgender from a very young age. The violence, sexual harassment and humiliation she faced are far beyond explanation. We could get a glimpse of patriarchal society which suppressed gender expressions of Laxmi from these lines. Here the term inadequate is connoting he inadequacy of our gender divisions itself.

"As the eldest son of my parents, they expected me to be a man. They expected me to be manly, and eventually be the man of the house. I knew I couldn't fulfil these expectations because, inwardly, I did not feel like a man. On top of that, I was gay. Even if my parents overlooked my aberrations, society would not. I felt inadequate."

A Gift of Goddess Lakshmi by Manobi Bandyopadhyay presents itself as a fine specimen offering insights into the mental trauma of transgender. When we go through the following lines by Manobi

Bandyopadhyay, we could see her excellence and mastery in the use of language where she is able to imprint her emotions through a few introspective questions.

> I am one of them. All my life people have called me *hijra, brihannala, napungshak, khoja, launda* . . . and I have lived these years knowing that I am an outcast. Did it pain me? It maimed me. But time, to use a cliché, is the biggest healer. The adage worked a little differently in my case. The pain remains but the ache has dulled with time. It visits me in my loneliest hours, when I come face to face with the question of my existential reality. Who am I and why was I born a woman trapped in a man's body? What is my destiny?

Thus it can be observed that literary talent of a long oppressed class is adding more colour and flavour to Indian literature. Though they are voice of agonies, we could recover from such autobiographies, splendid levels of fancy and imagination narrating saga of troubles most touchingly.

V. REFORMATIVE POTENTIAL OF TRANSGENDER SELF WRITINGS

One of basic drives behind transgender self writing is undoubtedly a call for reformation in the diseased gender norms of our society. They clearly denote through the writings that the stereotypical male-female categories in which we divided our society often show not our understanding of human sexuality but the lack of it. For instance, when Bandyopadhyay asks for freedom and acceptance we could feel in her voice, a true urge for a reformation in the gender norms of the society which always terms a transgender as an outcast.

> Beneath my colourful exterior lies a curled up, bruised individual that yearns for freedom—freedom to live life on her own terms and freedom to come across as the person she is. Acceptance is what I seek. My tough exterior and nonchalance is an armour that I have learnt to wear to protect my vulnerability. Today, through my good fate, I have achieved a rare success that is generally not destined to my lot. But what if my trajectory had been different? I keep telling myself that this is my time under the sun, my time to feel happy, but something deep inside warns me. My inner voice tells me that the fame and celebration that I see all around is *maya* (illusion) and I should accept all this adulation with the detachment of a *sanyasi* (hermit).

Through her autobiography, *I Am Vidya: A Transgender's Journey, Living Smile* Vidya's aim is not to arouse pity or sympathy but she wants to acknowledge transgender as transgender itself.

> My expectations were simple: I wanted to live like all men and women. My being a tirunangai was natural, just as men are men, women are women, and cats are cats. Trouble arises when people do not understand this simple truth.

When Vidya point out that trouble arises from people not understanding gender fluidity as normal, she is actually denoting the insufficiency of binary divisions of gender. Her call for a reform is far fetching. Living Smile Vidya's autobiography suggests that though in our country, minorities and backward castes have their rights, rarely one talk for the fair treatment of transgender as a minor category and try for an upliftment in their downtrodden status.

Similarly, *Me Hijra, Me Laxmi* and *Red Lipstick: The Men in My Life* by Laxminarayan Tripathi powerfully voices for a change in the gender based demarcations. From family, friends, relatives, colleagues, to ultimate law makers need to educate themselves about the inner turmoil faced by a transgender. Mere acceptance of their being is what a transgender demands and if a country could not provide that it cannot be called just and equal. When a society forces transgender to be man or woman against their whims and fancies, the ultimate result will be a life of suppression or a drive towards suicide for them. When Laxmi utters the following lines we could see how she is struggled with the expectations of a family put on her which is against her actual gender self.

> But where was I in all this? How could I fit into such a scenario? True, I didn't have to support a family. But, I too straddled many worlds, without belonging to any. As the eldest son of my parents, they expected me to be a man. They expected me to be manly, and eventually be the man of the house. I couldn't fulfil these expectations because, inwardly, I did not feel like a man. (37)

Coming to A. Revathi's self writings *The Truth about Me: A Hijra Life story* and *A Life in Trans Activism* are specially noted for their essence of trans activism. We could see the power of her writing, when she says that her aim is not to seek sympathy but to show the society the ability of a transgender and the fact that they too have rights.

> As a hijra I get pushed to the fringes of society. Yet I have dared to share my innermost life with you – about being a hijra and also about doing sex work. My story is not meant to offend, accuse or hurt anyone's sentiments. My aim is to introduce to the readers the lives of hijras, their districts culture, and their dreams and desires. I hope now that by publishing my story, larger changes can be achieved. I hope this book of mine will make people see that hijras are capable of more than just begging and sex work. I do not seek sympathy from the society or the government. I seek to show that we hijras do have the right to live in this society. (Revathi, v-vi)

Thus, it can be understood that transgender self writings are powerful in informing people about the intensity of oppression and seeking to bring about reformation in the society which always places a transgender aloof or detached from the mainstream.

VI. CONCLUSION

A voyage through Indian literature reveals the fact that transgender autobiographies are an integral part of it. Though elite literature tried to portray transgender in dim light, with the coming of authentic self writings by transgender themselves, long unheard agonies of a subaltern group are brought to the forefront. Just like the respect and recognition they received from our ancient literature, after reading such autobiographies one will start to acknowledge the rights of transgender. The literary output and reformative capacity of trans writings are absolutely laudable. Such writings are true record of the discrimination transgender community faces from the gender norms and regulations of Indian society which always placed them apart from the centre of gender classifications. A reformation in the binary divisions of gender as male and female is what voiced and hoped by transgender writers and India can be termed completely democratic when the wishes of such a section are properly recognised.

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Density functional theory, spectroscopic and hydrogen bonding analysis of fenoxycarb–water complexes

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ABSTRACT

The spectroscopic properties of Fenoxycarb (FC) and its water complexes were studied by adopting experimental and computational methods. The optimized geometrical parameters obtained from computational methods were compared with experimental studies. Density functional theory (DFT), Natural bond orbital analysis (NBO) is used to explain different types of hydrogen bonds in the molecule and its water complexes. The FT-IR and FT Raman spectra of FC were studied by vibrational energy distribution analysis (VEDA.4) using potential energy distribution (PED) analysis. Charge analysis explains the charge transfer within the molecule. Potential energy scan (PES) had been performed. The reactivity of the molecule using various descriptors such as Fukui function, local softness, electrophilicity, electronegativity, hardness, HOMO-LUMO energy gap were calculated and discussed. Intramolecular interactions were calculated by Hirshfeld surface analysis and fingerprint plots. The ^{1}H, ^{13}C NMR spectra were recorded and analysed. UV visible spectrum of the compound was recorded for the acetone solvent and electronic properties were computed by time dependent (TD-DFT) level with CAM B3LYP approach. FC was screened for its insecticidal activity. Molecular docking studies were conducted to predict its insecticidal activity.

1. Introduction

Fenoxycarb is an insect growth regulator with juvenile hormone activity (JHA) [1]. Fenoxycarb (FC) has the chemical formula $C_{17}H_{19}NO_4$ and systematic name Ethyl N-[2-(4-phenoxyphenoxy) ethyl]carbamate. It is produced industrially as an insect growth regulator with juvenile hormone activity [2]. This highly selective anti-insect agent, a third generation insecticide, is commonly used in integrated pest management practices [3]. The crystal structure of the title compound as reported by Kuhs et al. [4]. To the best of our knowledge there is no complete description of vibrational spectroscopic studies on experimental and theoretical calculations of FC have been performed. This influenced us to do the molecular geometry, spectral analysis, structural activity relationship, hydrogen bonding analysis and insecticidal activity of the compound by experimental techniques and density functional theory.

The title molecule composed of two parts such as aromatic and aliphatic separated by an ether bridge. The aromatic part combines two benzene rings (Ring 1 and Ring 2), separated by another ether bridge. The aliphatic part is made up of an ethylene ($-CH_2-CH_2$), carbamate (-NHCOO) and an ethyl ($-CH_2-CH_3$) group [1].

Vibrational spectroscopy combined with quantum chemical computation has been recently used as an effective tool in the vibrational analysis of biological compounds, since the computational results can help in the unambiguous identification of vibrational modes as well as bonding and structural features of complex organic system. In this present work, the efforts have been taken to predict the complete description of the molecular geometry, vibrational frequencies and natural bond orbital (NBO) analysis, hydrogen bonding interaction and insecticidal activity of FC and its water complexes. DFT calculations were performed by using Gaussian 09 program, B3LYP method was used to optimize the geometrical structure and changes in the vibrational characteristics of FC and its water complexes: FC with one water molecule (FCW_1), FC with two water molecules (FCW_2), FC with three water molecules (FCW_3) and FC with four water molecules (FCW_4), due to the

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extensive hydrogen bonding interactions. In order to take into account the effect of intermolecular interaction on geometrical parameters and vibrational spectroscopic analysis, we have considered the cluster built up from FC with water (FCW_1, FCW_2, FCW_3 and FCW_4) complexes and the molecule linked by N−H···O, C−H···O and O−H···O hydrogen bonds.

2. Experimental details

The title compound FC was purchased from Sigma Aldrich (St.Louis, MO, USA) with 99.5% purity and used without further purification. The room temperature fourier transform infrared spectra of the title compound was measured in the region 4000-400 cm^{-1}, at a resolution of +1 cm^{-1}, using PerkinElmer spectrometer equipped with mercury vapour lamp and globar as source. The FT-Raman spectrum in the range 3500−50 cm^{-1} was also recorded for the powdered sample with the 1064 nm line provided by an Nd-YAG laser employed as the excitation source and analysed on Bruker RFS 27 FT-Raman spectrometer. The spectral resolution is 2 cm^{-1}. The UV−Visible spectrum of FC was examined in the range 190−900 nm using CARY100 BIO UV−Visible spectrophotometer in acetone solvent. The ^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE111 500 MHz (AV500) instrument. The insecticidal activity of FC was analysed by well diffusion method against *Sitophillus oryzae*.

3. Computational details

All geometric structure calculation have been carried out using Gaussian 09 package and Gauss view molecular visualizing program package which has provide itself to be extremely useful to get a clear knowledge of optimized parameters, vibrational wavenumber, electronic structure properties and other molecular properties [5,6]. The geometry is fully optimized at Beck 3-Lee-Yang-Parr (B3LYP) level with standard 6-31G(d) basis set [7]. The computed wavenumbers were scaled by 0.9614 [8]. Additionally the calculated vibrational frequencies are clarified by means of the Potential energy distribution (PED) analysis of all fundamental vibrational modes by using Veda.4 program [9]. The initial geometry of the title compound has been taken from crystallographic information file (CIF) [10]. The theoretical tool Fukui function was performed by UCA-FUKUI software to understand the chemical reactivity the condensed Fukui function and related local and global parameters are calculated [11]. Potential Energy scan (PES) was performed to obtain a stable geometry of the compound. UV visible spectra, electronic transition, excitation energy and oscillator strength were computed with Time Dependent DFT (TD-DFT) level with CAM B3LYP 6-31G(d) and CAM B3LYP 6−311++G(d,p) basis sets [12]. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra [13].

The natural bonding orbital (NBO) calculations were done at the B3LYP method in order to investigate the optimized geometry corresponding to hydrogen bonding. The hyperconjugative interaction energy was deduced from second order perturbation approach. Atomic charges, donor-acceptor NBO hyperconjugative interactions, dipole moment, HOMO-LUMO energy gap were also computed [14]. Hirshfeld surface analysis of FC have been constructed from CIF files in order to identify the interactions using crystal explorer 3.1 [15]. Docking was performed with two different proteins (pdb ID: 2RCK and 3AY8) and the ligand using molecular docking software Auto Dock 4.2 [16].

4. Results and discussions

4.1. Potential energy scan analysis

The PES scan with B3LYP/6-31G(d) level of theoretical approximation was performed in order to identify the most stable conformer. In the present work the dihedral angles ϕ_1 ($H_2-C_1-C_5-O_8$), ϕ_2 ($C_{16}-O_{19}-C_{20}-C_{21}$) and ϕ_3 ($C_{23}-O_{30}-C_{31}-C_{32}$) for FC; ϕ_{1a} ($H_2-C_1-C_5-O_8$) and ϕ_{2a} ($C_{16}-O_{19}-C_{20}-C_{21}$) for FCW_1 are selected for the analysis to identify the minimum energy structure, it is also the relevant coordinate for conformational flexibility with the molecule. During the calculation, all the geometrical parameters were simultaneously relaxed while the dihedral angles are varied in steps of 10° up to 360° and are listed in Supplementary Tables S1a−S1e and the PES curves are plotted with relative energy and dihedral angle and are shown in Supplementary Figs. S1a−S1c.

For the rotation ϕ_1 and ϕ_{1a} minimum energy has been obtained at 60°. The difference is in relative energy is due to the influence of water molecule. The energy barrier obtained from both ϕ_1 and $\phi 1a$ as 14 kJ/mol. Energy barrier is the energy difference between the most stable conformer and unstable conformer. To define the potential position of FC with respect to the ethoxy group the dihedral angle ϕ_2 is selected. For this rotation, the first broad maximum is obtained at the angles 70°, 80°, 90° and 100°. These are almost energically equal barrier about ~9 kJ/mol. The second broad minimum obtained at 250°, 260°, 270° and 280° with almost energically equal barrier. These are isomer structure of each other. Global minimum is obtained at 180° due to the $H_{18}\cdots H_{26}$ (2.319 A°) steric repulsion [17]. For $\phi_{2a,}$ global minimum energy is obtained at 180° and two sharp peaks obtained as global maximum at 60° and 240° with barrier energy 10 kJ/mol. The difference in energy barrier between ϕ_2 and ϕ_{2a} is due to the influence of water molecule. i.e, $N_{11}-H_{12}\cdots O_{42}$ ($H_{12}\cdots O_{42} = 2.021$ A°) hydrogen bonding interaction.

For the rotation performed by dihedral angle ϕ_3, the minimum energy is located at 200° and the maximum energy is at 270°. Here the phenyl ring rotation energically attains barrier energy of 3.6 kJ/mol. The saddle point at 180° shows the possibility of weak $C_{32}-H_{37}\cdots O_{30}$ ($H_{37}\cdots O_{30} = 2.533$ A°) hydrogen bonding interaction. The above analysis reveals that the interaction with water molecule decreases the energy. Rotation about dihedral angle $\phi_1(H_2-C_1-C_5-O_8)$ shows minimum energy and is more stable structure. Hence this structure is used for the further calculations.

4.2. Molecular geometries

The experimental geometrical parameters (bond length, bond angle and dihedral angle) for FC with atom numbering scheme adopted in computation is shown in Fig. 1 and its water complexes (FCW_1, FCW_2, FCW_3 and FCW_4) are also shown in Supplementary Figs. S2a−S2d. The calculated values were compared with X-ray diffraction results [10]. The bond length, bond angle and dihedral angles obtained by computation along with the experimental values are listed in Supplementary Tables S2a−S2c.

Due to strong $O_{48}-H_{49}\cdots O_8$ hydrogen bonding ($O_8\cdots H_{49} = 1.942$ A°) interaction in FCW_3 and FCW_4, the C_5-O_8 bond length is increased in comparison with FC, FCW_1 and FCW_2. The C_9-O_8 bond length in FC and its all water complexes is reduced by the influence of $N_{11}-H_{12}\cdots O_8$ hydrogen bonding in comparison with the C_5-O_8 bond length. In FCW_2, FCW_3 and FCW_4, the C_9-O_{10} bond length is increased than that of FC and FCW_1 due to $O_{45}-H_{46}\cdots O_{10}$ hydrogen bonding interaction with water.

$N_{11}-H_{12}$ bond length of FC is lengthened while comparing with all water complexes due to $N_{11}-H_{12}\cdots O_{42}$ hydrogen bonding, in which the H … A distance in $FCW_{3,}$ $O_{42}\cdots N_{11}$ bond distance is

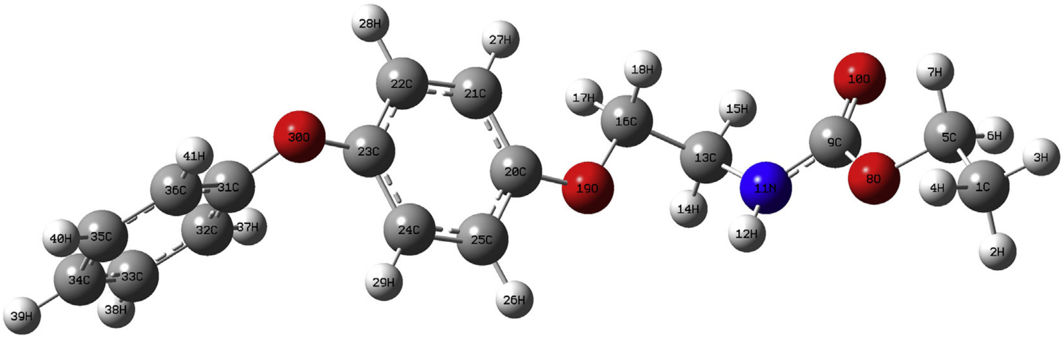

Fig. 1. Optimized molecular structure of Fenoxycarb (FC).

measured as 1.870 A° which is the strongest and stable hydrogen bonding. The N_{11}–C_{13} bond length is increased in FC and its water complexes, when comparing with C_9–N_{11} bond length due to the C_{13}–$H_{15}\cdots N_{11}$ hyperconjugative interaction. The bond length C_{16}–O_{19} is increased than that of C_{19}–O_{20} due to C_{16}–$H_{18}\cdots O_{19}$ hyperconjugative interaction in FC and its water complexes, by which FC and its water complexes C_{20}–C_{21} bond length is contracted while comparing with C_{20}–C_{25}. By the attachment of phenoxy group in all complexes, C_{23}–O_{30} bond length is increased when comparing with O_{19}–C_{20}.

The hydrogen bond formation is associated with elongation of X–H bond and shortening of X–Y bonds, these leads to the strongest intramolecular hydrogen bonding. The structural parameters of hydrogen bonds in FC water complexes are listed in Table 1. In FCW_1, the largest $\Delta R_{X\text{-}H}$ (0.017 Å) is found in O_{42}–$H^{W}_{43}\cdots N^{FC}_{11}$ and O_{42}–$H^{W}_{43}\cdots O^{FC}_{19}$, which indicates that they are the strongest intermolecular interactions. The shortest $R_{H\ \ldots\ Y}$ (1.930 A°) indicates the most stable complex among the two interactions. In FCW_2, O_{45}–$H^{W}_{46}\cdots O^{FC}_{10}$ is the most stable complex which is having $\Delta R_{X\text{-}H}$ value 0.019 Å and X … Y value 1.870 Å. In FCW_3, there is one intramolecular interaction (N_{11}–H^{FC}_{12}...O^{FC}_{8}) and one intermolecular hydrogen bonding interaction (N_{11}–H^{FC}_{12}...O^{W}_{42}). But among these interactions $R_{H\ \ldots\ Y}$ is the shortest in N_{11}–$H_{12}\cdots O_{42}$ (1.870 Å), which is the most stable in FCW_3 complex. In FCW_4, N_{11}–H^{FC}_{12}...O^{FC}_{8} and O_{48}–$H^{W}_{50}\cdots O^{FC}_{8}$ having largest $\Delta R_{X\text{-}H}$ value (0.017 Å), which is the strongest interaction. Among which O_{48}–$H^{W}_{50}\cdots O^{FC}_{8}$ ($R_{H\ \ldots\ Y} = 1.998$ Å) shows the most stable complex. The Hydrogen bond parameters $\delta R_{H..Y}$ is calculated from H-donor and H-acceptor [18]. In the present study, while comparing all water complexes O_{45}–$H_{46}\cdots O_{10}$ (FCW_2) and N_{11}–$H_{12}\cdots O_{42}$ (FCW_3) intramolecular hydrogen bonding shows most stable nature. Among these interactions, N_{11}–$H_{12}\cdots O_{42}$ seems to be strongest hydrogen bond due to the interaction of water molecule with N_{11}–H_{12} bond. This should be clear that N_{11} acts as highly effective donor, which is supported by natural charge analysis.

Table 1
Structural parameters of hydrogen bonds in FC water complexes.

Complex	H bond	$R_{X\text{-}H}$	$\Delta R_{X\text{-}H}$	$R_{H\ \ldots\ Y}$	$\delta R_{H\ \ldots\ Y}$	∢X–H...Y
FCW_1	O_{42}–$H^{W}_{43}\cdots O^{F}_{19}$	0.977	0.017	1.93	0.790	167.0
	O_{42}–H_{43} ....N^{F}_{11}	0.977	0.017	2.756	−0.036	91.2
FCW_2	O_{42}–$H^{W}_{43}\cdots N^{F}_{11}$	0.977	0.977	2.764	−0.044	88.7
	O_{45}–$H^{W}_{46}\cdots O^{F}_{10}$	0.979	0.979	1.870	0.850	168.2
	N_{11}–$H^{F}_{12}\cdots O^{W}_{42}$	1.021	0.010	1.983	0.767	150.0
	N_{11}–$H^{F}_{12}\cdots O^{F}_{8}$	1.029	0.018	2.38	0.370	69.5
FCW_3	O_{45}–$H^{W}_{46}\cdots O^{F}_{10}$	0.978	0.018	1.885	0.835	167.3
	O_{48}–$H^{W}_{49}\cdots O^{F}_{8}$	0.977	0.018	1.942	0.778	173.2
	N_{11}–$H^{F}_{12}\cdots O^{W}_{42}$	1.029	0.018	1.870	0.880	156.1
	N_{11}–$H^{F}_{12}\cdots O^{F}_{8}$	1.028	0.017	2.388	0.362	69.30
	O_{42}–$H^{W}_{43}\cdots O^{F}_{19}$	0.975	0.015	2.026	0.694	152.1
FCW_4	O_{42}–$H^{W}_{43}\cdots N^{F}_{11}$	0.975	0.015	2.848	−0.128	80.6
	O_{45}–$H^{W}_{46}\cdots N^{F}_{11}$	0.977	0.017	3.260	−0.540	108.0
	O_{48}–$H^{W}_{49}\cdots O^{F}_{8}$	0.977	0.017	1.998	0.722	151.3
	C_1–$H_4\cdots O_8$	1.095		2.649		62.4
FC	C_{13}–$H_{15}\cdots O_{10}$	1.092		2.410		102.3
	C_{16}–$H1_8\cdots N_{11}$	1.098		2.738		64.7
	C_{13}–$H_{14}\cdots O_{19}$	1.096		2.613		65.1
	N_{11}–$H_{12}\cdots O_8$	1.011		2.334		71.6
H_2O	OH	0.960				

The C–C–C bond angles in ring 1 (C_{20}–C_{21}–C_{22}, C_{21}–C_{22}–C_{23}, C_{23}–C_{24}–C_{25}) and ring 2 (C_{31}–C_{32}–C_{33}, C_{32}–C_{33}–C_{34}, C_{33}–C_{34}–C_{35}) are ≈ 120° (Table 1b), which shows the aromatic character of the rings. Dihedral angles C_5–O_8–C_9–O_{10} and C_5–C_8–C_9–N_{11} in ethyl carbamate group shows that the non hydrogen atoms are co-planar but in FCW_3 and FCW_4, the planarity is distorted due to the influence of N_{11}–$H_{12}\cdots O_{42}$ and O_{48}–$H_{49}\cdots N_{11}$ hydrogen bonding [19]. The dihedral angles C_{16}–O_{19}–C_{20}–C_{21} and O_{19}–C_{20}–C_{21}–C_{22} show that the phenoxy and ethylene group are planar in nature. C_{24}–C_{23}–O_{30}–C_{31} and C_{22}–C_{23}–O_{30}–C_{31} shows that the two phenoxy groups are non planar in nature. It shows the non planarity of the title compound. The self-consistent field (SCF) energy, zero point vibrational energy and dipole moment are listed in Supplementary Table S3. The increasing order of SCF energy, zero point vibrational energy and dipole moment is due to the presence of water molecule which can form intermolecular interaction with the FC molecule.

4.3. Vibrational spectral analysis

The FC molecule has 41 atoms, and it has 117 normal modes of vibration. The calculated vibrational frequencies, the measured infrared, and Raman band positions and their assignments are listed in Table 2. For visual comparison, the observed and calculated FT-IR and FT-Raman spectra of FC are presented in Figs. 2 and 3 respectively.

4.3.1. Carbamate group vibration

The carbamate group HNCOO appears in many biological compounds. It combines the characteristic of esters and amides with certain characteristics [20]. The vibrations belonging to N–H stretching always occur in the region 3450-3390 cm^{-1}, which being the characteristic region allowed for ready identification of structural features [21]. In this study, the FT-IR band observed at 3314 cm^{-1} is assigned to N_{11}–H_{12} stretching vibration, which is red shifted (76 cm^{-1}). The calculated value lies at 3388 cm^{-1}, which indicates the weakening of N–H bond resulting in proton transfer to the neighbour oxygen (N_{11}–$H_{12}\cdots O_8$). The PED of this mode is 100%, thus suggesting that this is pure mode. The red shift of N–H stretching wave number in the IR spectrum from the computed wave number indicates the weakening of N–H bond which

Table 2
FT IR, Raman and computed vibrational bands of FC and its water complexes their assignments at B3LYP Level.

IR	RAMAN	Wavenumber					Assignments	IR	Raman
		FC	FCW$_1$	FCW$_2$	FCW$_3$	FCW$_4$		Intensity	Intensity
3314vs		3388	3345	3318	3183	3202	υ_{sy}N11H12(100)	5	0
3102vw		3108	3111	3111	3111	3099	υ_{sy}C21H27(83)	1	0
3099vw		3099	3097	3099	3099	3098	υ_{sy}C32H37(87)	0	0
	3097vw	3097	3097	3096	3095	3096	υ_{sy}C24H29(98)	1	0
	3095vw	3094	3094	3094	3094	3095	C34H39(14)+C36H41(75) 20a	2	0
	3090vw	3090	3092	3092	3091	3085	C21H27(16) 20b	1	0
		3085	3085	3085	3085	3085	υ_{sy}C24H29(98)	5	0
3075vw	3075vw	3083	3078	3076	3076	3083	υ_{asy}C24H29(96)	2	0
3067 m		3070	3071	3070	3070	3071	C33H38(92)	2	0
	3065vs	3067	3063	3063	3062	3063	C36H41(75)	0	0
3041vw	3043vw	3028	3018	3038	3041	3029	υ_{asy}C13H15(88)	0	0
	3028vw	3019	3016	3020	3024	3020	υ_{asy}C1H2(81)	6	0
3012vw	3012 m	3011	3010	3012	3015	3015	υ_{asy}C1H4(98)	4	0
2970 m	2969 m	2989	2987	2999	3000	3007	υ_{asy}C5H6(81)	1	1
	2957 m	2959	2977	2962	2992	2967	υ_{asy}C13H15(79)+ υ_{asy}C16H18(79)	11	2
	2950 m	2953	2951	2954	2961	2965	υ_{sy}C5H6(98)	4	1
2938vw		2943	2942	2943	2945	2943	υ_{sy}C1H2(98)	3	1
2930 m	2929s	2942	–	–	–	–	υ_{sy}C13H15(81)+ υ_{sy}C16H18(13)	0	1
	2875 m	2903	2919	2942	2935	2921	υ_{sy}C16H17(93)+ υ_{sy}C13H14(93)	5	0
1688vs	1688 m	1746	1736	1700	1721	1714	υ_{sy}O10C9(79)	45	0
	1606 m	1611	1611	1610	1610	1606	C22C23(56)+βH26C25C24(10) 8b	3	3
	1593 m	1594	1594	1594	1594	1592	C32C33(51)+ βH37C32C33(14) 8a	8	1
1588 m	1589 m	1585	1586	1586	1586	1586	C31C32(57) 8b	3	0
1551vs	1526 m	1575	1576	1575	1575	1575	C20C21(26) 8b	2	0
1508vs	1508vw	1509	1536	1557	1575	1570	υ_{sy}N11C9(19)+υO8C9(19)+βH2C1H4(12) +β_{Sciss}H12N11C9(32)	33	0
1491s	1497w	1498	1498	1496	1496	1495	βH17C16H18(16)+βH27C21C22(46) + βH38C33C34(46) 19a	37	0
	1485 m	1486	1489	1489	1489	1489	βH12N11C9(11)+βH2C1H4(50)	14	0
	1480vw	1481	1482	1480	1481	1481	βH17C16H18(53)	17	0
	1474vw	1475	1477	1469	1470	1478	β_{asydef}H17C16C18(60)	44	0
	1467vw	1470	1469	1466	1466	1467	β_{twis}H3C1H4(66)+τH2C1C5O8(14)+β_{asydef}H6C2H7(76)	2	0
1461 m	1459 m	1458	1458	1458	1461	1459	β_{asydef}H2C1H3(76)+τ H2C1C5O8(24)+βH6C5H7(66)	1	0
	1444 m	1447	1447	1446	1449	1446	βH41C36C35(42) 19b	0	0
1426 m	1426w	1442	1432	1444	1447	1435	βH15C13H14(87)	3	0
	1412vw	1410	1412	1411	1411	1406	υ_{sy}C21C22(37)+βH26C25C24(31)+βC20C21C22(11)	0	1
	1404vw	1393	1393	1395	1399	1396	β_{sydef}H3C1H4(56)+τH6C5O8C9(20)	3	1
1391 m	1391w	1383	1378	1382	1381	1386	βH5C6H7(18)+τH18C16O19C20(47)	2	0
	1376w	1363	1366	1365	1365	1368	β_{sydef}H3C1H4(56)+τH6C5O8C9(16)+ β_{wag}H5C6H7(18)+ τH17C16O19C20(13) τH15C13N11C9(14)	4	0
1366	1365w	1354	–	–	–	–	υO30C23(23)+τH6C5O8C9(36)+τH14C13N118C9(10)+ β_{wag}H3C1H4(34)	2	0
	1316w	1315	1314	1315	1315	1314	υ_{sy}C35C36(47)+βH39C34C35(32)+β_{twis}H5C6H7(46)	1	0
	1307w	1303	1303	1302	1302	1298	C20C21(15)+C24C23(12)+βH39C34C35(20)	3	0
1296s	1296 m	1291	1294	1293	1293	1290	C20C21(11)+C35C36(11)+βH26C25C24(34)+ β_{wag}H6C5H7(34)+β_{twis}H17C16H18(16)+ β_{twis}H2C5H6(34)	4	0
	1282w	1281	1282	1281	1281	1279	υO30C23(23)+υ_{asy}C35C36(11)+βH26C25C24(39) 3	2	0
1274 m	1277 m	1269	1281	1279	1277	1278	βH14C13N11(23)+τH15C13N11C9(20)+ βH15C13H14(23)+ β_{wag}H18C16H17(20)	27	0
	1254w	1255	1254	1269	1273	1268	βH7C5C1(72)	0	0
1251vs	1249w	1252	1253	1254	1254	1262	υ_{sy}O19C20(16)+ υ_{sy}O30C23(16)	2	0
1230s	1235w	1226	1248	1250	1250	1247	H17C16H18(32)	30	1
	1220w	1217	–	–	–	–	υ_{sy}O19C20(16)+υ_{sy}O30C31(10) +βH14C13N11(10)+ β_{twist}H17C16H18(32) β_{twist}H7C5H6	87	1
	1212w	1205	1211	1212	1213	1201	υO8C9(23)+υ_{sy}N11C9(30)+βH12N11C9(32)	100	1
1194 m	1195s	1185	1187	1186	1187	1182	υ_{sy}O30C31(15)+ υO30C23(28)+βH27C21C22(16) 18b	3	0
1160 m	1194s	1153	1154	1153	1154	1152	βH37C32C33(66) 9a+βH13C15H14(35)	1	0
	1153 m	1149	1149	1149	1149	1152	β_{twist}H13C15H14(64)+ τH2C1C5O8(25)	1	0
	1139w	1146	1149	1149	1149	1147	β_{wag}H2C1H3(34)+βH26C25C24(46) 9a	2	1
	1133w	1143	1145	1148	1143	1143	βH40C35C36(70) 15	2	1
1120 m	1121 m	1143	1143	1143	1129	1128	υ_{sy}N11C13(63)+O8C5(63)+O8C9(63)	6	1
1107 m	1106 m	1107	1108	1106	1106	1104	υ_{sy}C1C5(11)+C21C22(11)+ O8C5(63))+ υO30C23(28)+τH2C1C5O8(14)	1	1
	1100w	1096	1100	1099	1100	1094	τH2C1C5O8(14)+βH26C25C24(30) 15	4	1
	1091w	1093	1095	1092	1095	1092	βH26C25C24(29) 15	2	0
	1076w	1067	1066	1066	1067	1066	βH41C36C35(42) 18b	1	0
1060s	1058w	1054	1042	1042	1043	1040	υ_{sy}N11C13(96)+ υ_{sy}O19C16(96)+ υ_{sy}C13C16(96)+β_{rock}H17C16H18(36)	13	0
1024w	1024s	1038	1034	1032	1023	1021	υ_{sy}C1C5(69)+ υ_{sy}N11C13(69)+ O8C5(69)	11	0
1009w	1002s	1013	1012	1013	1013	1012	υ_{sy}C33C34(49)+βC32C33C34(22) 18a	1	0
	1001w	992	993	992	992	994	N11C9(49)+O8C9(49)+βC20C21C22(64) 18b	2	0
	983vw	985	978	981	978	979	υ_{sy}C1C5(49)+ υ_{sy}C13C16(10)+ β_{rock}H15C13H14(18)+β_{twist}H7C5H6(29)	4	1
962vw	967vw	978	976	978	975	973	C33C34(23)+βC32C33C34(55) 17a	0	1
	931w	946	948	947	947	948	τH37C32C33C34(64)+τH37C32C33C34(15)	0	1
925vw	929w	924	925	924	924	941	β_{rock}H13C15H14(18)+τH37C32C33C34(72)+ τC31C32C33C34(15)	0	0
	910 m	915	917	915	919	925	C13C16(53)+τH26C25C24C30(74)+ υ_{sy}O19C16(53)	0	0
896w		914	905	908	914	916	C13C16(53)+τH26C25C24C30(74)	4	0

Table 2 (*continued*)

IR	RAMAN	Wavenumber					Assignments	IR	Raman
		FC	FCW$_1$	FCW$_2$	FCW$_3$	FCW$_4$		Intensity	Intensity
	904 m	902	902	905	907	906	τH27C21C22C23(75)	0	0
873 m	872 m	871	874	872	871	872	C1C5(11)+C21C22(11)+O8C5(11)+ O19C16(11)+O30C23(11)+τH17C16O19C20(70)	2	0
	860vw	860	860	860	857	857	C1C5(35)+C21C22 + O8C5 +opH12N11C9O8(81)	3	0
842s	841w	852	853	854	853	845	C5O8(16)+C21C22(16)+O30C23(16)+βC31C32C33(10)	5	0
818w	808 m	820	821	822	821	840	τH29C24C25C20(58)+opC24C22O30C23(17)	7	1
	797s	808	809	808	808	810	τH37C32C33C34(94)	0	0
	781w	791	799	805	800	803	βC31C32C33(10)	2	0
778w		787	787	788	789	786	τ H2C1C5O8(36)+β_{rock}H2C1H3(60)	0	0
763 m	765w	787	781	785	788	776	τH26C25C24C23(82)+opC21C20C22H27(82)	0	0
	745w	746	748	747	746	758	τH38C33C34C35(48)	6	0
736 m		735	734	732	730	752	opO10N11O8C9(85)	2	0
	709w	725	724	725	725	735	β_{rock}H17C16H18(16)+ β_{rock}H2C16H18(48)+τH38C33C34C35(34)	3	0
689 m		684	679	684	685	688	β_{sciss}O10C9O8(25)	2	0
666w		675	675	675	675	676	τH37C32C33C34(27)+τH31C32C33C34(57)	2	0
	639 m	630	632	632	631	673	βC21C22C23(57)+ β_{sciss}O10C9O8(48)+β_{wag}O10C9O8	0	0
	617w	608	608	609	611	610	βC32C33C34(71) 6a	0	1
	601vw	593	593	593	592	599	βC32C33C34(40) 6a	0	0
540w	534vw	564	563	563	564	560	βC22C23C30(44)	1	0
515w	530vw	507	513	516	513	516	υ_{sy}βC16C13N11(43)	2	0
	506vw	503	503	504	503	497	τH29C24C25C20(10)+opC24C22O30C23(17) +opC32C33C34C35 (57)	3	0
492w		496	485	486	486	485	β_{twis}O10C9O8(48)+opH12N11C9O8(73)	18	0
	489vw	486	–	–	–	–	τC32C33C34C35(12)+ opC32C33C34C35 (57)	3	0
	449vw	445	444	446	446	443	βC1C5O8(37)+ β_{rock}O10C9O8(48)	0	0
		437	438	438	440	424	βC20C21C22(46)	0	0
		414	414	415	415	417	τH26C25C24C30(10)+τC20C21C22C23(70)	0	0
		408	408	407	407	407	τH37C32C33C34(15)	0	0
	373 m	359	359	364	366	375	βC16O19C20(53)	1	0
		355	356	356	355	351	τC21C22C23O30(12)+opC24C22O30C23(22)	0	1
	346 m	342	343	345	343	339	βC22C23C30(10)+βC16C19C20(24)	1	1
	333vw	331	331	337	335	329	βC36C31O30(27)	1	31
		294	296	299	297	297	βC9N11C13(40)	0	1
	236 m	255	256	255	275	270	τH2C1C5O8(91)	0	0
		221	225	230	241	238	βC36C31O30(10)+βC16O19C20(23)+ τC32C33C34C35(12)	1	1
		206	208	209	209	213	τH31C32C33C34(27)	0	1
	189 m	173	187	194	204	201	βC23C24C25(11)+τC21C22C23O30(26) +τH20C21C22C23(13)+τN11C13C16O19(15)	0	0
		161	168	154	167	159	βC1C5O8(31)+τN11C13C16O19(15)	1	0
	111vs	146	151	151	153	151	τN11C13C16O19(50)	0	1
		117	133	132	133	132	βC36C31O30(11)+βC1C5O8(33)	0	4
		105	106	107	104	102	τC5O8C9N11(58)	0	4
		77	82	79	81	87	βC23C24C25(15)+τC5O8C9N11(51)	0	3
	67s	61	63	65	55	54	τC1C5O8C9(62)	0	17
		42	48	51	47	35	τC1C5O8C9(59)	0	10
		31	32	33	27	–	βC23C24C25(14)+τC21C22C23O30(17) +τC5O8C9N11(12)	0	25
		28	26	27	–	–	τC1C5O8C9(49)	0	23
		26	24	26	24	24	τC1C5O8C9(68)	0	21
		12	14	13	15	16	τC13C16O19C20(65)	0	47
		9	7	10	11	12	τC9N11C13 τC9N11C13C16(74)	0	100

Υ_{asy}: antisymmetric stretching; $\upsilon_{sy:}$ symmetric stretching; β: inplane bending; β_{asydef}: antisymmetric deformation; β_{sciss}: scissoring; β_{wag}: wagging; β_{twis}: twisting; β_{rock}: rocking; op: out of plane bending; τ: torsion; s: strong; vs: very strong; m:medium; w:weak; vw: very weak.

resulting the proton transfer to the neighbouring oxygen atom. In water complexes, the theoretically calculated wavenumber in FCW$_3$ is observed at 3183 cm^{-1}. The largest shift is noted in FCW$_3$, in which $N_{11}-H_{12}\cdots O_{42}$ hydrogen bonding is the strongest one.

The CNH vibration in which nitrogen and hydrogen atoms move in opposite direction of carbon atom in the amide moiety generally appears at 1508 cm^{-1} in IR and Raman spectra and the CNH vibration in which N and H atoms move in the same direction of carbon atoms in the amide group appears at 1212 cm^{-1} in Raman corresponding calculated value is at 1205 cm^{-1} [22]. The CN stretching vibration coupled with NH in plane bending is active in the region 1375 ± 55 cm^{-1}. In the present study the band at 1212 cm^{-1} in Raman, and the calculated value 1205 cm^{-1} is assigned as C_9-N_{11} stretching mode. The wagging of NH is moderately active in the region 790 ± 70 cm^{-1} and the band at 842 cm^{-1} is assigned as this mode.

C=O stretching band strongly appears in the range 1740–1683 cm^{-1}. The electron attracting group attached to the nitrogen atom increases the frequency of absorption [23,24]. In the present study, the $C_9{=}O_{10}$ stretching mode is observed as very strong band at 1688 cm^{-1} in IR and medium band in Raman. In FCW$_2$, FCW$_3$ and FCW$_4$ the wavenumber is decreased compared with FC and FCW$_1$ due to the conjugation between C=O and water molecules by which there is $O_{45}-H_{46}\cdots O_{10}$ hydrogen bonding. The antisymmetric stretching of COO group vibration appears in the IR and Raman at 1508 cm^{-1}. COO deformation usually occurs in the region 650-510 cm^{-1}. Rocking inplane and out of plane deformation vibration are observed as strong bands in the region 760-400 cm^{-1}. The COO deformation coupled with rocking mode appears at 449 cm^{-1} in Raman which is good agreement with the theoretical value at 445 cm^{-1}. The wagging mode is appeared at 736 cm^{-1}in IR.

The C–O stretching mode always occurs in the region 1300-

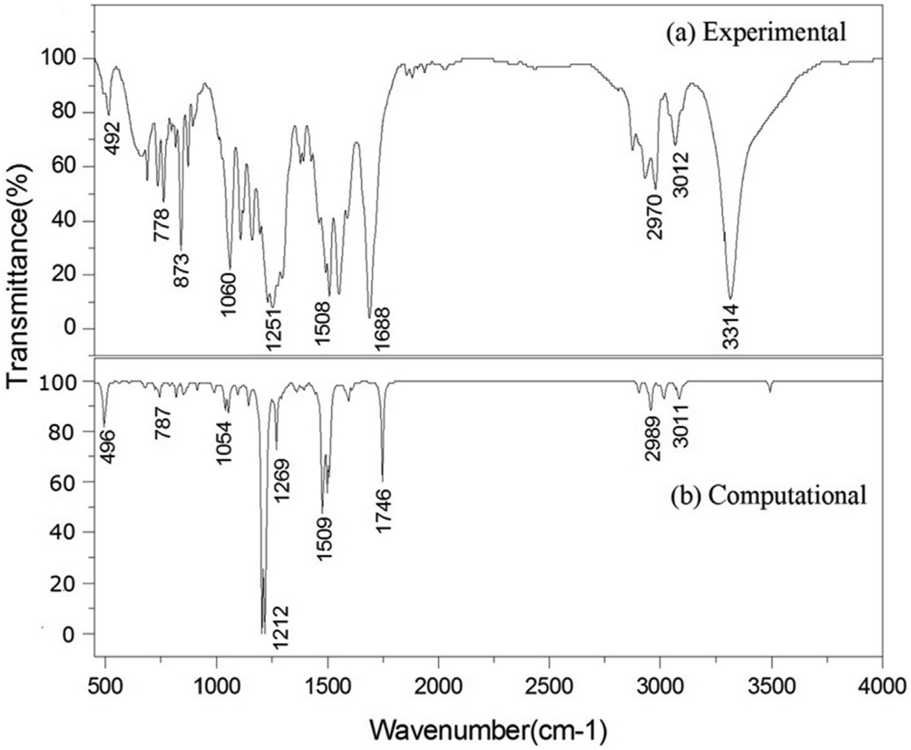

Fig. 2. Combined FT-IR spectrum of FC.

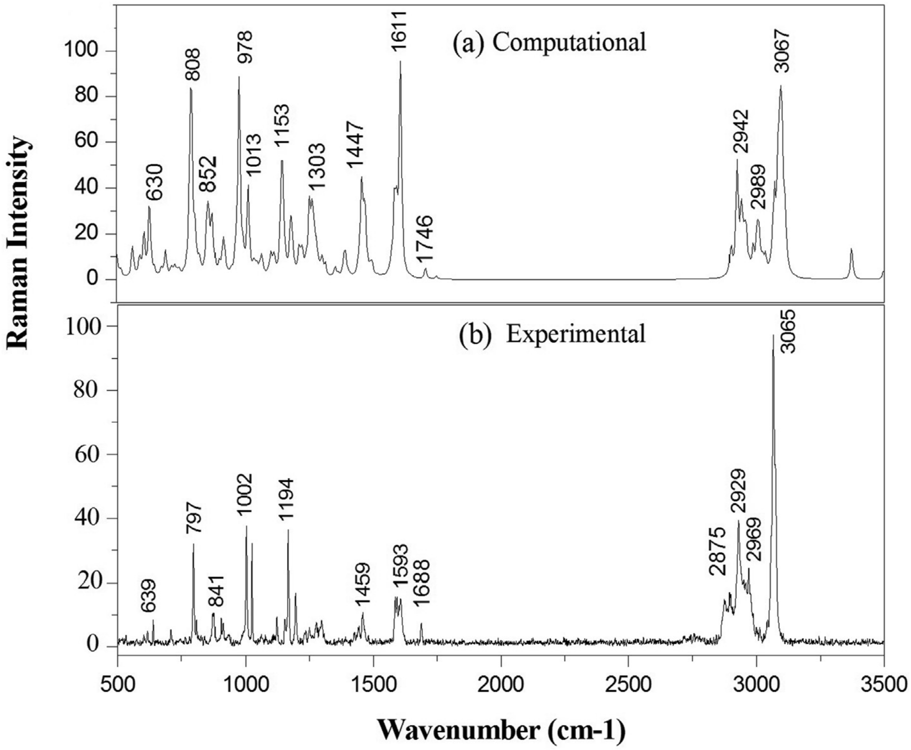

Fig. 3. Combined FT-Raman spectrum of FC.

1000 cm^{-1} [24]. The intensity of carbamate group increases due to the formation of hydrogen bond, it increases the intensity of IR and Raman bands. Thus the frequencies 1120, 1107, 873,842 in IR and 1121, 1106, 983, 877, 841 cm^{-1} in Raman are assigned to C_5—O_8 and C_9—O_8 modes. The in plane bending vibration of C—O are observed as mixed vibration of $\beta C_1C_5O_8$ at 449 cm^{-1} in Raman spectra where the calculated frequency is 445 cm^{-1} in FC. The out of plane bending modes also contribute to the mixed vibration of

$O_{10}N_{11}O_8C_9$ (85%), but shifted to high wavenumber value due to the effect of ethylene group attached to the carbamate group of the title compound.

4.3.2. CH_3 group vibration

The CH_3 group has 9 vibrational modes. The antisymmetrical stretching mode is expected in the range 2995−2930 cm^{-1}. The bands observed at 3012 cm^{-1} in IR and 3012, 3028 cm^{-1} in Raman corresponds to antisymmetric stretching. The corresponding calculated values are at 3011, 2989 cm^{-1}. The blue shifting of about 22 cm^{-1} is due to $C_1{-}H_4{\cdots}O_8$ hydrogen bonding interaction. The symmetric stretching modes give rise to strong band in the region 2930-2890 cm^{-1} [25]. For FC, it is observed at 2938 cm^{-1} in Raman and corresponding calculated values obtained at 2943 cm^{-1} is assigned with PED contribution of 98%.

The two deformation vibrations are possible in the CH_3 group, where the antisymmetric deformation vibration is observed in the region 1480-1435 cm^{-1} and symmetric vibration is in the region 1390-1360 cm^{-1}. For FC, the two antisymmetric deformation vibration modes are obtained at 1461 cm^{-1} in IR and 1459 cm^{-1} in Raman. The calculated values are at 1470, 1458 cm^{-1}. The symmetric deformation is observed at 1376 cm^{-1} in Raman. The inplane CH_3 rocking vibration is observed as medium band in IR at 1160 cm^{-1} and strong band in Raman at 1194 cm^{-1} with 60% PED. The out of plane rocking mode generally occurs in the region 1150-1080 cm^{-1}. For FC, this mode is observed in Raman at 1058 cm^{-1} and the corresponding calculated value is observed at 1054 cm^{-1}. The wagging vibrational mode is observed in Raman at 1139 cm^{-1}.

4.3.3. CH_2 group vibration

The CH_2 group has 6 vibrational modes. The antisymmetric and symmetric vibrations are generally observed in the region 2955-2950 cm^{-1} and 2880-2835 cm^{-1} respectively. In the present study, the CH_2 antisymmetric vibration is identified as medium band in Raman at 2969 cm^{-1} (C_5H_6) and 2957 cm^{-1} ($C_{13}H_{15}$) and $C_{16}H_{18}$). The symmetric band is observed as medium band in Raman at 2950 cm^{-1} (C_5H_6), 2929 cm^{-1} ($C_{13}H_{15}$ and $C_{16}H_{18}$). The C_5H_6 antisymmetric vibrations are shifted by about 14 and 70 cm^{-1} respectively due to the presence of $C_5{-}H_6{\cdots}O_8$ hyperconjugatve interaction. The corresponding calculated antisymmetric vibrations of $C_{13}H_{15}$are obtained at 2959, 2977, 2962, 2992 and 2967 cm^{-1} in FC, FW_1, FW_2, FW_3 and FW_4 respectively. The increase in wavenumber of FCW_3 is blue shifted due to the $C_{13}{-}H_{15}{\cdots}O_{45}$ hydrogen bonding interaction. The CH_2 deformation vibration is expected in the region 1463 ± 13 cm^{-1} [23]. For FC, this mode is observed at 1474, 1459 cm^{-1} in Raman and 1461, 1442 cm^{-1} in IR. It is clear that most of these modes are mixed modes of CH_2 and CH_3. The wagging vibration usually appears in the region 1382-1170 cm^{-1}. In our present study, these modes are expected in the region at 1296, 1274 cm^{-1} in IR and 1296, 1277 cm^{-1} in Raman. The twisting mode appears in between 1220, 1153 cm^{-1}. The rocking vibration of CH_2 group usually appears in the region 1174-724 cm^{-1}. The band observed at 983 and 931 cm^{-1} in Raman is assigned as rocking modes of CH_2 group, and the corresponding calculated values are obtained at 985 and 946 cm^{-1}.

4.3.4. Ring vibration

The stretching wavenumber of monosubstituted phenyl ring are expected in the region 3120-3010 cm^{-1}.In FC a weak band in IR at 3102 cm^{-1} is observed and the corresponding calculated value is observed at 3108 cm^{-1}. The mode 19b of monosubstituted phenyl ring is expected in the region 1470-1444 cm^{-1}. In Raman spectrum the medium band observed at 1444 cm^{-1} is correlated to 19b mode. The simultaneous activation of 8a, 8b and 19b mode clearly exhibit intermolecular charge transfer. The 8a mode is observed 1593 cm^{-1} in Raman spectra and the vibrational mode 8b extents from 1597 to 1562 cm^{-1}. FTIR spectrum shows a medium band at 1588 cm^{-1} and in Raman at 1589 cm^{-1} [26]. C−C stretching mode 14 of monoheavy substituted benzene is observed in IR and Raman as strong band at 1296 cm^{-1}.

There are five normal vibrations 3, 9a, 15, 18 and 18b for mono heavy substituted benzene characterising C−H in plane bending which occurs in the region 1300-999 cm^{-1}. A medium IR band is observed at 1160 cm^{-1} and strong band observed at 1194 cm^{-1} in Raman have been assigned to the mode 9a, which is enhanced due to the fact that this mode is coupled with the substituent oxygen. The corresponding calculated values of FC and its water complexes are found to be 1185,1187,1186,1187 and 1182 cm^{-1}. Normal mode 3 is active in Raman as weak band at 1307 cm^{-1}, while the normal mode 18 has been observed in Raman at 1002 cm^{-1} with strong intensity.

In diheavy substituted benzene mode 20b is observed in Raman as weak band at 3090 cm^{-1} which is expected in the region 3120-3020 cm^{-1}. The 19a mode is observed as strong band in FTIR at 1491 cm^{-1}, which generally occurs in the region 1530-1460 cm^{-1} [26]. The 8b mode appears as a medium band in Raman at 1605 cm^{-1}. The C−C stretching mode of phenyl ring is expected in the range 1650−1200 cm^{-1}. In the present work the CC stretching wavenumber is observed in FTIR spectrum at 1588, 1551, 1508, 1296 cm^{-1} and FT Raman at 1606, 1593, 1589, 1526, 1412, 1316, 1307, 1296, 1282 cm^{-1}. Here the $C_{20}{-}O_{19}$ and $C_{23}{-}O_{30}$ vibrations are observed as strong in IR at 1251 cm^{-1} and medium band in Raman at 1249 cm^{-1}.

4.3.5. Vibration due to water complex

The X−H stretching vibration frequencies of hydrogen bonds in FC and water complexes are listed in Supplementary Table S4. Stronger the hydrogen bond means the larger the shift value. In the present study the intramolecular $N_{11}{-}H_{12}{\cdots}O_{42}$ hydrogen bonds are calculated and the largest red shift value (−205 cm^{-1}) is found in FCW_3. This indicates that the N−H bond of carbamate group is red shifted because of the largest negative shift. The N_{11} atom also interact with water molecule ($N_{11}{-}H_{12}{\cdots}O_{42}$), which shows high interaction among the complexes. The $C_{13}{-}H^{FC}_{15}{\ldots}O^{W}_{45}$ hydrogen bond in FCW_2 and FCW_3 has a small blue shift values about $+10_{asy}$, 39_{sy} and $+13_{asy}$, $+39_{sy}$ respectively. This concludes the positive shift of hydrogen bond involving in the ethylene group. In this analysis the highest negative value of $\Delta\upsilon_{X\text{-}H}$ for $N_{11}{-}H_{12}{\cdots}O_{42}$ interaction in FCW_3 leads to the strongest binding interaction.

4.3.6. Liberation modes of water complex

The antisymmetric and symmetric vibration of water molecule normally occurs in 3756 cm^{-1} and 3652 cm^{-1} respectively. The antisymmetric stretching vibration is identified at 3652 cm^{-1} and symmetric vibration at 3500 cm^{-1} respectively in FCW_1. When increasing the number of water molecule, the strong hydrogen bond reduces to O−H force constant within the water molecule and reduces the stretching wave number [27]. The liberation mode of water molecule is listed in Supplementary Table S5.

The in plane deformation of water molecule is observed at 1650 cm^{-1}, which arises from vibration of water. The out of plane hydrogen bond liberation band is the most prominent spectroscopic manifestation of bulk water molecule. The liberation mode of water is detected in the spectral region between 900 and 300 cm^{-1} [28]. In FCW_1 wagging, twisting and rocking vibrations occurred at 884, 690, 574 cm^{-1} respectively.

4.4. NBO analysis

Natural Bond Orbital Analysis is an essential tool for studying intra and intermolecular bonding and interaction among bonds and also for investigating the hyperconjugative interaction in molecular system [29].The second order perturbation theory analysis by fock matrix in NBO basis corresponding to intramolecular bond of FC and its water complexes are listed in Supplementary Table S6.

In the present study there are various types of C—H···O, N—H···O, O—H···O hydrogen bonds in FCW_1, FCW_2, FCW_3 and FCW_4, complexes are possible. When the water molecule is added a strong intra molecular hydrogen bonding is exposed in NBO analysis by the interaction between the oxygen lone pair and N—H antibonding orbital $n(O_{42}) \rightarrow \sigma^*(N_{11}-H_{12})$ having hydrogen bonding interaction energy 18.786, 3.849 and 1.630 kJ/mol in FCW_1, FCW_2 and FCW_3 respectively. The lone pair of oxygen also donates its electron to σ type antibonding orbital of $N_{11}-H_{12}$. The possible hydrogen bonding and hyperconjugations of FC and its water complexes are listed in Table S7a and b.

The interaction between n_1 (N_{11}) and antibonding orbital $\sigma^*(O-H)$ shows the existence of strong N—H···O hydrogen bonding interaction in FCW_1, FCW_2 and FCW_3, which is supported by vibrational analysis. The downshift in N—H stretching wavenumber predicts red shift. $H_{12}\cdots O_{42}$ distance (2.221 A°) is shorter than that of van der Waals separation between the oxygen and hydrogen atom (2.720 Å) indicating the existence of strong N—H···O hydrogen bonding interaction. There is another interaction also, ie $O_{19} \rightarrow \sigma^*(O_{42}-H_{44})$ implies the existence of $O_{42}-H_{44}\cdots O_{19}$ hydrogen bond, which has the total stabilization energy 0.669 kJ/mol. In addition to the intermolecular hydrogen bonding there is C—H···O hyperconjugative interaction also. This is due to the lone pair oxygen atom $n_1(O_8)$ of carbamate group and antibonding orbital $\sigma^*(C_5-C_6)$ bond of ethyl group having $E^{(2)}$ value 3.766 kJ/mol. The lone pair N_{11} of carbamate group and antibonding orbital $\sigma^*(C_{13}-C_{14})$ bond of ethyl group having $E^{(2)}$ value 15.355 kJ/mol.The stabilization energy of ICT between $\sigma(N_{11}-H_{12}) \rightarrow \sigma^*(C_9-O_{10})$ of FC and FCW_3 are 15.732, 23.514 kJ/mol respectively. Also the ICT from $O_{45} \rightarrow \sigma^*(C_{16}-H_{18})$ in FCW_3 is one of the most important transition in FC water complexes. It shows the greater stability of the molecule with stabilization energy 100.918 kJ/mol while comparing with FCW_2, FCW_3 and FCW_4. The highest interaction predicts that these complexes could have strong stability and good biological activity.

4.5. *Charge distribution*

Atomic charge has used to describe the processes of electronegativity equalization and charge transfer in chemical reactions [30]. In FC and its water complexes the charge at C_9 (Supplementary Fig. S3) of carbon atom in carbamate group having more positive charge which is obvious due to the presence of the electron withdrawing nature of nitrogen and oxygen atoms, that withdrawn electron from the carbon atom of the carbamate group. However the result shows that the carbamate region leads to a redistribution of electron density symmetrically. Namely the charge of molecule show symmetric distribution due to the symmetry of carbamate group. Other positively charged carbon atoms (C_{20}, C_{23}, C_{31}) are attached to the electron withdrawing oxygen atoms.

The more negative charged atom C_5 shows the electron withdrawing nature of methyl group. The presence of larger negative charge on nitrogen (N_{11}) and oxygen and net positive charge on hydrogen atom may cause the formation of intramolecular interaction in solid form [31,32]. N_{11} shows reduction in negative charge at FCW_3 because of the strong and most stable $N_{11}-H_{12}\cdots O_{42}$ intramolecular hydrogen bonding interaction. The greatest positive charge observed at H_{12}, due to strong $N_{11}-H_{12}\cdots O_{42}$ intramolecular hydrogen bonding interaction, where the electrons are delocalized more towards the hydrogen atom with natural charges. This strong hydrogen bonding is supported by optimized parameter and vibrational analysis. The ethylene and ethyl groups are influenced by steric effect. This can be observed from the interatomic distance $H_{27}\cdots H_{18}$ (2.322 Å), $H_{27}\cdots H_{17}$ (2.353 Å), $H_7\cdots H_6$ (1.700 Å) and $H_4\cdots H_3$ (1.780 Å). H···H distance varies due to the intramolecular hydrogen bonding in water complexes. In FCW_3, the charge at H_{18} increases compared with FC and all other water complexes due to the presence of $C_{16}-H_{18}\cdots O_{45}$ hydrogen bonding ($O_{45}\cdots H_{18} = 2.630$ A°) and high stabilization energy $E^{(2)} = 100$ kJ/mol, which is supported by NBO analysis.

4.6. *Fukui function*

To illustrate chemical reactivity and selectivity, the Fukui function is adopted as the local density functional descriptors. With respect to electron changes its density changes in the region where a chemical group changes. It shows the tendency of the electronic density to deform at a given position upon accepting or donating electrons [33–35].

Condensed Fukui function and related local and global parameters calculated by UCA-FUKUI software is listed in Table 3. The hardness, softness, philicities, electrochemical potential, and fukui condensed functions obtained by UCA-FUKUI is shown in Supplementary Table S8. Local nucleophilicilty, local electrophilicity, local softness and local hardness calculated by UCA Fukui

Table 3
Condensed Fukui functions calculated with UCA-FUKUI for FC and water complexes.

Atoms	f+	f-	f0	Δf
C_1	0.0017	0.0024	0.0021	0.0007
H_2	−0.0032	−0.0042	0.0037	0.0010
H_3	−0.0080	−0.0096	0.0088	0.0016
H_4	0.0023	0.0010	0.0017	−0.0014
C_5	0.0015	0.0023	0.0019	0.0008
H_6	−0.0062	−0.0074	0.0068	0.0012
H_7	−0.0010	−0.0026	0.0018	0.0015
O_8	−0.0012	−0.0056	0.0034	0.0043
C_9	−0.0021	0.0013	0.0004	−0.0008
O_{10}	−0.0118	−0.0250	0.0184	0.0132
N_{11}	0.0055	−0.0149	0.0047	0.0094
H_{12}	0.0032	0.0003	0.0017	−0.0028
C_{13}	0.0027	0.0078	0.0052	0.0051
H_{14}	−0.0078	−0.0127	0.0103	0.0050
H_{15}	−0.0138	−0.0174	0.0156	0.0036
C_{16}	0.0090	0.0156	0.0123	0.0066
H_{17}	−0.0084	−0.0182	0.0133	0.0099
H_{18}	−0.0085	−0.0199	0.0142	0.0114
O_{19}	−0.0172	−0.0806	0.0489	0.0634
C_{20}	−0.0083	−0.0707	0.0395	0.0624
C_{21}	−0.0926	−0.04300	0.0678	−0.0495
C_{22}	−0.1023	−0.0332	0.0677	−0.0691
C_{23}	0.0188	−0.0560	0.0186	0.0373
C_{24}	−0.0917	−0.0208	0.0563	−0.0709
C_{25}	−0.1075	−0.0326	0.0700	−0.0749
H_{26}	−0.0381	−0.0310	0.0345	−0.0071
H_{27}	−0.0367	−0.0296	0.0332	−0.0071
H_{28}	−0.0341	−0.0289	0.0315	−0.0052
H_{29}	−0.0258	−0.0237	0.0247	−0.0021
O_{30}	−0.0123	−0.1009	0.0566	0.0886
C_{31}	0.0168	−0.0190	0.0011	0.0023
C_{32}	−0.0486	−0.0354	0.0420	−0.0132
C_{33}	−0.0831	−0.0112	0.0471	−0.0720
C_{34}	−0.0106	−0.0964	0.0535	0.0858
C_{35}	−0.0648	−0.0150	0.0399	−0.0498
C_{36}	−0.0793	−0.0420	0.0607	−0.0374
H_{37}	−0.0095	−0.0115	0.0105	0.0020
H_{38}	−0.0319	−0.0284	0.0302	−0.0034
H_{39}	−0.0323	−0.0288	0.0306	−0.0036
H_{40}	−0.0339	−0.0301	0.0320	−0.0037
H_{41}	−0.0290	−0.0245	0.0267	−0.0045

shown Supplementary Fig. S4.

It is found that the dual descriptor (Δf) value of O_{30} is highly positive, that is tendency to acquire electron and C_9 is electrophilic. Among all hydrogen atoms H_{18} is highly nucleophilic. It is clear that there is an eventual charge transfer in FC molecule from aromatic to aliphatic region. This is also supported in HOMO-LUMO analysis.

4.7. Hirshfeld surface analysis

The Hirshfeld of the title compound was pursued to elucidate the nature of intermolecular interaction and are illustrated in Supplementary Fig. S5 showing the surface that have been depicted over d_i, d_e, d_{norm}, shape index and curvedness. The d_{norm} surface reveals the close contacts of hydrogen bond donors and acceptors [36]. These spots are seen at O_{10} of carbamate group. The shape index curve represents the donor − acceptor pair. The interactions are visible on the Hirshfeld surface as well as finger print plots. The graphical representation of Hirshfeld finger print plot for the interaction of FC is shown in Fig. 4.

The d_e and d_i values show the closest external and internal distance from the given plot on Hirshfeld contact such as H···N (1%), H···O (20.5%), H···H (53%) and C···H (25.4%). The O···H interactions are represented by a spike indicating that oxygen atom contact with N−H in carbamate group. The shortest distance ($d_e + d_i$) for H···O interaction in FC is ~2.200 A° representing N−H···O hydrogen bonding. The percentage contributions of intermolecular interactions to the relative Hirshfeld surface reveals N−H···O (20.5%), where as more significant contributions come from H···H contacts (53%) show a sharp peak in Fig. 4,which is reflected in the scattered point in the fingerprint plot. The intermolecular interactions in the compound enhance the insecticidal activity of the FC molecule [37].

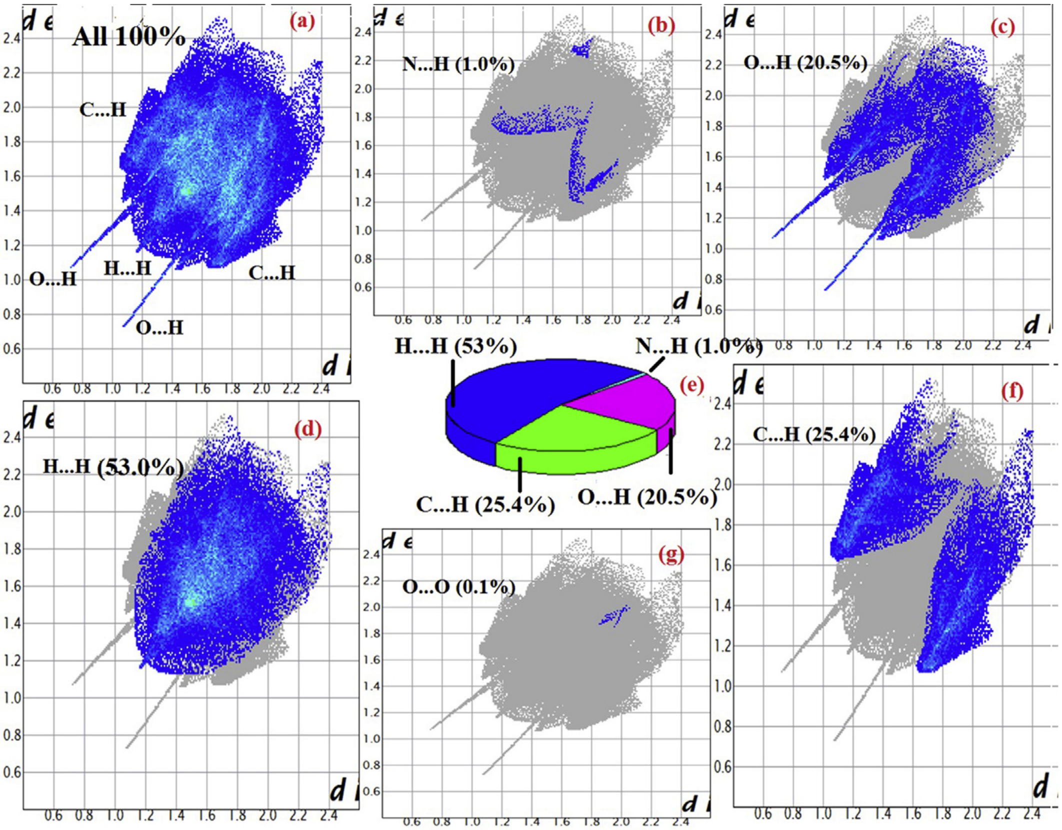

Fig. 4. 2D fingerprint plots of selected interactions of FC.

4.8. NMR spectral analysis

The ^1H and ^{13}C theoretical and experimental chemical shift of FC are listed in Table 4. The observed ^1H and ^{13}C NMR spectrum of FC in DMSO solution is shown in Fig. 5a and b. The shielding calculations of FC were carried out using 6-31G(d) basis set in DMSO solution. The isotropic shielding values were used to calculate the isotropic chemical shift with respect to tetramethyl silane. The agreement between the experimental and the calculated $^{13}C(R^2$-0.9826) and $^1H(R^2$-0.9925) are good. The correlation graphs between calculated and experimental ^1H and ^{13}C NMR chemical shifts of FC are shown in Supplementary Fig. S6.

The FC molecule having 17 different carbon atoms. Taking into account that the range of ^{13}C NMR chemical shift for analogous organic molecule >100 ppm, the accuracy ensures reliable interpretation of spectroscopic parameters. In the present work, ^{13}C NMR chemical shifts in the ring for FC molecule >100 ppm. Oxygen atom shows electronegative property. Therefore the chemical shift value of C_{20}, C_{23} and C_{31} in the ring has been observed at 150.25, 129.71, 158.57 ppm that are calculated at 141.37, 138.92 and 148.39 ppm respectively. Another carbon peaks are observed at 67.17, 40.19, 59.96 and 14.14 ppm due to C_{16}, C_{13}, C_5 and C_1 respectively. The C_9 atom is seated in between the electronegative oxygen and nitrogen atoms, therefore the calculated chemical shift value of C_9 is 155.29 ppm and its experimental value obtained is about 143.82 ppm. The chemical shift values of ethylene and ethyl groups attached to hydrogen atom experiences a lesser value of about 4.08 ppm and fairly agrees with the calculated value. The H_{12}

Table 4
The theoretical and experimental ^{1}H and ^{13}C chemical shifts of FC with respect to Tetra Methyl Silane (TMS).

Atom	Experimental (ppm)	Calculated (ppm)	Degeneracy
C_1	14.14	11.49	1
C_5	59.96	57.82	1
C_9	155.29	143.82	1
C_{13}	40.19	38.16	1
C_{16}	67.16	63.94	1
C_{20}	150.25	141.37	1
C_{21}	117.45	120.75	1
C_{22}	115.48	113.52	1
C_{23}	129.71	138.92	1
C_{24}	115.68	112.45	1
C_{25}	117.45	109.16	1
C_{31}	158.57	148.39	1
C_{32}	115.68	105.29	1
C_{33}	122.48	120.10	1
C_{34}	120.67	112.09	1
C_{35}	122.48	120.33	1
C_{36}	115.68	108.87	1
H_2	1.17	1.58	1
H_3	1.19	1.36	1
H_4	1.20	1.56	2
H_6	4.05	4.29	1
H_7	4.08	4.29	2
H_{12}	4.08	4.73	2
H_{14}	3.07	3.55	1
H_{15}	3.52	4.05	1
H_{17}	3.53	4.15	1
H_{18}	3.50	4.13	2
H_{26}	7.07	7.11	1
H_{27}	6.98	6.97	1
H_{28}	7.32	7.30	2
H_{29}	7.05	7.19	1
H_{37}	6.94	6.80	1
H_{38}	7.34	7.53	1
H_{39}	7.32	7.30	1
H_{40}	7.35	7.69	1
H_{41}	7.08	7.26	3

have a maximum chemical shift that shows the electron donating property of nitrogen atom.

4.9. UV visible spectral analysis

In order to understand the nature of electronic transfer with in FC molecule, TD-DFT level with CAM B3LYP calculations on electronic absorption spectra in acetone was performed and visualised in Supplementary Fig. S7. The λ-max value is obtained from the UV spectrum analysed theoretically with 6−311++G(d,p) and 6-31G(d) level of theory. The calculated UV absorption maxima theoretical electronic excitation energies and oscillator strength are given in Supplementary Table S9.

It is observed that the experimental absorption band centred at 212 nm for acetone. The corresponding calculated value obtained 215 nm in CAM B3LYP/6−311++G(d,p) level of theory. Furthermore CAM B3LYP/6-31G(d) level, the calculated value is recorded at 219 nm. All the transitions are assigned to $\pi \rightarrow \pi^*$. Based on the predicted dipole moment values, it is found that the dipole moment increases in going from gas phase to the solvent phase. While comparing the calculated wavelength with energy levels CAM B3LYP/6−311++G(d,p) is very close to the experimental value [38].

4.10. Frontier molecular orbitals

The frontier molecular orbital's HOMO, LUMO helps to exemplify the chemical reactivity and kinetic stability of the molecule and is very important parameter for quantum chemistry. The energy of the Highest Occupied Molecular Orbital (HOMO) is directly related to the ionization potential, Lowest Unoccupied Molecular Orbital (LUMO) energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures [39–41]. In HOMO of FC the electron distribution spreads over the phenoxy group and the LUMO is distributed over the carbamate group though ethylene moiety. The E_H and E_L values are calculated as −8.457 eV and −5.013 eV respectively. The ΔE value represents the smallest amount of energy needed for electronic excitation which belongs to $\pi \rightarrow \pi^*$ transition. In FC molecule the HOMO-LUMO energy value is predicted to be 3.444 eV. This value explains the eventual charge transfer interaction with in the molecule, which influences in the biological activity of the compound. The lower HOMO-LUMO energy gap indicates the FC molecule is highly reactive [42]. The frontier orbital (HOMO, LUMO) of FC is plotted in Fig. 6.

4.11. Global reactivity descriptors

Electronegativity (χ) chemical potential (μ), global hardness (η), global softness (S) and electrophilicity index (ω) are global reactivity descriptors, highly successful in predicting global reactivity trends on the basis of Koopmans's theorem [43,44]. Global reactivity descriptors are calculated [45]. The energies of frontier molecular orbitals (E_{LUMO}, E_{HOMO}) and global reactivity descriptors are listed in Table 5.

Higher the value of the electrophilicity index better is the electrophilic character. Thus, among all compounds, FCW_1 acts as a good electrophile as the molecule shows higher value for global electrophilicity index (ω) 0.4859 eV, as compared to compounds FCW_1, FCW_2, FCW_3 and FCW_4.

4.12. Docking studies

Molecular docking technology has been employed to understand the different binding modes of FC- ligand interactions. It also gives an idea about the binding energy of the compound with different proteins of the insecticidal strains [46,47]. Juvenile hormone proteins have been isolated from several insect species like *Bombyx mori, Heliothis virescens, Manduca sexta* and *Galleria mellonella* [48]. Among these, one protein from *Bombyx mori* (pdb ID, 3AYZ) and one protein from *Galleria mellonella* (pdb ID: 2RCK) are the objects of the present study. The conformational stability, hydrogen bond interactions, intermolecular energy and inhibition constant were analysed using AutoDock tools [49]. Ten different poses were generated for each ligand and ranked based on the binding affinity.

The binding affinities of FC with two target proteins were analysed using Molecular Docking studies. The present studies provided insights into inhibition of target insecticidal proteins by FC. Binding affinity, intermolecular interactions and inhibition constant are noted down for all ligand protein complexes. The binding mode of ligand with the two target proteins were effectively using Autodock tools and displayed in Fig. 7. Summary of hydrogen bonding and molecular docking results of FC with different protein targets are listed in Table 6 respectively.

Analysis of binding site revealed that FC exhibited a binding affinity of −6.32 kcal/mol and −3.48 kcal/mol with the proteins 2RCK and 3AY8. Both the compounds had one hydrogen bond interaction at VAL 55 and LYS 40 respectively. From the studies it is evident that the compound exhibited a significant effect against the target proteins and further analysis of the stability of the interaction would help in developing a potent lead molecule against the

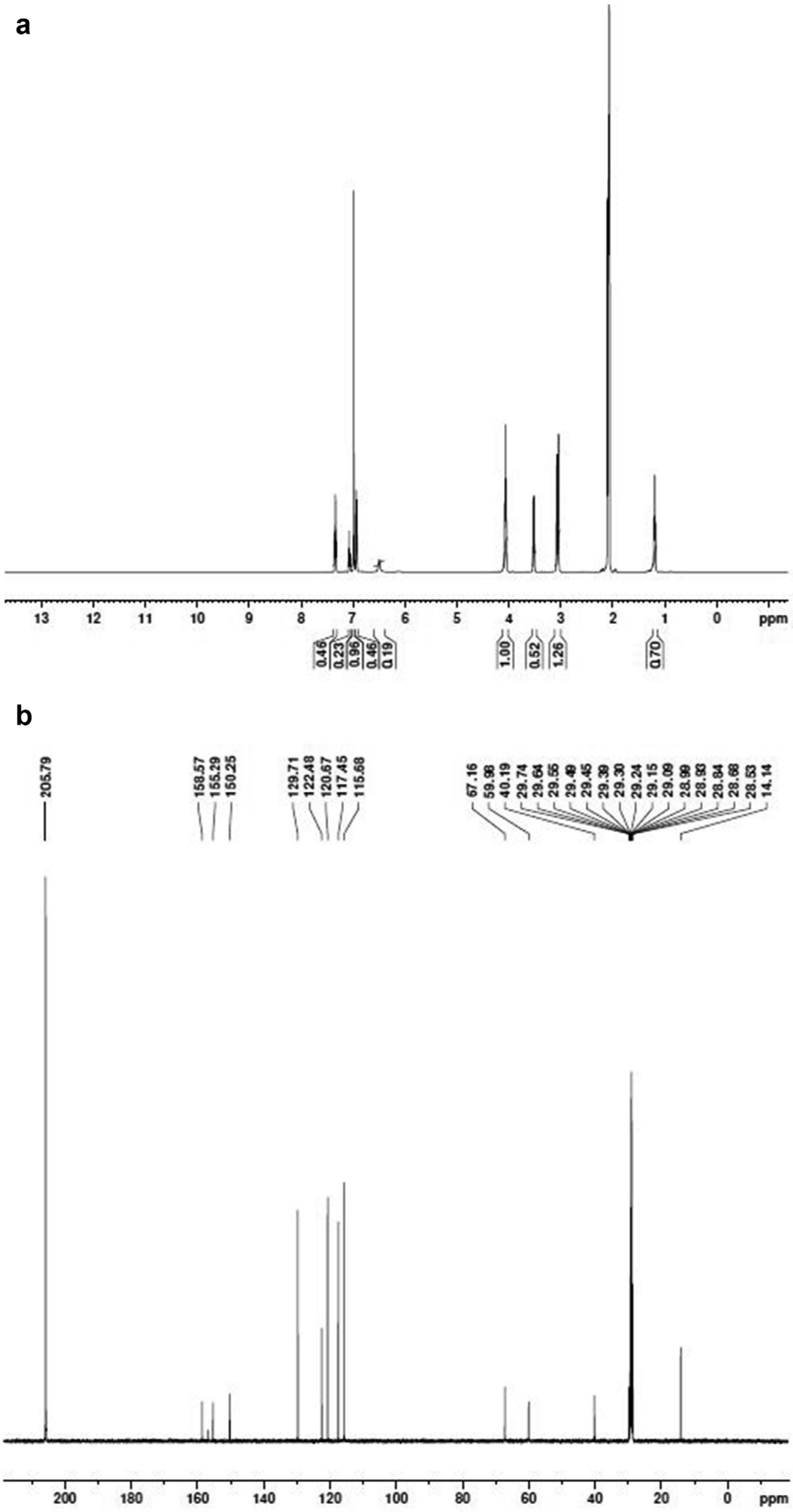

Fig. 5. a: The observed ^{1}H NMR spectra of the FC in DMSO solvent b: The observed ^{13}C NMR spectra of the FC in DMSO solvent.

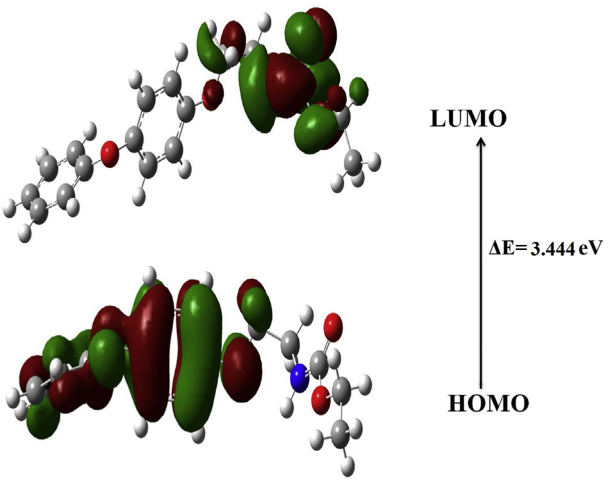

Fig. 6. Plot of frontier molecular orbitals of FC.

insects.

4.13. Insecticidal activity

The insecticidal activity of title compound was evaluated against *Sitophillus oryzae* [50]. The insects maintained as the feed supplement consisting of 2.5 kg pearl millet, 100 g powdered ground nut kernel, 5 g yeast and 5 g sulphur were mixed well in a sterile plastic tray and was infested with collected larvae; it was covered with fine cloth for ventilation. 5 gms of rice were sterilized by means of UV rays. After sterilization the feed was coated with different concentrations of title compound (62.5, 125, 250, 500 and 1000 ppm). It was allowed to dry under aseptic condition for 24 h. After coating the compound 20 larvae were inoculated and the mortality was checked for 3 days. Supplementary Table 10 shows the number of larvae inoculated with different concentrations and the graphical representation of insecticidal activity with different concentration is shown in Supplementary Fig. S8. It shows the high activity in high concentrations of FC compound. It is found that the activity increases with increase in concentration. Presence of carbamate group is responsible for the insecticidal activity [51].

5. Conclusion

In the present work, the geometric parameters of Fenoxycarb and its water complexes were theoretically calculated and compared with the experimental results. Due to the interaction with water molecule, the C_5—O_8 bond length is increased in FCW_3. N_{11}—$H_{12}\cdots O_{42}$ in FCW_3 seems to be the strongest hydrogen bond due to interaction of water molecule with N_{11}—H_{12} bond. In vibrational analysis largest shift is noted in FCW_3 due to N_{11}—$H_{12}\cdots O_{42}$ hydrogen bonding. C_9 in carbamate group is more positive, which shows the redistribution due to the symmetry in carbamate group. When water molecule is added, the stability of the compound increases. Condensed fukui function and related local and global parameters reveal that O_{30} is highly positive and have a tendency to acquire electron. Among all hydrogen atoms H_{18} is highly nucleophilic, this is clear that there is an eventual charge transfer in FC molecule from aromatic to aliphatic region.

Table 5
Calculated energy values of FC and its water complexes.

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO}-E_{LUMO} (eV)	I	A	χ	μ	η	S	ω
FC	−8.457	−5.013	−3.444	8.457	5.013	6.735	−6.735	1.722	0.290	13.170
FCW_1	−8.489	−5.010	−3.479	8.489	5.010	6.749	−6.749	1.739	0.287	13.095
FCW_2	−8.482	−5.014	−3.469	8.482	5.014	6.748	−6.748	1.734	0.288	13.127
FCW_3	−8.490	−5.012	−3.479	8.490	5.012	6.751	−6.751	1.739	0.287	13.101
FCW_4	−8.624	−5.020	−3.604	8.624	5.020	6.822	−6.822	1.802	0.277	12.913

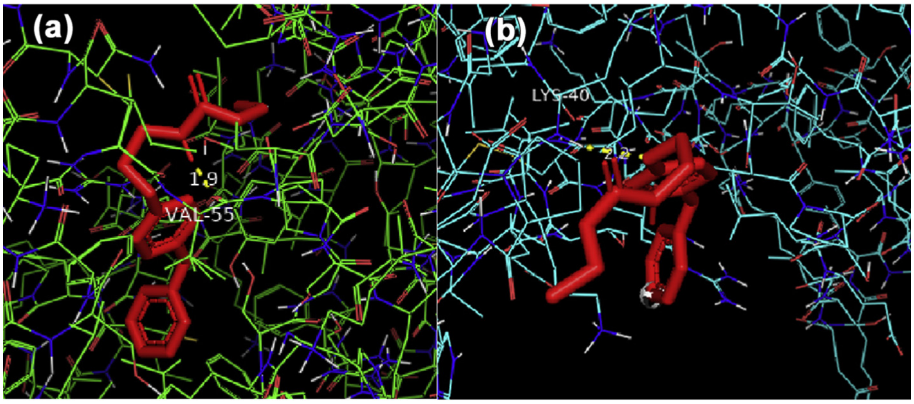

Fig. 7. Molecular docking of FC with different protein targets.

Table 6
Molecular docking results of FC with different protein targets.

Ligand	Target-proteins PDBID	No. of hydrogen bonds	Bounded residues	Binding energy (Kcal/mol)	Estimated Inhibition constant (μ_M)	Reference RMSD(Å)
FC	2RCK	1	VAL 55	−3.48	2.79	68.78
	3AY8	1	LYS 40	−6.32	23.34	34.89

Intramolecular interactions have been studied by Hirshfeld surface analysis and its fingerprint plots. The absorption maximum is observed at 212 nm for acetone solvent. H_{12} have maximum chemical shift due to the electron donating property of N_{11} atom. The compound exhibited a significant effect against the target proteins.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2019.127201.

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Spectroscopic, quantum mechanical and docking studies on organochlorine insecticides by density functional theory

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ABSTRACT

In the present study, the structural and spectral analysis for comparative study of Methoxychlor and its related compounds calculations were performed with the help of DFT with B3LYP/6-311G(d,p) level of theory. The experimental results of FT-IR, FT-Raman were compared with computed results. Detailed interpretations of the vibrational spectra were carried out with the aid of NCA and vibrational wavenumber scaled by WLS method. The electron distributions in various bonding, antibonding orbitals and $E^{(2)}$ energies have been calculated by NBO analysis. The stable position of MXC was identified by performing Potential Energy Scan analysis. The ^1H, ^{13}C NMR spectra were recorded and analysed. UV visible spectrum of the compound was recorded and electronic properties were computed by time dependent (TD-DFT) level. The molecular properties such as chemical reactivity descriptors HOMO, LUMO, MESP of title compound were calculated to get insight in to the stability and reactive site on the molecule. Hirshfeld analysis was carried out to investigate the intermolecular interaction in crystal structure and percentage of close contact with in the molecule. The biological activity in these molecules were analysed by molecular docking.

1. Introduction

Methoxychlor (MXC), an organochlorine insecticide, is widely used to preserve fruits, crops, vegetables and home gardens and it also effective against flies, mosquitoes, cockroaches and a wide variety of insects. MXC is structurally similar to DDT, which has been characterized as a persistent organic pollutant. MXC is considered the preferred alternative to DDT for its low toxicity and lower levels of persistence in the environment. Therefore, it has gradually replaced DDT for use in insect control programmes and to preserve fruits and vegetables [1]. Compared to DDT, methoxychlor is rapidly metabolized both in the environment and in living organisms, so it does not produce the long-lasting toxicity and bioaccumulation, which led to the cancellation of DDT. It also approved for use in forests, ornamental plants and insect control around houses, barns, and other agricultural premises [2]. MXC is a chlorinated insecticide with double ring structure and chemical formula $C_{16}H_{15}Cl_3O_2$. Methylchlor (MC) is also an insecticide with chemical formula $C_{16}H_{15}Cl_3$. Both MXC and MC show decreased insecticidal activity over DDT in some insects especially *lepidopterous* larvae due to vivo degradation in the insect body [3].

The literature review reveals that there was no detailed study on spectroscopic and quantum chemical calculations on organochlorine insecticides MXC and MC. This motivates to do the structural analysis, spectroscopic analysis, chemical reactivity and insecticidal activity of the molecules with density functional theory and MC has been selected to compare the structure activity relationship and docking studies with MXC by computational methods. In this attempt, a complete vibrational spectroscopic investigation have been performed on the compounds to give a detailed assignment of bands in FT-IR and FT Raman spectra on the basis of normal coordinate analysis (NCA) [4]. The calculated vibrational frequencies and band assignment were compared with those observed experimentally. The redistribution of electron density(ED) in various bonding and antibonding orbital and $E^{(2)}$ energies have been calculated by natural bond orbital analysis (NBO). This gives clear evidence of stabilization originating from the hyperconjugation of various intermolecular interactions. The HOMO and LUMO analysis

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have been used to elucidate information regarding charge transfer within the molecule [5]. Therefore, the present study provides complete information about spectroscopic, quantum chemical, chemical reactivity and biological studies under both theoretical and experimental approach.

2. Experimental techniques

The compound MXC in the solid form was purchased from Sigma Aldrich (St.Louis, MO, USA) company with 99% purity and used without further purification. The FT-IR spectrum of the MXC was recorded in the wavenumber range 4000–400 cm^{-1} by the KBr pellet technique using PerkinElmer Spectrophotometer equipped with mercury lamp and globar as source. The FT-Raman spectrum in the wavenumber range 3500–50 cm^{-1} was recorded by the BRUKER RFS 27: FT-Raman spectrophotometer using an Nd: YAG laser at 1064 nm as the excitation source with a resolution of 2 cm^{-1}. The UV–Visible spectrum of MXC was examined in the range 190–900 nm using CARY100 BIO UV Visible spectrophotometer in ethanol and cyclohexane solvents. The ^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE111 500 MHz (AV500) instrument.

3. Computational techniques

In computational methods, Gaussian 09 software program package was used [6]. The quantum chemical calculations were performed by DFT [7,8] method with the three parameter hybrid functional (B3) for the exchange part and the Lee-Yang-Par (LYP) correlation function with 6-311G(d,p) basis set [9]. The detailed interpretation of the vibrational spectra was carried out with the aid of normal coordinate analysis (NCA)[10]. MOLVIB program version 7.0 is used for NCA calculation [11]. Molecular Hirshfeld surface analysis and the related 2D finger print plots for the compound was calculated using Crystal explorer 3.1 programs [12]. The docking studies were performed using the molecular docking software, Autodock 4.2 [13]. The electronic transitions, excitation energies, absorbance and oscillator strengths were computed with the Time-Dependent DFT (TD-DFT) method and compared with UV–VIS spectra [14]. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra [15]. The total density of states (TDOS) was prepared by using the Gaussum 2.2 program [16] Gaussview 5.0.8 visualization program [17] has been utilized to the shape of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). To understand the chemical reactivity the condensed Fukui function and related local and global parameters are calculated by using theoretical tool UCA-FUKUI [18]. Docking was performed with two different proteins (pdb ID: 1C20 and 1EEA) and the ligand using molecular docking software Auto Dock 4.2 [19].

4. Results and discussion

4.1. Potential energy surface scan analysis

To identify the stable structure of MXC and MC conformational analysis is performed for $Cl_1–C_9–C_6–C_8$ (ψ_1) and $C_{12}–C_7–C_6–C_8(\psi_2)$. Torsional angles were varied from 0° to 360° rotations by a step of 10° using B3LYP 6-311G(d,p) basis set. The potential energy curve of the above tortional angles are shown in Supplementary Figs. S1a–S1b. Potential energy scan data is listed in Supplementary Tables S1–S2.

For rotation ψ_1 in MXC, the lowest energy is located at 60°, 180° and 300° with energies −5590017.449, −5590017.475 and −5590017.428 kJ/mol respectively. Among the three minima, the most stable energy is located at 60° due to $C_6–H_{22}\cdots Cl_3$ ($H_{22}\cdots Cl_3$ = 2.286A°) hydrogen bonding interaction. Maximum energy attained at 110°, 230° and 350° shows energy as −5589984.663,-5589984.033–5589985.549 kJ/mol. The barrier energy was obtained as ΔE = 33.4 kJ/mol. In MC, the minimum energy is located at 60°, 80°, 230° and 260°. These minimum energies are due to the steric repulsion ($H_{22}\cdots H_{24}$). The most stable energy is located at 260° with energy −5198842.194 kJ/Mol. The barrier energy was obtained as ΔE = 14.37 kJ/mol.

Rotation ψ_2 was located on the ring 1 region of both MXC and MC. In MXC, the global minimum energy was obtained at 230° with interatomic distance 2.732A° ($Cl_2\cdots H_{22}$) and steric repulsion. Maximum energy obtained at 170° and 350°are due to the $C_{13}–H_{25}\cdots Cl_2$ ($H_{25}\cdots Cl_2$ = 2.491A°) hydrogen bonding interaction. The potential barrier energy ΔE = 14.5, 14.66 kJ/mol in MXC and MC respectivly. In MXC and MC, further calculations were carried out for the stable structure as shown by PES technique.

4.2. Structural analysis

The optimized geometrical parameters of MXC and MC are calculated by B3LYP with 6- 311G (d,p) basis set. The calculated bond lengths, bond angles and dihedral angles of MXC compared with the experimental data [20] are listed in Tables 1a-1c. The agreement between theoretical and experimental results has been expressed by root mean square (RMSD) deviation using the

Table1a
Optimized bond length of MXC and MC at B3LYP/6-311G(d,p) level.

Bond length	Experimental Value (Å)	Calculated value (Å)	
		MXC	MC
$C_1–C_9$	1.781	1.806	1.804
$Cl_2–C_9$	1.813	1.812	1.812
$Cl_3–C_9$	1.785	1.806	1.806
$O_4–C_{18}$	1.377	1.362	–
$O_4–C_{20}$	1.471	1.421	–
$O_5–C_{19}$	1.359	1.362	–
$O_5–C_{21}$	1.463	1.421	1.096
$C_6–C_7$	1.525	1.528	1.529
$C_6–C_8$	1.533	1.528	1.529
$C_6–C_9$	1.526	1.561	1.56
$C_6–H_{22}$	1.136	1.093	1.093
$C_7–C_{10}$	1.403	1.402	1.397
$C_7–C_{12}$	1.380	1.394	1.399
$C_8–C_{11}$	1.407	1.403	1.398
$C_8–C_{13}$	1.389	1.395	1.399
$C_{10}–C_{14}$	1.380	1.385	1.392
$C_{10}–H_{23}$	1.144	1.084	1.085
$C_{11}–C_{15}$	1.403	1.384	1.391
$C_{11}–H_{24}$	1.041	1.085	1.085
$C_{12}–C_{16}$	1.410	1.394	1.390
$C_{12}–H_{25}$	1.141	1.082	1.082
$C_{13}–C_{17}$	1.411	1.396	1.392
$C_{13}–H_{26}$	1.142	1.081	1.081
$C_{14}–C_{18}$	1.390	1.399	1.396
$C_{14}–H_{27}$	1.089	1.083	1.085
$C_{15}–C_{19}$	1.401	1.399	1.397
$C_{15}–H_{28}$	1.143	1.083	1.085
$C_{16}–C_{18}$	1.376	1.397	1.399
$C_{16}–H_{29}$	1.079	1.082	1.086
$C_{17}–C_{19}$	1.381	1.396	1.397
$C_{17}–H_{30}$	1.033	1.082	1.085
$C_{20}–H_{31}$	1.101	1.096	1.095
$C_{20}–H_{32}$	1.007	1.096	1.093
$C_{20}–H_{33}$	1.014	1.089	1.092
$C_{21}–H_{34}$	0.974	1.096	1.092
$C_{21}–H_{35}$	0.944	1.089	–
$C_{21}–H_{36}$	0.927	1.096	–
RMSD		**0.0546**	**0.0419**

Table 1b
Optimized bond angle of MXC and MC at B3LYP/6-311G(d,p) level.

Bond Angle	Experimental (°)	Computational (⁰)	
		MXC	MC
$C_{18}-O_4-C_{20}$	117.4	118.6	_
$C_{19}-O_5-C_{21}$	120.1	118.5	_
$C_7-C_6-C_8$	111.7	113.3	113.1
$C_7-C_6-C_9$	112.3	113.6	113.7
$C_7-C_6-H_{22}$	108.8	106.1	106.1
$C_8-C_6-C_9$	113.4	115.5	115.5
$C_8-C_6-C_{22}$	103.8	105.3	104.3
$C_9-C_6-H_{22}$	106.1	101.5	101.6
$C_6-C_7-C_{10}$	118.8	119.5	119.3
$C_6-C_7-C_{12}$	122.9	122.8	122.7
$C_{10}-C_7-C_{12}$	118.2	117.7	117.9
$C_6-C_8-C_{11}$	114.2	117.2	117.3
$C_6-C_8-C_{13}$	126.4	125.3	125.0
$C_{11}-C_8-C_{13}$	119.3	117.4	117.7
$Cl_1-C_9-Cl_2$	105.5	107.1	107.2
$Cl_1-C_9-Cl_3$	102.3	108.6	108.6
$Cl_1-C_9-C_6$	116.8	114	114.2
$Cl_2-C_9-Cl_3$	108.3	107.5	107.5
$Cl_2-C_9-C_6$	109.4	109.4	109.3
$Cl_3-C_9-C_6$	111.6	109.9	109.8
$C_7-C_{10}-C_{14}$	120.9	121.5	121.1
$C_7-C_{10}-H_{23}$	123.9	119.6	119.6
$C_{14}-C_{10}-H_{23}$	115.1	118.9	119.2
$C_8-C_{11}-C_{15}$	121.2	121.8	121.4
$C_8-C_{11}-H_{24}$	117.9	119.4	119.5
$C_{15}-C_{11}-H_{24}$	120.6	118.8	119.1
$C_7-C_{12}-C_{16}$	121.8	121.6	120.8
$C_7-C_{12}-H_{25}$	124.9	120.0	120.2
$C_{16}-C_{12}-H_{25}$	113.1	118.3	119.0
$C_8-C_{13}-C_{17}$	120.2	121.6	120.8
$C_8-C_{13}-H_{26}$	123.8	120.6	120.6
$C_{17}-C_{13}-H_{26}$	115.9	117.9	118.6
$C_{10}-C_{14}-C_{18}$	119.6	120.1	121.0
$C_{10}-C_{14}-H_{27}$	123.6	121.4	119.3
$C_{18}-C_{14}-H_{27}$	116.5	118.6	119.6
$C_{11}-C_{15}-C_{19}$	118.0	120.1	121.0
$C_{11}-C_{15}-H_{28}$	122.9	121.3	119.3
$C_{19}-C_{15}-H_{28}$	118.8	118.6	119.6
$C_{12}-C_{16}-C_{18}$	118.6	119.8	121.3
$C_{12}-C_{16}-H_{29}$	117.3	119.1	119.2
$C_{18}-C_{16}-H_{29}$	124.6	121	119.4
$C_{13}-C_{17}-C_{19}$	119.5	120.1	121.6
$C_{13}-C_{17}-H_{30}$	119.9	118.9	119.0
$C_{19}-C_{17}-H_{30}$	120.4	121.1	119.4
$O_4-C_{18}-C_{14}$	115.2	115.9	_
$O_4-C_{18}-C_{16}$	123.6	124.8	_
$C_{14}-C_{18}-C_{16}$	121.3	119.3	117.7
$O_5-C_{19}-C_{15}$	112.6	116.0	_
$O_5-C_{19}-C_{17}$	125.6	124.9	_
$C_{15}-C_{19}-C_{17}$	121.8	119.1	_
$O_4-C_{20}-H_{31}$	94.8	111.5	_
$O_4-C_{20}-H_{32}$	93.9	111.5	_
$O_4-C_{20}-H_{33}$	116.1	105.8	_
$H_{31}-C_{20}-H_{32}$	124.1	109.4	107.3
$H_{31}-C_{20}-H_{33}$	117.8	109.2	107.6
$H_{32}-C_{20}-H_{33}$	113.9	109.2	108.1
$O_5-C_{21}-H_{34}$	92.71	111.5	107.4
$O_5-C_{21}-H_{35}$	101.7	105.8	_
$O_5-C_{21}-H_{36}$	102.5	111.5	_
$H_{34}-C_{21}-H_{35}$	125.6	109.3	_
$H_{34}-C_{21}-H_{36}$	107.3	109.4	_
$H_{35}-C_{21}-H_{36}$	123.9	109.3	_
RMSD		**4.371**	**4.587**

following equation

$$\mathrm{RMSD} = \sqrt{\frac{1}{n-1} = \sum_{i}^{n}\left(\gamma_{\mathrm{i}}^{\mathrm{cal}} - \gamma_{\mathrm{i}}^{\mathrm{exp}}\right)^2} \tag{1}$$

Table 1c
Optimized dihedral angle of MXC and MC at B3LYP/6-311G(d,p) level.

Dihedral Angle	Experimental Value (⁰)	Computational value (⁰)	
		MXC	MC
$C_{20}-O_4-C_{18}-C_{14}$	176.3	−179.9	_
$C_{20}-O_4-C_{18}-C_{16}$	−3.3	0.6	_
$C_{18}-O_4-C_{20}-H_{31}$	57.7	60.8	_
$C_{18}-O_4-C_{20}-H_{32}$	66.9	−61.8	_
$C_{18}-O_4-C_{20}-H_{33}$	178.4	179.5	_
$C_{21}-O_5-C_{19}-C_{15}$	170.1	179.3	_
$C_{21}-O_5-C_{19}-C_{17}$	11.4	−0.5	_
$C_{19}-O_5-C_{21}-H_{34}$	47.01	−61.0	_
$C_{19}-O_5-C_{21}-H_{35}$	174.8	179.7	_
$C_{19}-O_5-C_{21}-H_{36}$	−50.4	61.6	_
$C_8-C_6-C_7-C_{10}$	136.7	−129.5	−128.9
$C_8-C_6-C_7-C_{12}$	−41.3	48.2	49.0
$C_9-C_6-C_7-C_{10}$	94.5	96.1	97.0
$C_9-C_6-C_7-C_{12}$	87.5	−86.1	−85.2
$H_{22}-C_6-C_7-C_{10}$	22.7	−14.5	−14.0
$H_{22}-C_6-C_7-C_{12}$	−155.3	163.1	164.0
$C_7-C_6-C_8-C_{11}$	−88.4	94.0	95.3
$C_7-C_6-C_8-C_{13}$	91.0	−83.7	−82.2
$C_9-C_6-C_8-C_{11}$	143.4	−132.6	−131.3
$C_9-C_6-C_8-C_{13}$	37.2	49.8	51.2
$H_{22}-C_6-C_8-C_{11}$	28.7	−21.5	−20.0
$H_{22}-C_6-C_8-C_{13}$	−151.9	160.9	51.2
$C_7-C_6-C_9-Cl_1$	−63.7	58.3	58.0
$C_7-C_6-C_9-Cl_2$	65.2	−61.6	−62.1
$C_7-C_6-C_9-Cl_3$	−178.2	−179.5	−179.8
$C_8-C_6-C_9-Cl_1$	74.2	−75.0	−75.1
$C_8-C_6-C_9-Cl_2$	166.9	165.1	164.9
$C_8-C_6-C_9-Cl_3$	−50.3	47.3	47.1
$H_{22}-C_6-C_9-Cl_1$	172.6	171.7	171.5
$H_{22}-C_6-C_9-Cl_2$	−53.6	51.8	51.5
$H_{22}-C_6-C_9-Cl_3$	63.0	−66.0	−66.3
$C_6-C_7-C_{10}-C_{14}$	179.2	178.6	178.7
$C_6-C_7-C_{10}-H_{23}$	−1.11	−1.4	−1.6
$C_{12}-C_7-C_{10}-C_{14}$	−1.07	0.8	0.7
$C_{12}-C_7-C_{10}-H_{23}$	177.0	−179.3	−179.6
$C_6-C_7-C_{12}-C_{16}$	178.7	−178.9	−179.0
$C_6-C_7-C_{12}-H_{25}$	2.5	0.2	0.3
$C_{10}-C_7-C_{12}-C_{16}$	0.7	−1.1	−1
$C_{10}-C_7-C_{12}-H_{25}$	175.5	178.0	178.2
$C_6-C_8-C_{11}-C_{15}$	179.7	−177.5	−177.4
$C_6-C_8-C_{11}-H_{24}$	6.5	2.3	2.2
$C_{13}-C_8-C_{11}-C_{15}$	0.26	0.3	0.2
$C_{13}-C_8-C_{11}-H_{24}$	173.9	−179.9	180.0
$C_6-C_8-C_{13}-H_{17}$	179.7	177.7	177.5
$C_6-C_8-C_{13}-H_{26}$	1.05	−3.4	−3.3
$C_{11}-C_8-C_{13}-C_{17}$	−0.27	0.1	0
$C_{11}-C_8-C_{13}-H_{26}$	−179.6	179	179.2
$C_7-C_{10}-C_{14}-C_{18}$	1.04	0.0	−0.1
$C_7-C_{10}-C_{14}-H_{27}$	174.6	−179.9	179.9
$H_{23}-C_{10}-C_{14}-C_{18}$	−177.2	−180.0	−179.8
$H_{23}-C_{10}-C_{14}-H_{27}$	−3.6	0.2	0.2
$C_8-C_{11}-C_{15}-C_{19}$	0.5	−0.4	−0.5
$C_8-C_{11}-C_{15}-H_{28}$	−173.9	−179.9	179.9
$H_{24}-C_{11}-C_{15}-C_{19}$	174.5	179.8	179.9
$H_{24}-C_{11}-C_{15}-H_{28}$	0.1	0.2	0.2
$C_7-C_{12}-C_{16}-C_{18}$	−0.2	0.6	0.6
$C_7-C_{12}-C_{16}-H_{29}$	179.5	−180	−179.7
$H_{25}-C_{12}-C_{16}-C_{18}$	176.5	−178.5	−178.6
$H_{25}-C_{12}-C_{16}-H_{29}$	−3.9	1.0	1.0
$C_8-C_{13}-C_{17}-C_{19}$	−0.5	−0.3	−0.2
$C_8-C_{13}-C_{17}-H_{30}$	−174.8	179.4	179.8
$H_{26}-C_{13}-C_{17}-C_{19}$	178.9	−179.2	−179.4
$H_{26}-C_{13}-C_{17}-H_{30}$	4.5	1.0	0.6
$C_{10}-C_{14}-C_{18}-O_4$	179.9	180.0	–
$C_{10}-C_{14}-C_{18}-C_{16}$	−0.5	−1.0	−0.3
$H_{27}-C_{14}-C_{18}-O_4$	−5.9	−0.2	–
$H_{27}-C_{14}-C_{18}-C_{16}$	−174.6	179.3	179.7
$C_{11}-C_{15}-C_{19}-O_5$	170.8	−179.7	_
$C_{11}-C_{15}-C_{19}-C_{17}$	−1.2	0.1	0.4
$H_{28}-C_{15}-C_{19}-O_5$	5.1	−0.1	_
$H_{28}-C_{15}-C_{19}-C_{17}$	173.5	179.7	−179.9

(*continued on next page*)

Table 1c (*continued*)

Dihedral Angle	Experimental Value (^{0})	Computational value (^{0})	
		MXC	MC
$C_{12}–C_{16}–C_{18}–O_4$	179.6	179.7	–
$C_{12}–C_{16}–C_{18}–C_{14}$	0.1	0.3	0.0
$H_{29}–C_{16}–C_{18}–O_4$	−0.02	0.3	−179.6
$H_{29}–C_{16}–C_{18}–C_{14}$	−179.5	−179.1	−179.6
$C_{13}–C_{17}–C_{19}–O_5$	179.6	−180.0	–
$C_{13}–C_{17}–C_{19}–C_{15}$	1.3	0.2	0.0
$H_{30}–C_{17}–C_{19}–O_5$	−6.1	0.3	–
$H_{30}–C_{17}–C_{19}–C_{15}$	175.6	−179.5	−180.0

where N is the number of experimental or calculated data. The RMSD of bond lengths and bond angles are 0.0545 and 4.371 for MXC and 0.0419 and 4.587 for MC respectively [21]. The optimized structures and atom numbering of MXC and MC are shown in Fig. 1. In MXC, due to the substitution of electron donating group (OCH$_3$ groups) phenyl ring is distorted from the regular hexagonal structure. The $C_6–C_7$ and $C_7–C_8$ bond lengths are slightly larger than other C–C bonds indicate negligible configuration interaction between two phenyl rings systems, ie. $C_7–C_{10}$ (1.404A°), $C_7–C_{12}$ (1.394 Å), $C_8–C_{13}$ (1.395 Å) and $C_8–C_{11}$ (1.403 Å). The distortions observed in point are explained in terms of the change in hybridization effectuated by the substituent at the carbon site to which the groups are attached. As a result of the electron donating OCH$_3$ substitution, a shortening of the O–C bond and enlargement of the neighbouring $C_{14}–C_{18}$ and $C_{16}–C_{18}$ in Ring1 and $C_{15}–C_{19}$ and $C_{17}–C_{19}$ in Ring 2 bonds are observed.

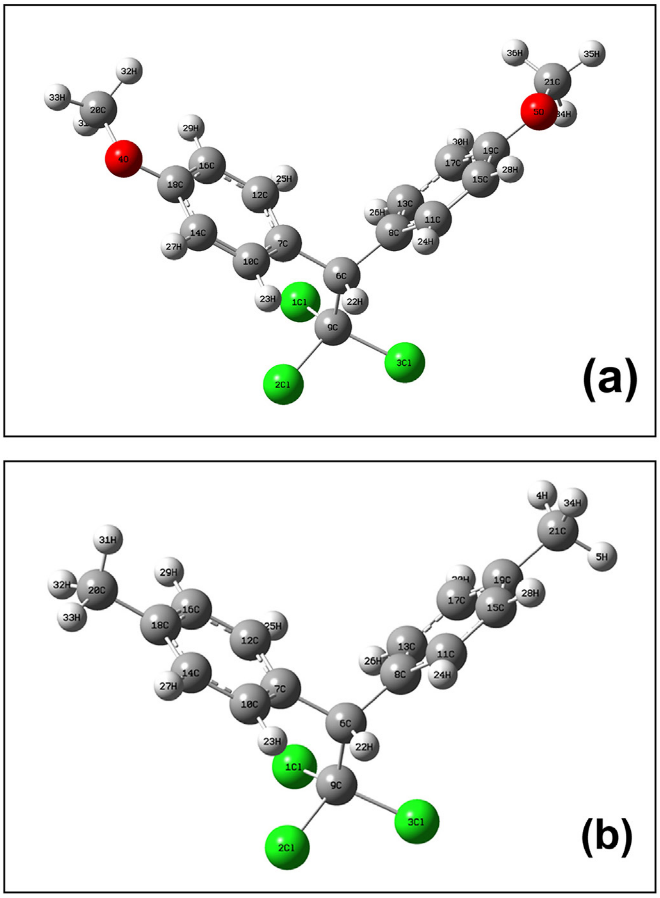


Fig. 1. Optimized molecular structure of (a) Methoxychlor(MXC) and (b) Methylchlor (MC).

In ring1, the change in bond angle $C_{14}–C_{10}–C_7$ and $C_{16}–C_{12}–C_7$ by 1.5°and 1.6° respectively and a reduction in endocyclic angle $C_{12}–C_7–C_{10}$ by 2.3°, together with the charge transfer interaction [22]. The DFT calculation also gives an increase in the angle $C_6–C_7–C_{10}$ by 0.5° from 120°at the C_7 position and this asymmetry of exocyclic angles reveals the repulsion between the H_{22} and the H_{23} atom. The asymmetry of the exocyclic angles $O_4–C_{18}–C_{16}$ and $O_4–C_{18}–C_{14}$ are significant at the C_{18} position, which gives repulsion between $O_4–C_{28}–H_{31,\ 32,\ 33}$ groups and H_{29} atom of the phenyl ring. The computed values of the above mentioned angles correlate well with the experimental results [20].

In MXC and MC the two phenyl rings are non planar with $C_{12}–C_7–C_6–C_8$ 48.1 A^0 and $C_{13}–C_8–C_6–C_7$ -83.7 A^0. The trichloro ethane moieties are twisted making $C_{12}–C_7–C_6–C_9$ -86.1 A^0 and $C_{13}–C_8–C_6–C_9$ 49.8 A^0 respectively. The more deviation in phenyl ring 1 region is due to the $C_{13}–H_{26}\cdots Cl_1$ hydrogen bonding interaction. The deviations in $C_7–C_6–C_9$, $C_8–C_6–C_9$, $C_6–C_9–Cl_3$, $C_6–C_9–Cl_1$, $C_6–C_9–Cl_2$ bond angles are due to the electronic coupling between trichloro ethane lone pair electrons and the phenyl ring π system. The short inter atomic distance $C_6–H_{22}\cdots Cl_3$ and $H_{22}\cdots H_{23}$ 2.285A°, $H_{22}\cdots H_{24}$ 2.229A° reveals the possibility of intramolecular hydrogen bonding interactions.

The cumulative effects of sterric interaction between $Cl_3\cdots C_8$ 3.104A°, $Cl_1\cdots C_7$ 3.273 Å, $H_{22}\cdots H_{23}$ 2.285 Å, $H_{22}\cdots H_{24}$ 2.229 Å induced the entire molecule from the planarity of the phenoxy rings. As it is evident from dihedral angles $C_7–C_6–C_9–Cl_1$ and $C_8–C_6–C_9–Cl_3$ which are calculated as 58.3° and 47.3° respectively. With respect to the ring 2, the trichloro ethane group and ring 2 have been deviated from their actual planarity. This can be identified with the aid of dihedral angle $C_{11}–C_8–C_6–C_9$ and $C_{11}–C_8–C_6–C_7$, values are calculated −132.6° and 93.9° respectively that confirmed the deviation from the actual plane with respect to the Ring 2. The bond angle are calculated Ring1-H_{22}; H_{22}-Ring 2, Ring1-Ring 2 with respect to C_6 atom which are 105.3, 106.1, 113.3A° respectively. The deviation from co planarity of trichloro ethane moiety with respect to phenyl ring plane is also an outcome of intramolecular charge transfer state which reflected in the geometry by their dihedral angles $C_{12}–C_7–C_6–C_9$, $C_{10}–C_7–C_6–C_9$, $C_{13}–C_8–C_6–C_9$, $C_{11}–C_8–C_6–C_9$ are −86.1,96.1,49.8,-132.6° respectively.

Chlorine is very electro negative as they cause inductive withdrawal. This leads to intramolecular hydrogen bonding interaction [23]. The noticeable deviation from experimental C–H bond lengths may arise from the low scattering factors of hydrogen atoms in XRD data. $C_{11}–H_{24}$, $C_{15}–H_{28}$, $C_{17}–H_{30}$, $C_{13}–H_{26}$, $C_{12}–H_{25}$, $C_{16}–H_{29}$, $C_{14}–H_{27}$ and $C_{10}–H_{23}$~1.15A° with respect to the experimental value 0.93A° of ring C–H bond distance. The $O_4\cdots H_{32}$ and $O_5\cdots H_{35}$ distances are 2.088A°, 2.011A° respectively, which are shorter than the sum of related Van der waals radii.

4.3. *Vibrational analysis*

The MXC compound consists of 36 atoms and has 102 normal vibrational modes. The comparative representations of theoretically predicted FT-IR and FT- Raman spectra at B3LYP/6-311G(d,p) level of theory along with the experimental results of are shown in Figs. 2 and 3. The theoretical and experimental frequencies are calculated and listed in Table 2. Further, the relative and absolute intensities are tabulated. The local symmetry co-ordinates are listed in Supplementary Tables S3a–S3b. The theoretical values show slight deviation from the experimental one, since the theoretical wavenumbers are obtained from the isolated molecule in the gaseous phase and the experimental wavenumbers are obtained from the isolated molecule in solid state [24]. The fundamental

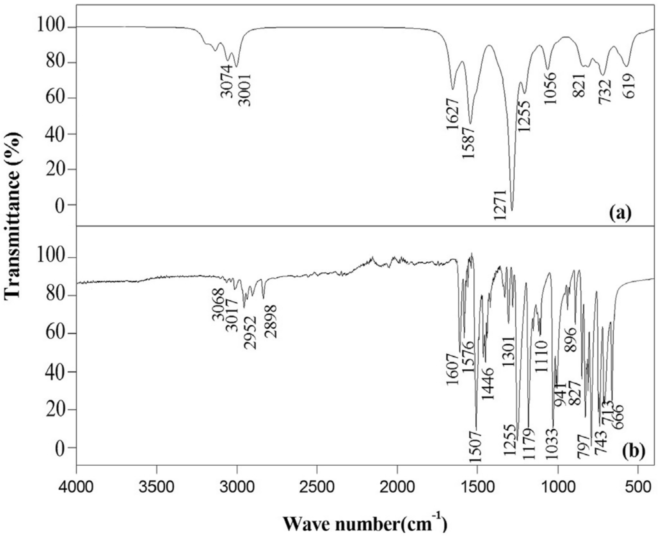


Fig. 2. Combined FT-IR (a) theoretical (b) experimental spectrum of MXC.

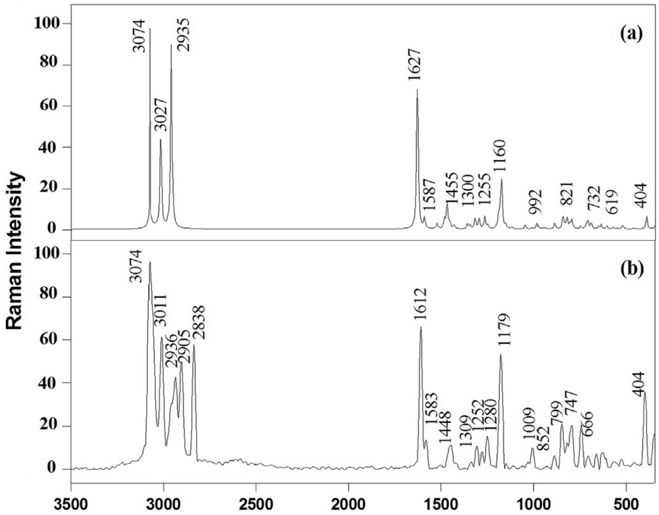


Fig. 3. Combined a) theoretical (b) experimental FT-Raman spectrum of MXC.

modes of MXC have been assigned based on vibrational concept and explanations are provided in the following sections.

4.3.1. *Methoxy group vibrations*

The vibrations of O—CH$_3$ group are described by nine normal modes which are associated with CH$_3$ group, namely asymmetric stretch, symmetric stretch, in-plane stretch, inplane bending, symmetric bending, in-plane rocking, out-of plane rocking, out-of-plane stretch, out-of plane bending modes and twisting modes [25]. The asymmetric and symmetric stretching modes of CH$_3$ group attached to the oxygen atom are usually shifted due to electronic effects [26]. The CH$_3$ asymmetric stretching vibrations are expected in the region 3000-2930 cm^{-1}. In the present study, the medium intense Raman and weak IR bands identified at 2936 and 2952 cm^{-1} were assigned to C—H stretching vibration. The CH$_3$ symmetric stretching vibrations are expected in the region 2830-2815 cm^{-1}. A strong band observed at 2898 cm^{-1} in the FT-IR spectrum leads blue shifting due to C$_{20}$—H$_{33}$···O$_4$ hyperconjugative interaction. The calculated value at 2882 cm^{-1} is good agreement with the experimental value. The computed values are obtained at 2882 and 2881 cm^{-1}.

The asymmetric and symmetric deformation vibrations of methyl group normally appear in the region 1465-1440 cm^{-1} and 1390-1370 cm^{-1}, respectively and the rocking vibrations of CH$_3$ modes usually appear in the region 1070-1010 cm^{-1} [27]. Asymmetric deformation observed at 1446 cm^{-1} in IR and 1448 cm^{-1} in Raman. The CH$_3$ rocking modes calculated at 1160 and 1159 cm^{-1} are in good agreement with the bands observed at 1179 cm^{-1} in FT-IR and FT-Raman spectra. The relatively large value of IR and Raman wavenumber of the rocking mode suggests the presence of hyperconjugation [28]. The CH$_3$ twisting vibrations have been observed at 1160 and 1159 cm^{-1}. The OCH$_3$ vibration is assigned in the region 1000-100 cm^{-1}. Methoxy group attached to an aromatic ring gives υ_{asy} and υ_{sy} in C—O—C in the range 1310—1210 cm^{-1} and 1010 cm^{-1} respectively. The O—C stretching is observed at 1301 cm^{-1} in IR and 1309, 1280 cm^{-1}in Raman. The C—O—CH$_3$ in plane bending is observed as a highly mixed mode in the region 600—200 cm^{-1}. The O—CH$_3$ torsion mode has been observed at 213 cm^{-1} in FT-Raman spectra.

4.3.2. *CH—Cl$_3$ vibrations*

The C—H stretching vibrations normally observed in the region 3000-2800 cm^{-1} [29]. In the present study the C—H stretching vibration at 3017 cm^{-1} in IR and 3011 cm^{-1} in Raman. The blue shifting of 17 cm^{-1} and 11 cm^{-1} in C—H stretching mode is due to strong C$_6$—H$_{22}$···Cl$_1$ intramolecular hydrogen bonding interaction. However, vibrational coupling with other groups may result in a shift in the absorption band as high as 840 cm^{-1}. In MXC, the bands 628 cm^{-1} (vs) in FT-Raman spectrum has been identified as C—Cl stretching vibration with theoretically calculated value 619 cm^{-1}.

The stretching modes of both phenyl rings are predicted at higher wave number than the symmetric stretching modes of CCl$_3$ group [30]. For the C—Cl group belongs to carbon atom expected the stretching, rocking and out of plane deformation as in aromatic C—H groups [31]. In MXC, it is observed at 404 cm^{-1} in Raman spectrum and the corresponding calculated value obtained at 404 cm^{-1}. The CCl$_3$ deformation vibrations are calculated at 297, 215 and 207 cm^{-1} and the corresponding rocking modes obtained at 191 and 182 cm^{-1}. Torsion modes of both rings were predicted at lower wave number. The calculated C—Cl in-plane deformation vibrational band is at 303 cm^{-1}.

4.3.3. *Ring vibration*

The heteroaromatic structure shows the presence of the C—H stretching vibration in the region 3085—3055 cm^{-1}, which is the characteristic region for the identification of the C—H stretching vibration [32]. For the C—H stretching vibrations we have observed the bands at 3074 in Raman spectrum. The calculated value observed at 3074 cm^{-1} ring 2 and 3068 cm^{-1} ring 1 respectively.

The C—C stretching modes of the phenyl group are expected in the range 1650—1200 cm^{-1}. The actual positions of these modes are determined by the form of substitution around the ring [33]. The selection rule allows five normal modes 8a, 8b, 19a, 19b and 14 for the tangential C—C stretching mode in asymmetrically disubstituted benzene derivatives. DFT computation shows vibration modes 8a and 8b at 1552 and 1628 cm^{-1}; The phenyl ring mode 8a manifests as very strong band in Raman at 1612 cm^{-1} and weak band in IR at 1607 cm^{-1} and its companion 8b appears as weak and medium band at 1576 and 1583 cm^{-1} in Raman. The calculated values also agree well with the experimental data. The mode 19a is observed as very intense band in IR at 1507 cm^{-1}. The mode 14 is expected in the range 1330—1240 cm^{-1}. In MXC mode 14 is identified as 1255 cm^{-1}in IR and 1252 cm^{-1} in Raman. The corresponding calculated value is found to be 1255 cm^{-1}.

Table 2
Detailed assignment of fundamental vibrations of MXC by normal coordinate analysis.

IR	Raman	MXC	MC	Assignment	IR Intensity	Raman Intensity
3068w	3074vs	3074	3073	υ_{asy}C13-H26+υ_{asy}C11-H24+υ_{asy}C15-H28+υ_{asy}C17-H30(98) **2**	31	100
		3068	3063	υ_{asy}C16-H29+υ_{asy}C12-H25+υ_{asy}C14-H27+υ_{asy}C10-H23(98)	36	9
		3060		υ_{asy}C13-H26(98)	39	6
		3057	3040	υ_{asy}C16-H29(99)	39	6
		3056	3034	υ_{asy}C13-H26(98)	39	2
		3054	3024	υ_{asy}C16-H29(99)	38	6
		3035	3024	υ_{asy}C16-H29(99)	31	9
3017w	3011s	3027	3023	υ_{asy}C6-H22(99)	32	18
		3001		υ_{asy}C20-H31(58)+υ_{asy}C20-H32(29)+υ_{asy}C20-H33(10)	47	10
2952w		3001		υ_{asy}C21-H35(58)+υ_{asy}C21-H34(29)+υ_{asy}C21-H36(10)	46	9
	2936 m	2935		υ_{asy}C20-H31(74)+υ_{asy}C20-H34(25)	6	6
		2934		υ_{asy}C21-H36(97)	6	5
	2905s	2934		υ_{asy}C21-H34(73)+υ_{asy}C21-H36(25)	6	4
2898w		2882		υ_{sy}C20-H33(87)+υ_{sy}C21-H35(8)	3	1
2839vw	2838s	2881		υ_{sy}C21-H34(87)+υ_{sy}C20-H32(8)	3	1
		1627	1628	υC13-C8(50)+υC7-C12(14)+βH30C13C17(15)+δ_{C}13-C8-C11(7) **8a**	51	53
1607 m	1612vs	1612	1624	υC16-C18(51)+υC11-C15(14)+βH30C17C13(6)+δ_{C}7-C12-C16(8)+βO4-C18-C14(6) **8a**	48	97
		1588	1586	υC16-C18(37)+υC11-C15(31)+βH30C17C13(8) **8b**	43	5
1576 m	1583 m	1587	1585	υC13-C18(37)+υC7-C12(31)+βH23C10C14(7)+βO4-C18-C16(7)+βH30C17C19(6)+βH26C13C14(8) **8b**	45	4
		1522	1522	υC13-C8(21)+υC7-C12(13)+βH30-C17-C13(30)+H23−C10−C7(7)+H27−C14−C10(6) **19a**	82	3
1507vs		1519	1519	υC13-C16(21)+υC13-C8(13)+βH25-C12-C16(7)+βO4-C18-C16(7)+ βH27-C14-C10(6)+βH23-C10-C7(18)+βH24-C11-C15(18) **19a**	80	2
		1482		δ_{H}34-C21-H35(54)+δ_{H}35-C21-H36(20)+δ_{H}34-C21-H36(10)+βO5-C21-H34(7)	50	11
		1482		βH31-C20-C32(54)+βH32-C20-C33(18)+δ_{H}34-C21-H36(7)	47	10
		1470		δ_{H}35-C21-H36(67)+δ_{H}34-C21-H35(26)	39	22
		1469		δ_{H}32-C20-H33(69)+δ_{H}31-C20-H33(24)	36	15
		1456		δ_{H}35-C21-H36(84)+βH30-C17-C13(6)	28	7
1446 m		1455		δ_{H}32-C20-H33(83)+βH29-C11-C15(6)	27	7
	1448 m	1435	1426	C13−C18(35)+C12−C16(31)+βH28-C15-C11(29)+βO4-C18-C16(7)+ρH22-C6C9(5)	22	4
1420w		1432	1423	C16−C18(38)+C8−C11(6)+βH29-C16-C18(20)+βH26-C13-C8(5)+ βH25-C12-C1(7)+βH27-C14-C18(8)	22	4
		1362	1395	υC12-C16(6)+βH28-C15-C11(16)+ρH22-C6-C8(41)	48	5
		1347	1358	υC12-C16(6)+βH22-C6-C9(25)+βH27-C14-H10(12)+βO4-C18-H14(12)	58	4
		1322	1344	υC12-C16(7)+υC8-C11(25)+βC6-C7-C12(6)+βH28-C15-C19(41)	88	10
		1319	1324	υC7-C12(31)+υC13-C8(10)+βH23-C10-C14(22)+βH24-C11-C15(8)+βH25-C12-C16(12)	95	9
1304 m	1309w	1300	1318	υC12-C16(7)+υC8-C11(35)+βC6-C7-C12(6)+βH24-C11-C15(7)+δ_{H}22-C6-C9(20) **3**	94	8
		1271	1292	υC18-O4(36)+υC7-C12(18)+βH23-C10-C7(19)+υC20-O4(8)+δ_{C}10-C7-C12(5)+δ_{C}32-C20-H33(5)	98	8
	1280 m	1268	1252	υC19-O5(33)+υC15-C8(21)+βH28-C15-C11(10)+υC20-O5(7)+δ_{C}17-C13-C8(6)	94	10
1255vs	1252 m	1255	1224	υC16-C18(21)+υC8-C11(6)+υC6-C7(15)+ρH22-C6-C8(22) **14**	100	5
		1200	1220	υC13-C18(21)+υC6-C8(12)+υC12-C16(8)+βH22-C6-C9(22)	76	6
		1197	1205	υC12-C16(6)+βH30-C17-C13(40)+βH29-C16-C18(13)+βH25-C12-C16(8)+βH27-C14-C10(8)	70	14
		1193	1203	υC7-C12(8)+βO4-C18-C16(6)+ρO5-C21-H36(53)+ρO5-C21-H34(18)	73	16
		1192	1196	υC10-C7(8)+ρO4-C20-H33(47)+ρO4-C20-H31(18)+βH29-C14-C10(7)	66	10
		1189		υC11-C15(21)+υC14-C10(8)+βH28-C15-C11(21)+βH23-C10-C14(13)+βH25-C21-C16(9)+βH29-C14-C10(7)	57	18
		1181		υC14-C10(26)+υC6-C7(17)+υC15-C19(7)+υC6-C8(7)+υC11-C15(21)+υC14-C10(8)	48	32
1179vs	1179s	1160	1181	O5−C21−H34(70)	31	5
		1159		ρO4-C20-H31(68)	30	5
		1132		C12−C16(7)+C11−C15(21)+βC24-C11-C15(45)+βH27-C14-C10(7)+βC6-C7-C10(6)	25	1
1110 m		1126	1138	C14−C10(22)+C15−C19(8)+βC29-C16-C18(19)+βH24-C11-C15(14)+ βC27-C14-C10(6)+βH25-C12-C16(7)	23	2
		1056	1133	C21−O5(69)+C15−C19(11)	45	1
		1055	1054	C20−O4(71)+C10−C7(12)	42	1
1030vs		1020	1053	C10−C7(5)+C15−C19(26)+βC29-C16-C18(10)+βC10-C7-C12(8)+δ_{C}15-C19-C17(38)	20	1
	1009 m	1020	1030	C18−C14(27)+C15−C28(5)+βH24-C11-C15(10)+δ_{C}10-C7-C12(42)+δ_{C}13-C8-C11(9)	19	1
		992	1030	C6−C8(7)+ΨC7-C12-C16-C18(38)+PC10−C7−C12−C16(17)+ΨC13-C8-C11-C15(8) **17b**	15	3

		964	1003	ΨC17-C13-O8-C11(31)+ωH24-C11-C15-C18(17)+ωH29-C16-C18-C18(9)+PC10−C7−C12−C6(7)	12	1
		962	1001	ΨC11-C15-C19-C17(35)+ωH24-C11-C15-C18(21)+ωC6-C7-C12-C10(11)+ ωH27-C14-C10-C8(6)+PC12−C6−C18−C14(7)	12	1
		952	994	ΨC15-C19-C17-C13(41)+ωH24-C11-C15-C18(11)+ωC6-C7-C13-C8(8)+PC13−C8−C11−C15(34)	12	1
945 m		945	953	ΨC10-C7-C12-C16(45)+PC10−C7−C12−C16(39)	12	1
		901		C6−C7(8)+C16−C18(7)+C13−C8(6)+ΨC18-C14-C7-C10(21)+ΨC16-C18-C14-C10(18)+δ_C8-C6-C9(9)	18	4
	852w	856	902	C11−C15(5)+ΨC13-C8-C11-C15(20)+ΨC11-C15-C19-C17(16)+ ωH30-C17-C13-C19(13)+δ_C8-C6-C9(12)+ρC6-C9-Cl3(5)	43	4
		846	854	ΨC10-C7-C12-C16(49)+ΨC18-C14-C10-C7(31)	46	11
		834	846	ΨC10-C7-C12-C16(30)+ΨC11-C15-C19-C17(12)+ΨC12-C16-C18-C14(6)+ ωH23-C10-C7(7)+ ωC6-C7-C12-C10(12)+ PC8−C11−C15−C19 + PC10−C7−C12−C16(7)	45	6
	824w	821	841	ωH28-C15-C19-C11(68)+ωC6-C7-C12-C10(7)+ΨC8-C11-C15-C19(6)+PC15−C19−C17−C13(7)	46	6
		818	836	ωH28-C15-C19-C11(29)+ωH25-C12-C16-C7(12)+ωH26-C13-C8-C17(10)+ωH27-C14-C10-C18(9)+ ΨC16-C18-C14-C10(18)+ΨC18-C14-C10-C7(13)	46	5
827 m		808	820	υC14-H27(6)+PC12−C16−C18−C14(19)+δ_C7-C6-C8(10)+ΨC12-C16-C18-C14(8)+P C6−C9−Cl3(6)+PC17-C13-C18-C11(6)	45	6
		801	804	PC18−C14−C10−C17(30)+PC15−C19−C17−C13(11)+ΨC10-C7-C12-C16(7)+ΨC17-C13-C8-C11(5)	43	9
797vs	799 m	761	796	PC12−C16−C18−C14(26)+ΨC16-C18-C14-C10(26)+PC15−C19−C17−C13(23)+ΨC11-C15-C19-C17(5)	41	1
743s	747 m	732	753	PC7−C12−C16−C18−C14(29)+ΨC14-C10-C7-C12(29)+PC11−C15−C19−C17(20)+ΨC19-C17-C13-C8(19)	53	2
		722	731	PC7−C12−C16−C18−C14(32)+ΨC18-C14-C10-C7(29)+PC13−C8−C11−C15(15)+ΨC17-C13-C8-C11(15)	56	6
713 m		704	723	PC7−C12−C16−C18−C14(28)+ΨC10-C7-C12-C16(27)+PC11−C15−C19−C17(20)+ΨC11-C15-C19-C17(19)	49	3
666s	666 m	666	704	PC16−C18−C16−C14−C10(30)+ΨC10-C7-C12-C16(19)+ΨC19-C17-C13-C8(12)	25	1
		650	670	υC12-C16(6)+βC6-C7-C12(5)+δ_C18-C14-C10(53)+δ_C15-C19-C17(8)+δ_C11-C15-C19(10)	23	2
	628w	619	653	υC9-Cl2(12)+PC12−C16−C18−C14(29)+δ_C15-C19-C17(8)+ΨC16-C18-C14-C10(15)+δ_C7-C6-C9(6)	32	1
		586	625	ΨC10-C7-C12-C16(37)+PC11−C15−C19−C17(13)+ΨC18-C14-C10-C7(11)+ ΨC19-C17-C13-C8(9)+PC14−C10−C7−C12(8)	43	1
		564	582	βC19-O5-C21(7)+ΨC16-C18-C14-C10(32)+ΨC10-C7-C12-C16(23)+ΨC8-C11-C15-C19(7)+ΨC11-C15-C19-C7(6)	43	1
		536		ΨC12-C16-C18-C14(54)+ΨC14-C10-C7-C12(41)	18	1
		530	544	ΨC8-C11-C15-C19(37)+ΨC10-C7-C12-C16(18)+ΨC11-C15-C19-C17(16)+ΨC16-C18-C14-C10(13)	17	2
		476	505	ΨC10-C7-C12-C16(31)+PC15−C19−C17−C13(7)+ΨC17-C13-C8-C11(27)+ΨC16-C18-C14-C10(10)+ PC16−C18−C14−C10(6)+ΨC8-C11-C15-C19(5)	7	0
		463	498	ΨC10-C7-C12-C16(40)+PC18−C11−C15−C19(5)+ΨC8-C11-C15-C19(12) +ΨC14-C10-C7-C12(5)+PC16−C18−C14−C10(6)	7	1
		429		ΨC12-C16-C18-C14(46)+ΨC19-C17-C13-C8(32)+ΨC12-C16-C18-C14(18)	4	0
		427	420	ΨC11-C15-C19-C17(56)+ΨC11-C15-C19-C17(43)	4	0
	404s	404	418	C9−Cl1(6)+ΨC12-C16-C18-C14(33)+PC7−C12−C16−C18(28)+PC11−C15−C19−C17(17)+ΨC11-C15-C19-C17(6)	3	3
		359	394	PC13−C8−C11−C15(55)+ΨC11-C15-C19-C17(20)+ΨC8-C11-C15-C19-C17(6)	3	1
		349	374	PC10−C7−C12−C16(48)+ΨC10-C7-C12-C16(33)+PC11-C15-C19-C17(6)	3	2
		312	360	βC18-O4-C20(24)+βC6-C8-C11(16)+βO5-C19-C17(6)+βH23-C10-C7(24)+ΨC12-C16-C18-C14(5)	3	1
		303	339	C9−Cl1(11)+ΨC10-C7-C12-C16(21)+δCl2-C9-Cl3(22)+βC19-O5-C21(7)+ρC6-C9-Cl3(7)+ΨC10-C7-C12-C16(6)	3	2
		297	320	C9−Cl2(23)+δCl1-C9-Cl2(22)	3	4
		265	299	δCl2-C9-Cl3(21)+βC19-O5-C21(18)+ΨC11-C15-C19-C17(10)+βC14-C18-C16(10) +βO5-C19-C17(7)+ΨC17-C13-C8-C11(10)	2	1
		250	292	ΨC8-C11-C15-C19(33)+ΨC10-C7-C12-C16(16)+ΨC8-C11-C15-C19(15)+ΨC16-C18-C14-C10(13)+τC19-O5-C21-H34(15)	2	1
		242	232	ΨC10-C7-C12-C16(50)+ΨC16-C18-C14-C10(19)+τC18-O4-C20-H31(16)+PC10-C7-C12-O16(5)	2	1
		215		C6−C7(14)+C6−C4(6)+ΨC10-C7-C12-C16(22)+ΨC4-C10-C7-C12(15)+βC6-C8-C11(5)+δCl2-C9-Cl3(12)	2	1
		207	223	βC6-C7-C12(11)+δCl1-C9-Cl2(16)+δ_C6-C9-Cl3(14)+ΨC10-C7-C12-C6(9)+ΨC8-C11-C15-C19(8)+PC11-C15-C19-C17(6)	2	2
		191	203	ΨC16-C18-C14-C10(43)+ΨC10-C7-C12-C16(26)+ρC6-C9-Cl2(7)	3	1
		182	197	ρC6-C9-Cl3(21)+βC6-C8-C11(13)+δCl1-C9-Cl2(7)+βO5-C19-C17(8)+δCl1-C9-Cl2(7)+ρC6-C9-Cl3(7)+βC19-O5-C21(6)	3	2
		168		ΨC16-C18-C14-C10(55)+ΨC10-C7-C12-C16(37)	3	1
		158		ΨC14-C10-C7-C12(36)+ΨC18-C14-C10-C7(26)+ΨC8-C11-C15-C19(16)+ΨC11-C15-C19-C17(14)	2	0
		108	162	τC14-C18-O4-C20(18)+ΨC14-C10-C7-C12(14)+τC21-O5-C19-C15(11)+βC8-C6-C9(9)+τC18-O4-C20-H31(11)+ΨC7-C12-C16-C18(6)	1	1
		101	115	τC21-O5-C19-C15(38)+τC14-C18-O4-C20(20)+τC19-O5-C21-H34(13)+τC18-O4-C20-H31(7)+δ_C8-C6-C9(6)	3	1
		93	68	τC14-C18-O4-C20(21)+τC21-O5-C19-C15(14)+ΨC10-C7-C12-C16(10)+τC18-O4-C20-H31(7)+τC19-O5-C21-H35(5)	1	3
		58	63	ΨC16-C18-C14-C10(39)+ΨC10-C7-C12-C16(34)+τH22-C6-C7-C10(8)+τC7-C6-C9-Cl2(8)	3	2
		50	56	ΨC14-C10-C7-C12(41)+ΨC12-C16-C18-C14(37)+ΨC8-C11-C15-C19(9)+ΨC16-C18-C14-C10(6)	4	1
		42	46	ΨC8-C11-C15-C19(23)+ΨC8-C11-C15-C19(16)+τC9-C6-C7-C12(8)+τH22-C6-C9-Cl1(12)+ΨC18-C14-C10-C7(8)+ΨC10-C7-C12-C16(7)	1	4
		30	37	ΨC12-C16-C18-C14(29)+ΨC16-C18-C14-C10(28)+ΨC15-C19-C17-C13(19)+ΨC11-C15-C19-C17(14)	2	4
		23	31	τC11-C8-C6-C9(40)+ΨC10-C7-C12-C16(14)+ΨC7-C6-C8-C10(9)+ΨC10-C7-C12-C16(6)+τC9-C6-C7-C10(5)	1	2

υ_{asy}: asymmetric stretching; υ_{sy}: symmetric stretching β:bending; δ:deformation; ρ:rocking; δ:twisting; P:puckering; ψ:asymmetric torsion; τ:torsion.

The in-plane bending mode 3, 9b and 18a are found to be simultaneously active in both IR and Raman because of symmetry lowering of the molecule; in addition such deformation changes the bond length between the carbon atoms, which build the charge transfer axis and the polarizability of such π conjugated system. Mode 3 is active as medium band at 1301 cm^{-1} in IR and 1309 cm^{-1} in Raman. The C–H plane bending vibrations usually occur in the region 1390-990 cm^{-1} [32]. The calculated value observed at 1322, 1319 cm^{-1}. The C–H out of plane deformation is usually observed between 1000 and 700 cm^{-1} [34,35]. In MXC, the C–H out of plane vibration was observed 827 cm^{-1} in IR and 824 cm^{-1} in Raman and calculated value observed at 821 cm^{-1}. The C–C vibration occurs in the region 1625-1430 cm^{-1}. In MXC the wavenumbr 1446 cm^{-1} in IR and 1148 cm^{-1} in Raman have to be assigned to the C–C vibration.

4.4. NBO analysis

A useful aspect of the NBO method is that it provides information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and intermolecular interactions. These delocalization effects can thus be depicted as a charge transfer from the highest occupied bonding orbitals into unoccupied antibonding orbitals and their importance can be more quantitatively characterized through a second-order perturbative treatment that gives the energy lowering associated with such interactions [36]. The strength of the delocalization interaction can be estimated by the second-order energy lowering E^2:

$$E^{(2)} = \Delta E_{i,j} = q_i \frac{F_{(i,j)^2}}{\varepsilon_j - \varepsilon_i} \quad (1)$$

The donor-acceptor interaction results have been tabulated in Supplementary Table S4. The OCH_3 group attached to the phenyl rings are the electron donating group. The energy for the lone pair interaction $O_4 \rightarrow C_{20}–H_{33}$ and $O_5 \rightarrow C_{21}–H_{35}$ are 12.678 kJ/mol. This increases the lengthening of C–O bonds that gives clear evidence of the resonance of asymmetric phenyl ring increased by electron donating oxygen atom. The intramolecular hyperconjugative interactions are performed by the orbital overlap between π(C–C) and π*(C– C) bond orbitals, as well as the $\sigma(C_6–C_9)$ and σ*(C–Cl) which results in ICT causing stabilization of the system. The electron density at three conjugated π bands and π* bands of the phenyl rings as well as the σ bond of trichloroethane and the π* band of the C–Cl clearly demonstrate a strong delocalization between π electron donor OCH_3 and acceptor trichloroethane via a conjugated path.

The intramolecular hyperconjugative interactions are formed by the orbital overlap between π(C–C) and π*(C–C) bond orbitals which results intramolecular charge transfer ICT causing stabilization of the system. These interactions are observed as an increase in electron density ED in C–C anti-bonding orbital that weakens the respective bonds [37]. The π electron cloud movement from donor to acceptor can make the molecule highly polarized and causes ICT, which is responsible for the bioactivity of MXC. The possible hydrogen bonding and hyperconjugative interactions are listed in Table 3. The energy of hyperconjugative interactions $\sigma(O_4) \rightarrow \sigma^*(C_{20}–H_{33})$ and $\sigma(O_5) \rightarrow \sigma^*(C_{21}–H_{35})$ become strong as 14.57 kJ/mol. The electron density is transferred from $\sigma(O_4) \rightarrow \sigma^*(C_{20}–H_{33})$ showing both the shortening and blueshift. The intramolecular charge transfer is one of the causes of insecticidal activity of the compound.

Table 3
Hydrogen bonding and hyperconjugative interactions In MXC and MC.

Compound	Donor	ED(e)	Acceptor	ED(e)	E^2 (KJ/mol)
MXC	$n_1(Cl_1)$	1.949 −0.346	$\sigma^*(C_6–H_{22})$	0.02 0.392	2.503
	$n_1(O_4)$	1.963 −0.545	$\sigma^*(C_{20}–H_{33})$	0.009 0.396	14.586
	$n_1(O_5)$	1.963 −0.545	$\sigma^*(C_{21}–H_{35})$	0.009 0.395	14.586
	$n_1(Cl_3)$	1.939 −0.328	$\sigma^*(C_{13}–H_{26})$	0.017 0.456	2.792
MC	$n_1(Cl_1)$	1.987 −0.978	$\sigma^*(C_6–H_{22})$	0.02 0.39	2.134
	$n_1(Cl_3)$	1.988 −0.975	$\sigma^*(C_{13}–H_{26})$	0.017 0.456	2.176

[a] $E^{(2)}$ means stabilization energy in kJ/mol.

4.5. Natural population analysis

The mulliken and natural charge analysis played an important role in determining the vibrational properties of atoms. In the present study, mulliken and natural atomic charge between MXC and MC were calculated by B3LYP level. The calculated mulliken and natural atomic charges are shown in Supplementary Table S5. In MXC, the mulliken atomic charge of C_9 become more negative shows the direction of delocalization and the natural atomic charges are more sensitive to the change in the molecular structure than mulliken's net charges [38]. The charge analysis on MXC and MC shows that the presence of electronegative oxygen atom O_4/O_5 imposes very high natural charge on the carbon atom enormous positive charge between C_{18}/C_{19} and C_{20}/C_{21} [39]. The presence of lone pair electron and methyl group having hyperconjugative interaction in MXC. Compounds with OCH_3 group attached to aromatic ring containing methyl groups are influenced by sterric effect. This can be observed from the increase in inter atomic distance $H_{27} \cdots H_{32}$ (2.340 A^0) and bond angles $C_{14}–C_{18}–O_4$ 115.9, 124.4 A^0 in MXC and MC respectively. This leads to increase in charge H_{27} (0.216 and 0.209e) and H_{35} (0.186 and 0.164e) in MXC and MC respectively. The results can, however, better represent in graphical form as given Supplementary Fig. S2.

It is observed that all carbon atoms having negative charge except C_{18} and C_{19} and all the hydrogen atoms are positive charge. The charges on C_{18}, C_{19} of the carbon atom attached to oxygen atom are more positive than the other carbon because of the electron withdrawing nature of the oxygen atom. The magnitude of atom C_6 and C_7 situated at the para position is positive which suggesting an extensive C–H⋯Cl hyperconjugative effect from both the rings to the trichloro ethane, more negative charged carbon C_6 confirms the electron withdrawing nature of the ethane group.

4.6. UV vis spectral analysis

UV spectral analysis of MXC has been investigated by TD DFT method. The calculated results involving the vertical excitation energies, oscillator strength(f) and absorption wavelength were carried out and compared with measured experimental spectra in cyclohexane and ethanol solvents were listed in Table 4. As can be seen from the UV visible spectra, absoption maximum values have been found to be 255 nm and 262 nm in π→π* cyclohexane and ethanol solvents respectively. The corresponding calculated values are obtained at 245 nm cyclohexane and 255 nm in ethanol. The experimental and computed UV visible absorption spectra of MXC are shown in Supplementary Figs. S3a–S3b. This shows that the molecule allows strong transition with high excitation coefficient [40]. The very strong band arise in the aromatic system due to

Table 4
Experimental and calculated absorption wavelength, energies and Oscillator strengths of MXC using the TD-DFT method in cyclohexane and ethanol solvents.

Solvent	Transition feature	Oscillator strength (f)	CI Expansion coefficient	Excitation energy (eV)	Calculated wave number (nm)	Experimental value (nm)	Assignment
Cyclohexane	H→L	0.041	0.198	5.065	244.79	255	$\pi \rightarrow \pi^*$
Ethanol	H→L	0.046	0.217	5.069	254.57	262	$\pi \rightarrow \pi^*$
Gas	H→L	0.025	0.174	5.083	243.90		

$\pi \rightarrow \pi^*$ transition which was supported by NBO analysis.

4.7. NMR analysis

NMR is one of the most effective spectroscopic techniques for organic molecule characterisation. To provide a definite assignment and analysis of ^1H and ^{13}C NMR spectra. Theoretical calculation on the chemical shift of MXC is performed by Gauge independent atomic orbital (GAIO) method in $CDCl_3$ solution. The calculated and experimental values together with the peak assignments of MXC for ^1H and ^{13}C NMR chemical shifts are shown in Supplementary Table S6. The shielding calculations of MXC were carried out using 6-311G(d,p) basis set in CDCl3 solution. The isotropic shielding values were used to calculate the isotropic chemical shift with respect to tetramethyl silane. The agreement between the experimental and the calculated $^{13}C(R^2$- 0.9892) and $^1H(R^2$-0.9576) are good. The correlation graphs between calculated and experimental ^1H and ^{13}C NMR chemical shifts of MXC are shown in Supplementary Fig. S4. Generally, the proton on phenyl ring is expected to give NMR signal in the region of 6–8 ppm [41]. The chemical shift of H_{26} observed at 7.53 ppm which is slightly different with calculated value. It is due to the $C_{13}–H_{26}\cdots Cl_1$ hydrogen bonding interaction. In ^1H NMR spectrum, methyl group near to the oxygen atom exhibit peak between 3 and 5 ppm. This greater deshielding is attributed to electronegative of oxygen atom [42].

Usually carbon atoms on phenyl ring are supposed to give NMR signals in the region 100–150 ppm [43]. In the present study, all carbon atoms on phenyl ring show the peaks in the expected range. The carbon C_6, linkage between two phenyl rings exposed a signal at 69.73 ppm. The calculated ^{13}C NMR chemical shift value of C_7 and C_8 atoms bonded with interconnect carbon atom is deshielded at 133.05 and 136.43 ppm respectively and corresponding experimental value at 131.14,130.67 ppm due to the higher electronic charge density around the ring. The methoxy carbon C_{20}/C_{21} atoms attached with oxygen with chemical shift value 55.23 ppm which closely with calculated value at 53.49 ppm. The signal assigned to C_9 in which the chlorine atom is attached at 102.5 ppm and the computed value is at 109.75 ppm. The peaks observed in C^{13} spectrum between 76 and 77 ppm belongs to solvent peaks [44]. The relationship between the experimental and computed ^1H and ^{13}C NMR chemical shifts of MXC are given in Fig. 4a-b.

4.8. HOMO and LUMO analysis

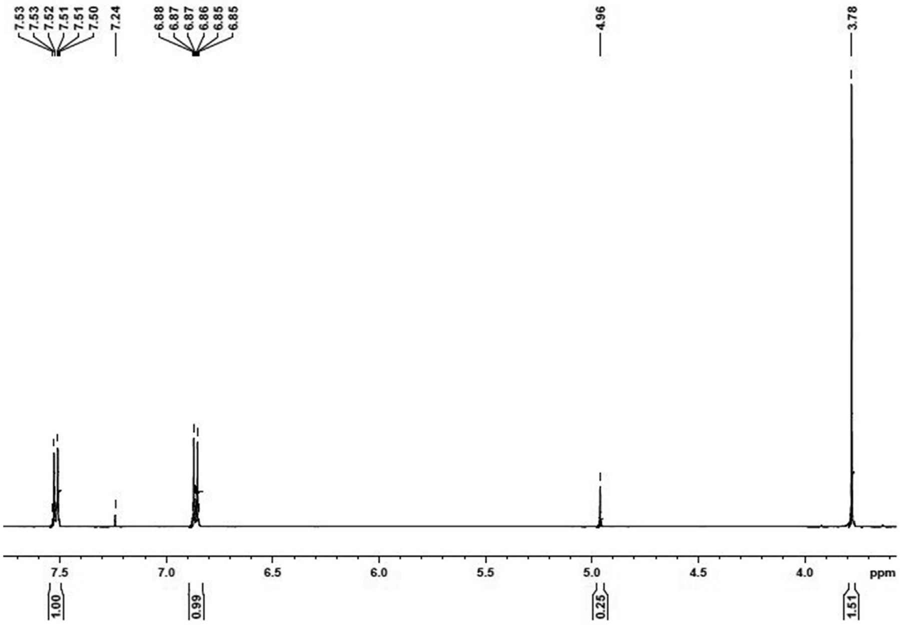
Molecular orbital and their properties such as energy are very useful for physicists and chemists. This is also used by the frontier electron density for predicting the most reactive position in p-electron systems and also explains several types of reaction in conjugated system [45,46]. The eigen values of HOMO and LUMO and their energy gap reflect the chemical activity of the molecule. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one-electron excitation from the highest occupied molecular orbital HOMO to the lowest unoccupied orbital LUMO. The most of the HOMO and LUMO are delocalized as π nature over the whole C=C bond. The molecular orbital plots of the frontier orbitals for the ground state of MXC and MC including the HOMO and the LUMO are shown in Fig. 5. From the figure, the electron density of the HOMO is larger than LUMO which lead to intramolecular charge transfer from two phenyl rings to the trichloro ethane and vice versa. The lowering of HOMO–LUMO energy gap 3.713 eV reflects the possibility of the intramolecular charge transfer from HOMO to LUMO [47].

To understand the structure of molecule and their reactivity the parameter values such as ionization potential (IP), chemical hardness(η), chemical potential (μ), electron affinity (A), global chemical softness (s), Electronegativity (χ), Electrophilicity(ω) have been calculated using HOMO and LUMO orbital energies [48]. The calculated energy values of MXC and MC are listed in Table 5. Due to the presence of intramolecular charge transfer interaction the electrophilicity index value is increased and hence enhance the bio activity of the molecule.

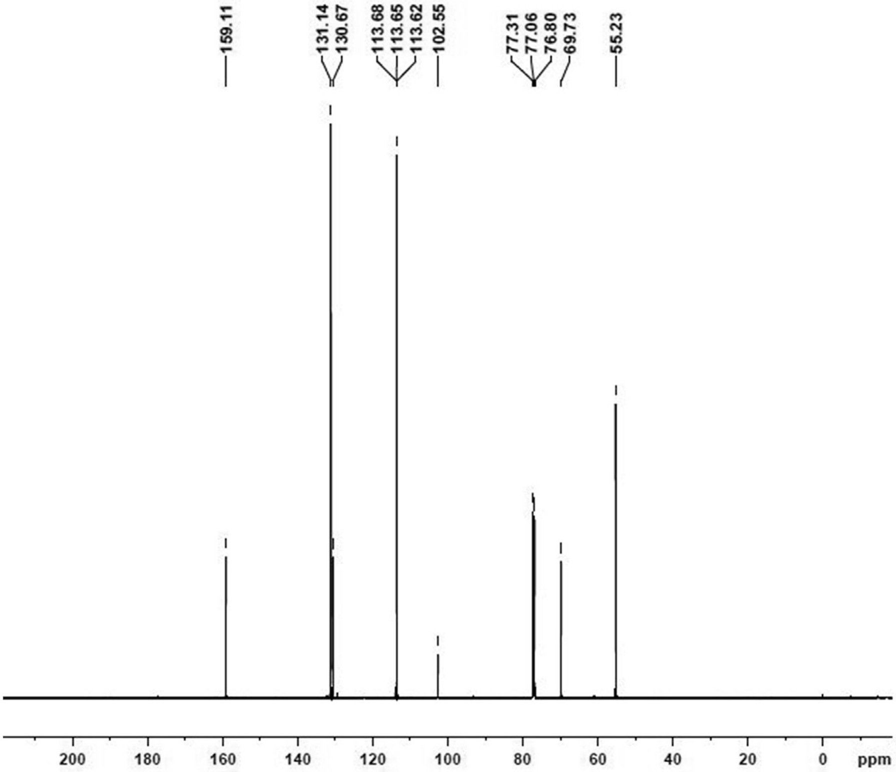
4.9. Hirshfeld surface analysis and MEP analysis

Although the determination of the solid state structure was established with the observation of the crystallographic study, but in a visual manner to elucidate the unique intermolecular interactions present in the structure of the complexes, we carried out the Hirshfeld surface analysis. The Hirshfeld surface analysis is special for a specified crystal structure and set of spherical nuclear electron densities, and it indicates the possibility of further insight to molecular crystal interaction. The Hirshfeld surfaces of both the crystal structures have been mapped over d_{norm}, shape index and curvedness [49]. The surfaces are shown as transparent for the visualization of the molecular moiety, in a similar orientation for both structures, around which they were calculated. The dominant O⋯H interactions are viewed by the bright red area of d_{norm} surface and light red spots are due to C–H⋯O interactions. The shape index and curvature surfaces were shown to give proper details on each donor-acceptor pair and to detect how much shape the surfaces are properly divided into patches, respectively. The C–O⋯C intermolecular interactions appear as two distinct spikes in the fingerprint plots in Fig. 6. The C–H⋯O intermolecular interactions appear as two distinct spikes in the fingerprint plots. Complementary regions are visible in the Supplementary Fig. S5. Finger print plots where one molecule acts as donor $de > di$ and the other as an acceptor $de < di$.

The d_e and d_i values show the closest external and internal distance from the given plot on Hirshfeld contact such as C⋯H (11.2%), C⋯Cl (8.7%), H⋯H (42.4%), H⋯Cl (20.3%), O⋯H (10.1%) and C⋯Cl (6.2%). The O⋯H interactions are represented by a spike indicating that oxygen atom contact with C–H in methyl group. The shortest distance $d_e + d_i$ for H⋯O interaction in MXC is ~2.200A° representing C–H⋯O bonding. The percentage contributions of intermolecular interactions to the relative Hirshfeld surface reveals C–H⋯O (11.2%), where as more significant contributions come from H⋯H contacts (42.4%) show a sharp peak in Fig. 6, which is reflected in the scattered point in the fingerprint plot [50]. The intermolecular interactions in the compound enhance the insecticidal activity of the MXC molecule.



a



b

Fig. 4a. The observed ^{1}H NMR spectra of the MXC in $CDCl_3$ solvent.The observed ^{13}C NMR spectra of the MXC in $CDCl_3$ solvent.

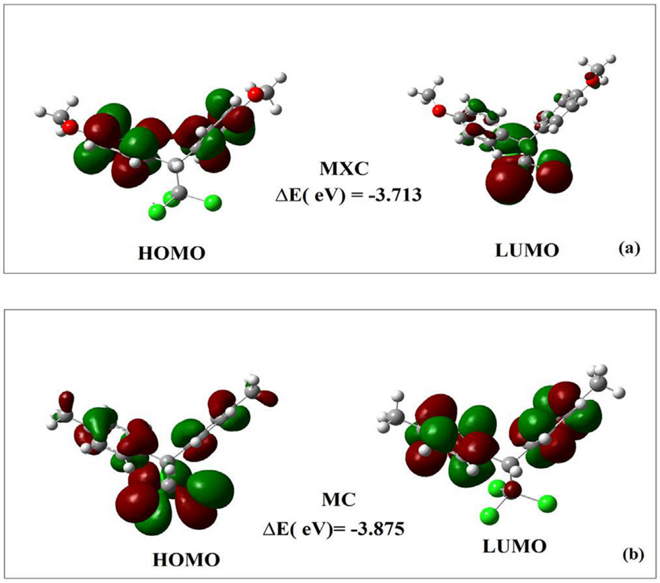


Fig. 5. Plot of frontier molecular orbitals of MXC and MC.

Table 5
Calculated energy values of MXC and MC.

Parameter	MXC	MC
HOMO	−0.325	−0.335
LUMO	−0.188	−0.192
ΔE(eV)	−3.713	−3.875
Ionization Poteneтial	0.325	0.335
Electron Affinity	0.188	0.192
electronegativity (χ)	−0.256	−0.263
Chemical potential(μ)	0.256	0.263
Hardness(η)	0.068	0.071
Softness(S)	7.325	7.006
electrophilicity index(ω)	0.481	0.486

MEP is very helpful computed technique to illustrate the charge distributions nucleophilic and electrophilic poisons on the functional groups as colour-indicators like: blue e-poor < green < yellow < orange < red e-rich [51]. Therefore, the MEP analysis served to support the Hirshfeld Surface Analysis interactions result. The nucleophilic positions in the molecule which indicated by red-colour were placed at methoxy groups, the blue high electrophilic was detected on phenyl rings as seen in Supplementary Fig. S6. The presence of the blue H-donor and red colours H-acceptor in the desired molecule open the possibility to form different types of H-bonds, which were already observed theoretically by Hirshfeld Surface Analysis.

4.10. Fukui function

The Fukui function is adopted as the functional discriptors of local density to illustrate chemical reactivity and selectivity. It reveals the relative energy site in the molecule [52]. The condensed or atomic Fukui functions on the jth atom site are given as per the following equations for an electrophilic $f_{j}^{-}{}_{(r)}$, nucleophilic and free radical attack $f_{j}^{+}{}_{(r)}$, on the reference molecule, respectively is

$$f_{j}^{-} = q_{j}(N) - q_{j}(N-1) \quad (3)$$

$$f_{j}^{+} = q_{j}(N+1) - q_{j}(N) \quad (4)$$

$$f_{j}^{0} = 1 \Big/ 2\left[q_{j}(N+1) - q_{j}(N-1)\right] \quad (5)$$

For the neutral, anionic or cationic chemical species q_j is the atomic charge at the jth atomic site. The concept of generalized philicity is proposed by Chattaraj et al. [53], containing informations about known various global, local reactivity and these electivity descriptors. The dual descriptor is the difference between nucleophilic and electrophilic attack in the fukui function. If $\Delta f(r) > 0$, the specific site is favoured for electrophilic attack.

The condensed fukui function value calculated using UCA-Fukui in MXC is shown in Supplementary Table S7. It is observed that the atoms C_6 and C_9 has higher f^+ value, which shows the possible site for nucleophilic attack and C_7 have higher f^- value which indicates the possible site of electrophilic attack. It is found that the dual descriptor (Δf) value of C_{19} is highly positive, that is tendency to acquire electron and $Cl_1$is electrophilic. Among all hydrogen atoms H_{22} is highly neucleophilic. It is clear that there is an eventual charge transfer in MXC molecule from aromatic to trichloro ethane region which also supported in HOMO-LUMO analysis.

4.11. Docking studies

Docking was performed to analyse that the best fit site for ligand molecule in protein. Minimum energy obtained from optimized structure at B3LYP level theory and docking for different receptors. In the present work, the compounds have been docked with different protein receptors 1C20 (*drosophila melanagaster)* and 1EEA *(acetylcholisterase)* [54–57]. The target proteins are selected from protein data bank RCSB PDB. The ligand with protein interaction was studied and visualized using Discovery studio visualization. Figure shows the best ranked ligand-target protein complexes with H-bonding interaction. Docking studies listed in Table 6 and the binding mode of ligand with the two target proteins were effectively using Autodock tools and displayed in Figs. 7–8.

In the binding model, the residue LYS 454 present in active site of target *drosophila melanagaster* is attached to the MXC through a single hydrogen bond C—H···Cl 1.69A° which represented by dashed lines. The ligand MXC shows bond energy −7.52 kCal/mol with target protein activity 1C20. For IEEA receptor, the binding affinity represented by MXC and MC are −7.03 and −6.8 kCal/mol '1 respectively. The hydrogen bond interaction decides the properties and nature of the proteins and bio molecules. From the docking studies, it is evident that trichloroethane group involved in hydrogen bond formation with the target enzyme which shows the insecticidal active site of MXC.

5. Conclusion

Vibrational spectral analysis is carried out using FT IR and Raman spectroscopy in the insecticidal molecule Methoxychlor. Potential energy scan analysis explained most stable structure. The structural parameters and vibrational frequencies of MXC and its related compound have been studied theoretically by DFT (B3LYP) calculation to support experimental results. Peculiar blue shift was noticed as an outcome of C—H···Cl hyperconjugative interaction. Natural charge analysis elucidates the electron withdrawal nature of ethane group. The experimental UV—visible spectrum exhibit absorption peak in ethanol and cyclohexane solvents showed $\pi \rightarrow \pi^*$transition. The chemical shift values (with respect to TMS) were compared with the experimental data and were a very good agreement both for ^{1}H and ^{13}C. Hirshfeld surface analysis and

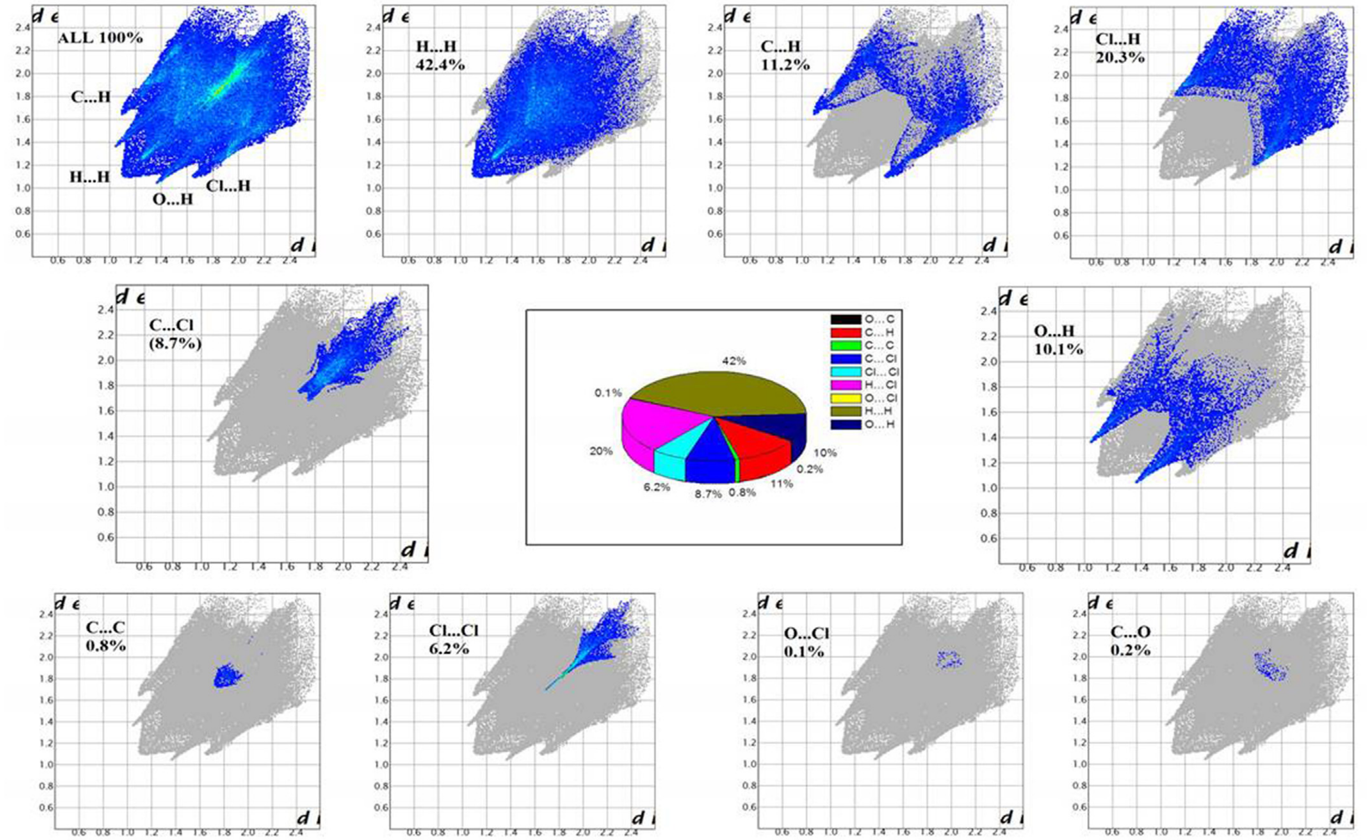


Fig. 6. 2D fingerprint plots of selected interactions of MXC.

Table 6
Molecular docking results of MXC with different protein targets.

Protein (PDB:ID)	Compound	Binding Residue	Bond energy	H-Bond distance (A^0)	Incubation constant (μm)	Binding affinity (k/cal)
1C20	MXC	LYS 454	−8.58	1.69	6.37	−7.52
		LYS 133		2.03		
	MC	LEU 540	−7.71	2.04	10.08	−6.82
1EEA	MXC	GLN 74	−8.52	1.93	7.07	−7.03
		TYR 74		2.15		
	MC	TYR 70	−8.42	1.96	3.05	−6.8

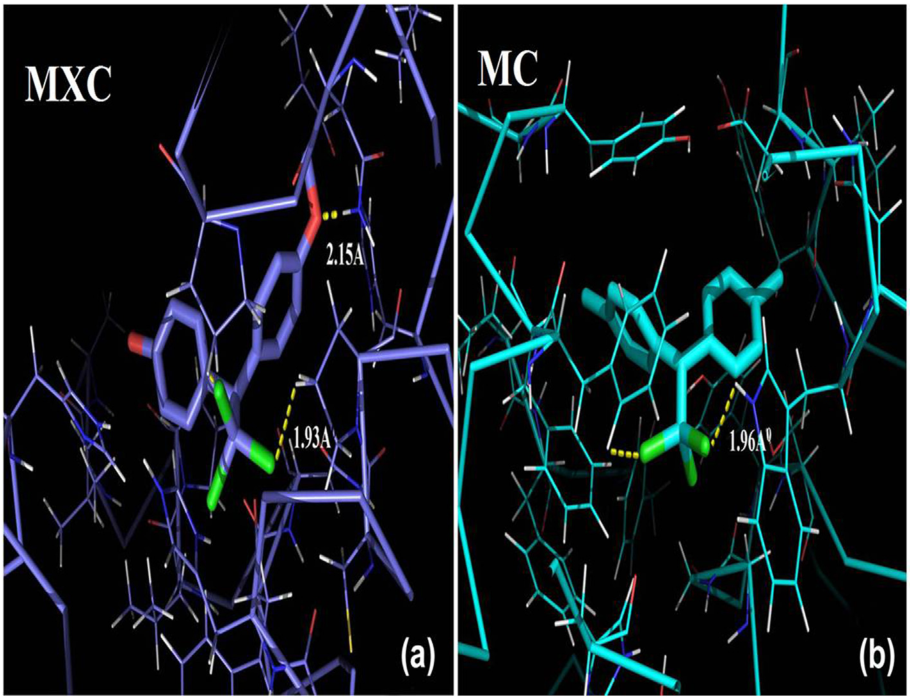


Fig. 7. Molecular docking of (a) MXC and (b) MC with pdb id: 1C20.

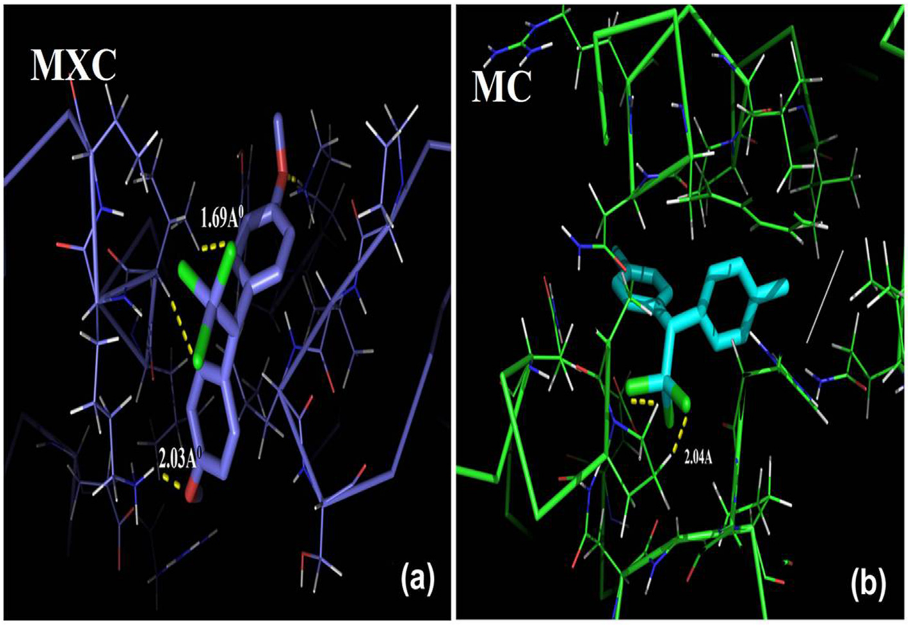


Fig. 8. Molecular docking of (a) MXC and (b) MC with pdb id: IEEA.

associated 2D fingerprint plots were showed the intermolecular interaction of the title molecule in the crystal structure. It is also observed the percentage contribution of intermolecular interaction which enhanced the insecticidal activity of the title compound. Molecular electrostatic potential analysis served to support Hirshfeld surface analysis. Nucleophilic position is indicated by red colour placed at methoxy group. Molecular docking studies obviously reveal LYS 454 presents active site in *drosophila melanagaster* through single C—H···Cl hydrogen bonding with target protein activity (1C20).

CRediT authorship contribution statement

L.S. Anju: Data curation, Writing - original draft, Formal analysis. **D. Aruldhas:** Conceptualization, Methodology, Supervision, Writing - review & editing. **I. Hubert Joe:** Software, Visualization. **Nimmy L. John:** Software, Validation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2020.127904.

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STRATEGIC FOR INTERNATIONAL FINANCE IN DEVELOPMENT OF NATION

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Abstract

International Finance is an important part of financial economics. It mainly discusses the issues related with monetary interactions of at least two or more countries. International finance is concerned with subjects such as exchange rates of currencies, monetary systems of the world, foreign direct investment (FDI), and other important issues associated with international financial management. Like international trade and business, international finance exists due to the fact that economic activities of businesses, governments, and organizations get affected by the existence of nations. It is a known fact that countries often borrow and lend from each other. In such trades, many countries use their own currencies. Therefore, we must understand how the currencies compare with each other. Moreover, we should also have a good understanding of how these goods are paid for and what is the determining factor of the prices that the currencies trade at. International trade is one of the most important factors of growth and prosperity of participating economies. So this study conduct how to improve international finance in developing country

Author Keywords

International finance, Foreign direct investment, Exchange rate, Capital market, Monetary system

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DFT AND VIBRATIONAL SPECTROSCOPIC STUDY ON PYRIMIDINE DERIVATIVE INSECTICIDE

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ABSTRACT

A complete vibrational analysis of (6-methyl-2-thiophen-2-ylpyrimidin-4-yl) *N*,*N*-dimethylcarbamate (MTPD) was performed by using theoretical information using density functional theory based on scaled quantum chemical approach. The structural and spectroscopic data of the molecule were obtained from B3LYP with 6-31G(d) basis set calculations. The complete vibrational distributions were performed on the basis of the potential energy distribution (PED) of the vibrational energy distribution analysis (VEDA 4) program. The stable geometry of the compound has been determined from potential energy surface scan. The calculated HOMO and LUMO energies show that charge transfer occur within the molecule. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the modes of vibration. Natural charge analysis and molecular electrostatic potential (MESP) has been calculated.

Keywords: Pyrimidine, Vibrational analysis, reactivity, UCA Fukui, MESP

1. INTRODUCTION

Pyrimidine represents one of the most active classes of compounds, possessing a wide spectrum of biological activity [1]. It belongs to the family of nucleic acids and is of great interest, since they control the manufacture of protein and the functions of cell in living organisms. Pyrimidine does not exist in nature but in the form of its different derivatives are found as a part of more complex systems and are widely distributed. Pyrimidine and its derivatives are known for their biological activity and have related much attention from spectroscopists, drug, clinical and industrial researchers because of their therapeutic importance [2]. Nitrogen containing cyclic compounds has been increasing interest because of their utility in various applications. They are present in wide variety of drugs, biologically active compounds including insecticidal agents [3]. The current study is to focus on the significance of pyrimidine and its derivative as insecticidal agents to the development of more potent and effective insecticidal agents.

In the present study the molecular structure of (6-methyl-2-thiophen-2-ylpyrimidin-4-yl) *N*,*N*-dimethyl - carbamate (MTPD) is described. The purpose of this work is to investigate the performance of DFT method in predicting geometry and vibrational spectra of the title compound. The natural bond orbital (NBO) analysis, Molecular electrostatic potential should help us to understand the structural and spectral characteristics and bioactivity of the compound.

2. MATERIALS AND METHODS

All geometric structure calculation have been carried out using Gaussian 09 package and and Gauss view molecular visualizing program package, which has provided itself to be extremely useful to get a clear knowledge of optimized parameters, vibrational wavenumber, electronic structure properties and other molecular properties [4]. The geometry is fully optimized at Beck 3-Lee-Yang-Parr (B3LYP) level with standard 6-31G(d) basis set [5]. The computed wavenumbers were scaled by 0.9614 [6]. Additionally the calculated vibrational frequencies are clarified by means of the Potential energy distribution (PED) analysis of all fundamental vibrational modes by using Veda.4 program [7]. The theoretical tool Fukui function was performed by UCA-FUKUI software to understand the chemical reactivity the condensed Fukui function and related local and global parameters are calculated [8]. Potential Energy scan (PES) was performed to obtain a stable geometry of the compound.

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry

Complete geometrical parameters were performed within the C_1 point group symmetry for the title compound (MTPD), the optimized geometries are shown in fig. 1 and are listed in table 1. The optimized structure parameters (bond length, bond angle, dihedral angle) of TMPD was calculated at DFT B3LYP/6-31G(d) basis set. The optimized geometries give nearly non planar structure to the compound. The backbone of the MTPD molecule consists of one methyl pyrimidine and a dimethyl carbamate.

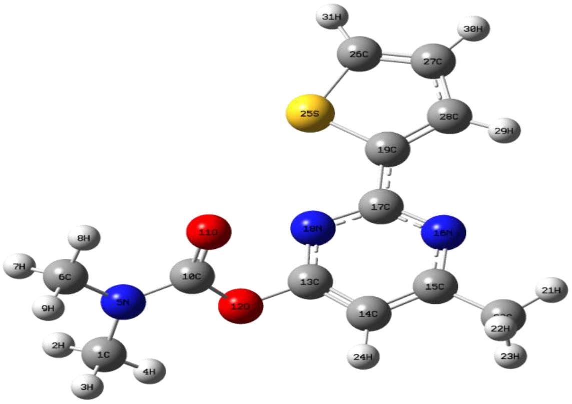

Fig. 1: Optimized structure of MTPD

Table 1: Optimized structure parameters of MTPD

Bond Length	Exp. value	Calculated value	Bond Angle	Exp. value	Calculated value	Dihedral angle	Exp. value	Calculated value
(A^0)			(^{0})			(^{0})		
C_1-H_2	0.98	1.098	H_2-C_1-H_3	109.5	108.1	H_2-C_1-N_5-$_{C6}$	69.3	55.6
C_1-H_3	0.98	1.098	H_2-C_1-H_4	109.5	109	H_2-C_1-N_5-C_{10}	-104.9	-122.3
C_1-H_4	0.98	1.087	H_2-C_1-N_5	109.4	110.7	H_3-C_1-N_5-C_6	-50.8	-63.6
C_1-N_5	1.456	1.455	H_3-C_1-H_4	109.5	109	C_3-C_1-N_5-C_{10}	-104.9	118.4
N_5-C_6	1.457	1.455	H_3-C_1-N_5	109.5	109.7	H_4-C_1-N_5-C_6	-170.7	175.8
N_5-C_{10}	1.337	1.361	H_4-C_1-N_5	109.5	110.3	H_4-C_1-N_5-C_{10}	15.1	-2.2
C_6-H_7	0.98	1.098	C_1-N_5-C_6	117.1	116.5	C_1-N_5-C_6-H_7	55.2	-61.7
C_6-H_8	0.98	1.089	C_1-N_5-C_{10}	124.9	125.1	C_1-N_5-C_6-H_8	175.2	178.3
C_6-H_9	0.98	1.098	C_6-N_5-C_{10}	117.9	118.4	C_1-N_5-C_6-H_9	55.2	58.1
C_{10}-O_{11}	1.213	1.211	N_5-C_6-H_7	109.5	110.3	C_{10}-N_5-C_6-H_7	-130.2	116.4
C_{10}-O_{12}	1.37	1.399	N_5-C_6-H_8	109.5	108.9	C_{10}-N_5-C_6-H_8	-10.24	-3.6
O_{12}-C_{13}	1.398	1.373	N_5-C_6-H_9	109.5	110.4	C_{10}-N_5-C_6-H_9	109.7	-123.8
C_{13}-C_{14}	1.382	1.394	H_7-C_6-H_8	109.5	109.4	C_1-N_5-C_{10}-O_{11}	176.8	176.1
C_{13}-N_{18}	1.314	1.321	H_7-C_6-H_9	109.5	108.4	C_1-N_5-C_{10}-O_{12}	-4.0	-7.5
C_{14}-C_{15}	1.401	1.397	H_8-C_6-H_9	109.5	109.5	C_6-N_5-C_{10}-O_{11}	2.7	-1.8
C_{14}-C_{24}	1.512	1.083	N_5-C_{10}-O_{11}	126.2	126.4	C_6-N_5-C_{10}-O_{12}	-178.1	174.6
C_{15}-N_{16}	1.333	1.342	N_5-O_{10}-O_{12}	111.5	110.6	N_5-C_{10}-O_{12}-C_{13}	176.0	154.6
C_{15}-C_{20}	1.501	1.506	O_{11}-C_{10}-O_{12}	122.3	122.9	O_{11}-C_{10}-O_{12}-C_{13}	-4.8	-28.8
N_{16}-C_{17}	1.345	1.342	C_{10}-O_{12}-C_{13}	115.2	118.4	C_{10}-O_{12}-C_{13}-C_{14}	87.0	132.2
C_{17}-N_{18}	1.351	1.348	O_{12}-C_{13}-C_{14}	119.2	117.9	C_{10}-O_{12}-C_{13}-N_{18}	-95.7	-52
C_{20}-H_{21}	0.98	1.096	O_{12}-C_{13}-N_{18}	114	118.3	O_{12}-C_{13}-C_{14}-C_{15}	175.7	175.9
C_{20}-H_{22}	0.98	1.096	C_{14}-C_{13}-N_{18}	126.8	123.7	O_{12}-C_{13}-C_{14}-C_{24}	-4.2	-4.5
C_{20}-H_{23}	0.981	1.094	C_{13}-C_{14}-C_{15}	113.4	116.1	N_{18}-C_{13}-C_{14}-C_{15}	-1.1	0.3
			C_{14}-C_{15}-N_{16}	122.7	121.4	N_{18}-C_{13}-C_{14}-C_{24}	178.9	179.9
			C_{14}-C_{15}-C_{20}	121.6	122	O_{12}-C_{13}-N_{18}-C_{17}	-177.0	-176.5
			N_{16}-C_{15}-C_{20}	115.8	116.6	C_{14}-C_{13}-N_{18}-C_{17}	-0.02	-0.9
			C_{15}-N_{16}-C_{17}	117.4	116.6	C_{13}-C_{14}-C_{15}-N_{16}	1	0.4
			N_{16}-C_{17}-N_{18}	125	127	C_{13}-C_{14}-C_{15}-C_{20}	-179.0	179.9
			C_{13}-N_{18}-C_{17}	114.7	115.3	C_{14}-C_{15}-C_{20}-H_{21}	-163.3	123.1
			C_{15}-C_{20}-H_{21}	109.5	110	C_{14}-C_{15}-C_{20}-H_{22}	-43.2	-119.2

Continued…

	C_{15}-C_{20}-H_{22}	109.5	111.8	C_{14}-C_{15}-C_{20}-H_{23}	76.8	1.9
	C_{15}-C_{20}-H_{23}	109.4	110	N_{16}-C_{15}-C_{20}-H_{21}	16.8	-57.3
	H_{21}-C_{20}-H_{22}	109.5	109	N_{16}-C_{15}-C_{20}-H_{22}	136.8	60.4
	H_{21}-C_{20}-H_{23}	109.5	107	N_{16}-C_{15}-C_{20}-H_{23}	-103.2	-178.6
	H_{22}-C_{20}-H_{23}	109.5	108.9	C_{15}-N_{16}-C_{17}-N_{18}	-1.6	-0.5
				N_{16}-C_{17}-N_{18}-C_{13}	1.5	1.1
				C_{14}-C_{15}-N_{16}-C_{17}	0.3	-0.3
				C_{20}-C_{15}-N_{16}-C_{17}	-179.8	-179.8

Pyrimidine ring is found to be near planar within small twist exo C_{13}, C_{17}, C_{15} bond angles (N_{18}-C_{13}-O_{12}, O_{20}-C_{13}-C_{14}, N_{16}-C_{17}-S_{19}, C_{14}-C_{15}-N_{16}, C_{14}-C_{15}-C_{20}) notably deviate from the expected triagonal angle and so transfer of electrons is possible between the pyrimidine ring and side chain atoms and this results in the molecular crowding effect arising from steric requirements which is responsible for biological activity. Decrease the endo cyclic angles of C_{13}-N_{18}-C_{17}, C_{13}-C_{14}-C_{15}, C_{15}-N_{16}-C_{17} and the corresponding increase in the endo cyclic angles N_{14}-C_{13}-N_{18}, N_{16}-C_{15}-C_{14}, N_{16}-C_{17}-N_{18} are due to the negative inductive effect in the pyrimidine ring. Lowering of bond angles N_5-C_{10}-O_{12} and C_{10}-O_{12}-C_{13} is due to the charge transfer from pyrimidine ring through carbamate group to the thiophene ring. In the molecule, the dimethyl carbamate part C-H, C-N, C-O, C-C bond lengths are almost identical. But when compared the C_{13}-C_{18} bond length is slightly decreased and C_{16}-C_{17} and C_{18}-C_{17} bond length is increased due to the attachment of thiophene ring. The C_{16}-C_{17}-N_{18} bond angle is calculated in MTPD as 125.8 A°. This is difference is due to the attachment of thiophene groups. This also clears the C_{13}-N_{18}-C_{17} bond angle (116.0 A°).

3.2. NBO Analysis

NBO analysis gives the role of intermolecular hydrogen bonding interaction in the compound. This is carried out by considering all possible interaction between filled donor and empty acceptor. For each donor (i) and acceptor (j), the stabilization energy (E^2) associated with the delocalization i⟶j is determined as

$$E^{2} = \Delta Eij = qi(Fi,j)2 \Big/ Ej - Ei$$

Where, q_i is donor orbital occupancy, E_i,E_j are the diagonal elements, F_{ij} is the off diagonal NBO fock matrix element.

Table 2: Possible Hydrogen bonding and hyper-conjugative interactions for MTPD

	Donor	ED (e)	Accepter	ED (e)	E^2 (kJ/mol)
Hydrogen bonding	n_1(O11)	1.815	σ*(C6-H8)	0.009	4.226
		-0.239		0.471	
	n_1(O12)	1.935	σ*(C1-H4)	0.007	3.18
		-0.557		0.462	
	n1(N5)	1.688	σ*(C1-H2)	0.015	18.995
		-0.247		0.433	
Hyperconjugation	n1(N5)	1.688	σ*(C1-H3)	0.016	21.84
		-0.247		0.432	
	n1(N5)	1.688	σ*(C6-H7)	0.014	21.004
		-0.247		0.437	
	n1(N5)	1.688	σ*(C6-H9)	0.014	18.702
		-0.247		0.436	

Table 2 shows the most relevant hydrogen bonding and hyper-conjugative interactions for the compound performed by NBO analysis. The hyper-conjugative interactions are formed by the orbital overlap between σ bond orbital to σ*anti-bonding orbital, which results in intramolecular charge transfer causing the stabilization of the system. These interactions can be identified by finding the increase in electron density in the anti-bonding orbital.

C-H…O intramolecular hydrogen bonds are possible in MTPD. $C_1…O_{12}$ and $C_6…O_{11}$ distance 2.702 A °and 2.789 A° which are shorter than the sum of related vander Walls radii. The corresponding C-H-O angle is 104.2 A°.

3.3. MESP Analysis

Molecular electrostatic potential represents a point in the space around the molecule to provide an indication of net electrostatic effect produced at the point by the total charge distribution of the molecule and correlate with dipole moment and chemical reactions. The MSEP has been employed as an informative tool of chemistry to describe different physical and chemical features including non-covalent interactions in complex biological system. The Molecular Electrostatic Potential (MESP) is the most useful electrostatic property to study the relation between structure and activity. The molecular electrostatic potential at the surface are presented by distant colours. Red represents the region of most electronegative electrostatic potential. Blue represent the region of the most positive electrostatic potential. Green represents place of zero potential, potential increases in the order red< orange<green<blue. The red region refers to the area would favour interaction and lone pair region predicting site of hydrogen bonding donor. The computed molecular electrostatic potential for MTPD is shown in fig 2. The carbonyl group shows the negative potential or donor nature. This gives the evidence for the possibility of C-H…O hydrogen bonding.

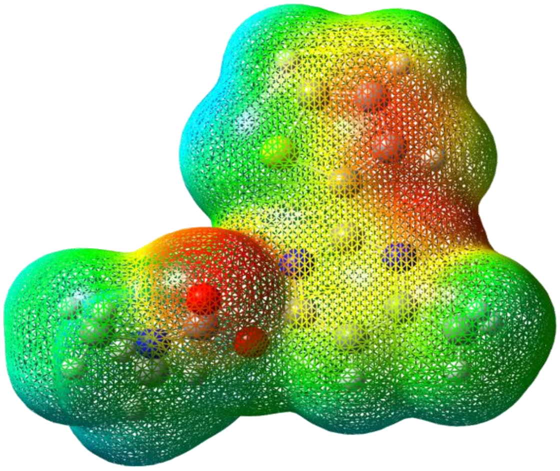

Fig. 2: Molecular electrostatic potential for MTPD

3.4. PES Analysis

A detailed potential energy surface (PES) scan study on dihedral angles N_{16}-C_{15}-C_{20}-H_{21} (φ_1) and H_2-C_1-N_5-C_6 (φ_2) have been performed at B3LYP/6-31G(d) level. The PES scans were carried out by minimizing the potential energy in all geometrical parameters by changing the torsion angle at every 10° for a 360° rotation around the bond. The PES scan are shown in fig 3 .In both the rotations minimum energy is obtained at 60°, 10° and 300°. For φ_1 the minimum energy obtained at 60° is due to the steric interaction $H_{23}…H_{24}$ (2.472 A°) where the stability is increased. The maximum energy is obtained at 360° due to the C_{20}-$H_{21}…N_{16}$ interaction ($H_{21}…N_{16}$ = 2.714 A°).

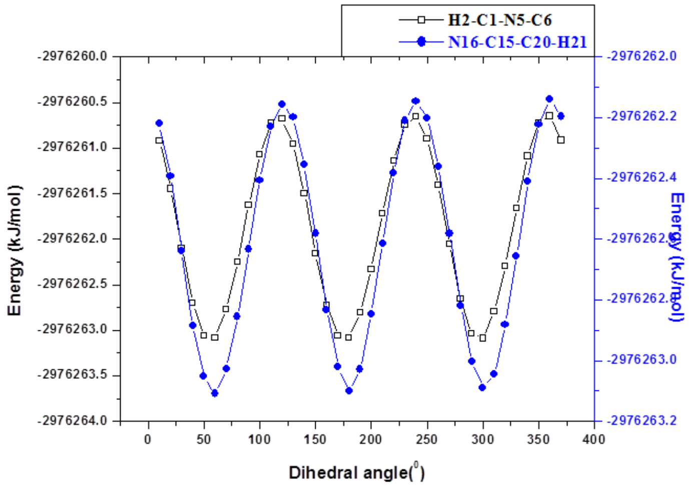

Fig. 3: Potential energy Scan curve of MTPD

3.5. Charge Analysis

The natural charge of title compound is shown in Fig 4. The result shows that the substitution of thiophene ring by pyrimidine ring leads to the redistribution of electron density.

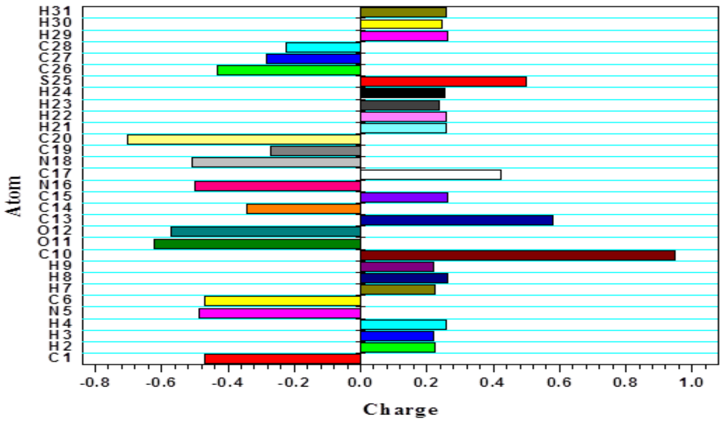

Fig 4: Charge analysis of MTPD

The compound shows that the presence of two large electronegative atom and one nitrogen atom impose very high charge on carbon atom (C_{10}) of the carbamate group. Charge of N_{18} is decreased by the influence of C_{25}-H_{26}...N_{18} hyperconjugative interaction. It is worthy to mention that C_{10}, C_{13}, C_{17} and C_{15} atoms exhibit positive charge while other carbon atoms exhibit negative charge. C_{20} having maximum negative value because of the attached electron donating methyl group. The charge on H_8 in methyl group shows the maximum magnitude of 0.264e among the hydrogen atom due to the C_6-H_8...O_{11} hydrogen bonding interaction.

3.6. Vibrational Analysis

The MTPD has 31 atoms with 87 modes of vibrations. The molecule does not exhibit symmetry and hence belongs to the C_1 point group. The assignment of MTPD was done by theoretical calculations. The theoretical IR spectrum is shown in fig 5. The detailed vibrational assignments of calculated frequencies have been reported in the table 3.

Table 3: The detailed vibrational assignments of calculated frequencies of MTPD

Calculated IR wave number	Assignments with PED	IR intensity	Raman intensity
3139	υC27H30(14)+υC26H31(80)	0	0
3126	υC26H31(85)+ υC27H30(12)	0	1
3115	υC14H24(99)	0	1
3099	υC26H31(18)+ υC27H30(73)	1	0
3086	υC1H2(63)+ υC6H7(63)	1	1
3072	υC6H8(92)	0	1
3024	υ_{asy}C20H21(94)	2	25
3001	υ_{asy}C20H21(96)	1	8
2966	υC1H2(21)+ υC6H7(25)+ υC6H9(46)	4	5
2960	υ_{sy}C1H2(71)+ υC6H7(25)	6	4
2942	υ_{sy}C20H21(95)	2	4
2922	υ_{sy}C1H2(10)+ υC6H9(53)	13	8
2915	υ_{sy}C1H2(70)+υC6H9(17)	8	7
1772	υO11C10(77)+ υN5C10(12)	47	1
1568	υC16N15(14)+υN18C13(14)+υC13C14(38)+υN16C15(10)	33	6
1550	υC16N15(34)+υN18C13(34)+βC19C17N16(31)+υC14C15(31)	16	5
1533	υC19C28(54)+υC26C27(54)+υC17C19(11)+ βH29C28C27(12)+βH30H27C26(12)	18	6
1504	βH2C1H3(70)+βH7C6H9(70)	8	11
1473	βH2C1H4(23)+βH2C1H3(24)+ βH7C6H9(24)+βH2C1H3(24)+βH7C6H8(31)	4	57
1469	βH2C1H3(51)+βH7C6H9(51)+βH7C6H8(16)+τH8C6N5C1(11)	4	48
1460	βH2C1H4(57)+βH7C6H8(22)	6	36
1456	βH21C20H22(69)+opC20H2C15H22(14)	9	51
1446	βH21C20H22(84)++opC20H2C15H23(13)	7	5
1434	υC19C28(47)+υC26C27(47)+υC17C19(11)	22	1
1432	βH2C1H4(57)+βH3C1H4(57)+βH8C6H9(17)	20	1
1405	βH8C6H9(51)	6	1
1402	υN1613C15(41)+βH24C14H13(10)	6	3
1392	υN5C10(14)+βH21C20H22(20)	13	2

Continued...

1380	βH21C20H22(38)	8	100
1369	υN16C15(70)+υN18C13(10)+υC17C19(11)+βH21C20H22(27)	11	3
1335	υC16N15(15)+υN18C13(15)+υC13C14(11)+υC14C15(10)	37	4
1324	υC19C28(17)+υC26C27(17)+βH31C26H27(17)	17	1
1243	opC6H7N5H9(10)	8	1
1240	υN16C15(73)+υN18C13(10)	7	0
1209	υC19C28(13)+υC26C27(13)+βH29C28C27(52)+βH30H27C26(52)	3	0
1147	υO12C10(40)+υO12C13(10)+υN5C1(52)+βH24C14H13(37)	17	0
1144	βH7C6H8(10)+opC1H4N5H2(33)+τH8C6N5C1(31)	19	1
1123	υN5C10(12)+ υO12C10(21)+ υO12C13(21)+ βN5C10O11(10)+opC1H4N5H2(33)+opC6H7N5H9(12)+	100	1
1104	υC19C28(10)+υC26C27(10)	17	0
1099	βH7C6H8(10)+opC1H4N5H3(36)+τH8C6N5C1(33)+ βH21C20H22(18)	9	0
1071	υC19C28(13)+υC26C27(13)+βH31C26C27(48)+βH29C28C27(11)	1	0
1052	υN5C1(17)+opC6H7N5H9(31)	2	1
1032	βH21C20H22(13)++opC20H2C15H23(70)	3	2
1027	υC19C28(24)+υC26C27(24)+βH29C28C27(11)+βH30H27C26(11)	5	1
1013	υO12C10(22)+υO12C13(22)+υN5C1(12)+υN5C6(12)	6	1
990	υC14C15(10)+βC14C13N18(10)+opC20H2C15H22(41)	1	0
964	υN16C15(10)+υN18C13(10)+ βC14C13N18(15)++opC20H2C15H22(13)	0	2
945	υO12C10(20)+υO12C13(20)+υC15C20(10)+ υN5C1(26)+υN5C6(26)	1	5
893	τH29C28C19C17(81)+βH29C28C27(79)	0	0
849	βC17C19C28(26)+opC14C13C15H24(17)	1	0
841	βC17C19C28(33)+opC14C13C15H24(23)	3	0
832	τH29C28C27C26(84)+τH31C26S25C19(84)	1	0
816	βC17C19N28(34)+opC14C13C15H24(15)	4	0
799	υN5C1(10)+υN5C6(10)+opC14C13C15H24(35)	2	0
770	τC15N6C17CN18(58)+τC15C4C13N18(18)	2	1
723	υS25C19(41)+βC17C19C28(42)	1	1
715	opO11N5O12C10(69)	1	1
694	τH29C28C27C26(86)	6	1
672	τC15C4C13N18(18)+opO11N5O12C10(19)+ τC17N18C13O12(12)	2	0
635	βN5C10O12(12)+βC19S25C26(31)	1	2
629	βN16C17N18(12)+βC19S25C26(29)	1	1
599	βN5C10O11(24)+τC15N16C17N16(10)	1	0
569	τC19C28C27C26(11)++τC15N16C17N16(30)	0	0
551	τC19C28C27C26(71)	0	0
534	υC15C20(15)+βC13N18C17(42)	1	0
508	βC13N18C17(11)+βN5C10O12(12)+βC14C13O12(19)+ βC10O12O13(19)+βC14C15C20(11)	0	0

Continued...

457	τC19S25C26C27(80)	0	0
431	υO12C10(10)+υO12C13(10)+βC1N5C10(52)	1	0
368	βC6N5C10(43)	2	0
342	υC17C19(13)+βN16C17N18(12)+βC14C15C20(14)+ βC6N5C10(11)	0	0
329	βC19C17N16(10)+βC17C19C28(42)+βC14C13O12(19)+ βC10O12O13(19)+βC6N5C10(16)	0	0
272	υC17C19(14)	0	0
248	τC17N6C17CN18(58)++τC15N16C17N16(11)	0	0
231	τC17C19S25C26(19)+τC17C19S25C26(14)+ τC15C4C13N18(14)+τC15N16C17C19(12)	0	0
221	opC6C1C10N5(63)	0	0
214	βN5C10O12(12)+βC14C15C20(14)+opC6C1C10N5(11)	0	0
178	τC13C4C15C20(48)	0	0
143	τH4C1N5C6(43)+τC1N5C10O12(18)	0	0
127	τH4C1N5C6(37)	0	0
96	βC17C17N16(13)+τC17C19S25C26(22)+ τC15N16C17C19(31)	0	0
94	τC1N5C10O12(41)+opC6C1C10N5(10)	0	0
70	τH4C1N5C10(70)	0	0
65	τC20H21C5N16(47)	0	0
58	τC20H21C5N16(43)	0	0
47	τC17N18C13O12(17)	0	0
30	τC13O12C10N5(40)+τC1N5C10O12(11)	0	0
21	τC13O12C10N5(50)	0	0

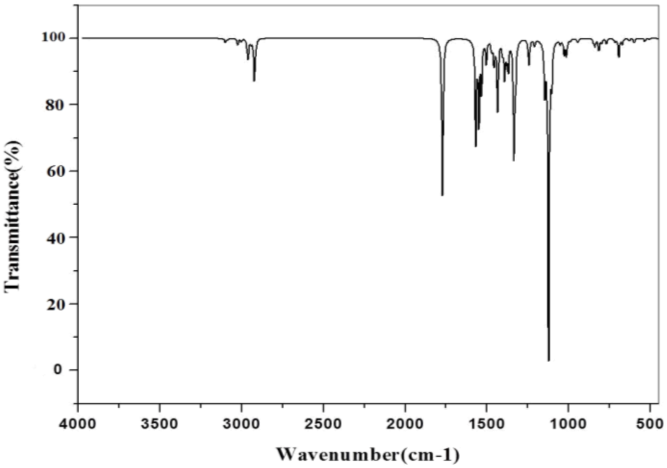

Fig. 5: Theoretical IR spectrum of MTPD

3.6.1. Pyrimidine ring vibration

Spectral region around 3100-3000 cm^{-1} [9] is the characteristic region of C-H vibrations in the heteroatomic structure. However, in tri-substituted pyrimidine with only one free ring hydrogen atom and the band is very weak which is observed at 3115 cm^{-1}.

Due to C-C and C-N stretching vibrations, strong absorption in pyrimidine was observed at 1600-1500 cm^{-1}. The fundamental bands due to the coupled C-C and C-N stretching vibrations of pyrimidine ring moiety in TMPD have been observed at 1568 cm^{-1}. Another significant mode to discuss is the ring breathing mode, a distinctive mode for cyclic molecules that is recognized as a powerful band at 964 cm^{-1}. In this regard, this assignment is consistent with different derivatives of pyrimidine. [10–14]. Usually an in plane deformation vibration is at higher than the out of plane vibration. In the present study, the bands observed at 620 cm^{-1} is attributed to ring in-plane bending modes. The ring out-of-plane bending mode is established at 508cm^{-1}.

3.6.2. Thiophene ring vibration

The CH stretching vibrations are expected to appear in the region 3100– 3000 cm^{-1}, with multiple weak bands.

The nature of substituents does not have much effect on the bands in this region [15, 16]. CH stretching vibrations of the molecule is observed at 3099 cm^{-1}. The CH in-plane bendings vibrations appear as sharp but weak to medium bands in the region 1100–1500 cm^{-1}region. The in plane bending mode is observed at 1027 cm^{-1}. These bands are not sensitive to the nature of substituents. The out of plane bending vibrations occur in the wavenumber range 800-1000 cm^{-1}. In TMPD, the out of plane bending mode is observed at 816 cm^{-1}. It is difficult to distinguish the C-S bands in thiophene. This can be clarified by the shorter bond duration and greater polarity of the thiophene C-S bond. [17]. The C-S stretching mode is predicted to occur at 691, 707 $cm^{-1}$and is observed at 743 and 771 cm^{-1} [18].

3.6.3. C=O vibrations

The stretching vibrations of C = O are generally found in the region 1850–1600 cm^{-1} region [19, 20]. In TMPD, the C=O vibrations is observed as very strong band at 1770 cm^{-1}.

3.6.4. Methyl group vibration

For the assignment of CH_3 group frequencies, basically nine fundamentals can be associated to CH_3 group, namely symmetric stretch; asymmetric stretch , in-plane bending, symmetric bending, in-plane rocking, out-of-plane rocking and twisting hydrogen bending modes. In addition to that, out-of-plane stretch, and, out-of-plane bending, modes of the CH_3 group would be expected. The asymmetric stretching wave number is assigned at 3024, 3001$cm^{-1}$and symmetric stretching established at 2942 cm^{-1}. We have observed the symmetrical methyl deformation mode at 1369 cm^{-1}. The methyl in-plane-bending and out-of-plane bending deformation modes are observed at 1446 and 1380cm^{-1} respectively. The in-plane and out-of-plane rocking modes of TMPD observed at 1032 and 1099cm^{-1}. The calculated frequency 65cm^{-1} is attributed to methyl twisting mode.

3.6.5. $(N\text{-}CH_3)_2$ vibration

The CH_3 groups next to the nitrogen atom in amines are somewhat shifted. The symmetric stretch at 2830-2770 cm^{-1} is lowered in wave number and intensified and to stands out among other aliphatic bonds. Due to the possibility of C-H...O hydrogen bonding (C_1-H_4...O_{12} and C_6-H_8...O_{11}) there is a blue shift affected in the region 2915-2966 cm^{-1}. C–N vibrations usually absorb in the region 1350–1160 cm^{-1} [21]. In TMPD these vibrations are observed at 1354cm^{-1},1153cm^{-1} in FTIR and the corresponding calculated values observed at 1169, 1147 cm^{-1} PED percentages of about 70%, 40%.

3.7. HOMO LUMO Analysis

Highest Molecular orbital and Lower Molecular Orbital are very important parameter in quantum chemistry and these orbitals are known as FMO. HOMO can be considered as the outermost orbital which contains electrons representing the ability to donate electron while LUMO can considered the innermost orbital containing few places representing the ability to accept the electrons. The lower value of HOMO-LUMO value indicates both the intra molecular charge transfer within the molecule and lower chemical reactivity. The lower energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) explains eventual charge transfer within the molecule.

From the energy gap value it is observed that MTPD has lower band energy. It explains an eventual charge transfer interaction within the molecule and high chemical reactivity. The small value of H-L gap gives more number of charge transitions to occur between the thiophene ring to carbamate group through pyrimidine ring that can be effectively used for insecticidal activity [22]. According to calculation, the energy band (ΔE) of the molecule to the first excited state is

HOMO energy: -5.96 eV
LUMO energy: -1.37 eV
HOMO-LUMO energy gap: 4.59 eV

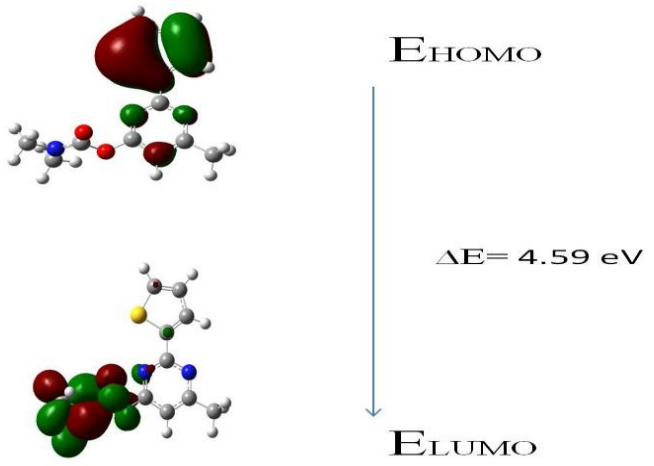

Fig. 6: HOMO and LUMO plot of MTPD

The HOMO LUMO energy gap explains the eventual charge transfer interaction taking place within the molecule. The frontier orbital (HOMO, LUMO) of MTPD is plotted in Fig.6.

By using HOMO and LUMO energy values for a molecule, electronegativity and chemical hardness can be calculated as follows:

Global reactivity descriptors are calculated using the energies of frontier molecular orbitals E_{LUMO} as $\chi = 1/2(E_{HOMO}+E_{LUMO})$, $\mu = -1/2\ (E_{HOMO}+E_{LUMO})$, $\eta = 1/2(E_{HOMO} - E_{LUMO})$, $S=1/2\eta$ and $\omega = \mu^2/2\eta$. The energies of frontier molecular orbitals (E_{LUMO}, E_{HOMO}) and global reactivity descriptors are listed in table 4. Energy gap of title molecule is calculated 4.590eV. A molecule with a small frontier orbital gap is generally associated with a high chemical reactivity and low kinetic stability. Larger the HOMO-LUMO energy gap, harder the molecule. Higher the value of the electrophilicity index better is the electrophilic character. The Zero point vibrational Energy, Dipole moment (D) and SCF Energy are calculated as 629.27kJ/mol, 2.822 and -1178.018 respectively.

Table 4: Global reactivity descriptors

Global reactivity descriptors	MTPD
Ionization potential (I)	5.960
Electron affinity (A)	1.370
Electro-negativity (χ)	3.665
Chemical potential (μ)	-3.665
Global hardness(η)	2.295
Global softness (S)	0.218
Electrophilicity index (ω)	2.926

3.8. Local reactivity descriptors

The Fukui function is a descriptor of local reactivity that shows the preferred regions where a chemical species will change its density when the number of electrons is modified. The Fukui function is a local reactivity descriptor that indicates the preferred areas where a chemical species changes its density when the number of electrons changes. The condensed or atomic Fukui functions on the jth atom site are given as per the following equations for an electrophilic $f_j^-(r)$, nucleophilic and free radical attack $f_j^+(r)$, on the reference molecule, respectively listed in table ().

$f_j^- = q_j(N) - q_j(N-1)$

$f_j^+ = q_j(N+1) - q_j(N)$

$f j^0 = 1/2\ [q_j(N+1) - q_j(N-1)]$

Morell et al. [23] proposed a dual descriptor ($\Delta f(r)$), defined as the difference between the nucleophilic and electrophilic Fukui function and is given by:

$$\Delta f(r) = [\ f^+(r) - f^-(r)]$$

If $\Delta f(r) > 0$, the site is favoured for a nucleophilic attack. If $\Delta f(r) < 0$, the site may be favoured for an electrophilic attack. Dual descriptors $\Delta f(r)$ gives a clear difference between nucleophilic and electrophilic attack at a particular region with their sign. It gives positive value for site where nucleophilic attack is possible and a negative value where electrophilic attack is possible.

Table 5: Condensed fukui function of FC molecule by UCA-FUKUI

Atoms	f^-	f^+	f^0	dual descriptor Δf
C1	-0.0108	-0.0046	0.0077	-0.006
H2	0.0234	0.0117	0.0175	-0.012
H3	0.0265	0.0167	0.0216	-0.0099
H4	0.0023	-0.0075	0.0026	0.0050
N5	0.0717	0.0104	0.041	-0.061
C6	-0.0105	-0.0047	0.0076	-0.006
H7	0.0217	0.0100	0.0158	-0.012
H8	0.0077	0.0027	0.0052	-0.005
H9	0.0264	0.0159	0.0211	-0.010
C10	-0.0099	-0.0073	0.0086	-0.003
O11	0.0453	0.0059	0.0256	-0.039
O12	0.0198	0.0119	0.0159	-0.008
C13	0.0048	0.0272	0.0160	0.0220
C14	0.1101	0.1235	0.1168	0.014
C15	0.0117	0.0337	0.0227	0.022
N16	0.0547	0.0382	0.0464	-0.017
C17	-0.017	0.1162	0.0496	0.099
N18	0.032	0.0446	0.0383	0.013
C19	0.121	0.0024	0.0617	-0.119
C20	-0.0126	-0.015	0.0138	0.002
H21	0.0196	0.0225	0.021	0.003
H22	0.0196	0.0229	0.0213	0.003
H23	0.0179	0.023	0.0205	0.005
C24	0.0264	0.0389	0.0327	0.013
S25	0.0667	0.1373	0.1020	0.0710
C26	0.1367	0.0981	0.1174	-0.039
C27	0.0433	0.0106	0.0270	-0.033
C28	0.0535	0.1065	0.0800	0.0530
H29	0.0293	0.0297	0.0295	0.0004
H30	0.0364	0.0383	0.0373	0.0020
H31	0.0325	0.0404	0.0365	0.0080

From the values reported in table 5 the nucleophillic attacking sites for the title compound are H_4, C_{13}, C_{14},

C_{15}, N_{18}, C_{20}, H_{21}, H_{22}, H_{23},C_{24}, S_{25}, C_{28}, H_{29}, H_{30}, H_{31}(positive value i.e. Δf (r)>0) and the electrophillic attacking sites are C_1, H_2, H_3, N_5, C_6, H_7, H_8, H_9, C_{10}, O_{11} ,O_{12}, N_{16}, C_{19}, C_{26}, C_{27}.(negative value i.e. Δf (r) < 0).

3.9. Molecular docking

The Docking study of MTPD was performed with two different proteins. Docking is performed for the different receptors (PDB ID-1JI6, 1DLC) and shown in table 6; autodock binding energies, binding residues and bond energy were obtained. Among them the inhibition of MTPD with 1DLC target protein has the lowest free energy -6.20 kcal/mol. Thus this possesses the highest potential binding affinity into the binding site of the molecule. Out of hundred docking runs converged on a top-ranked cluster (1DLC) as shown in Fig. 7, the best docked conformations are those found to have the lowest binding energy and the greatest number of members in the cluster, indicating good convergence. Carbamate group present in the active site of the target ASN 618 is attached to MTPD by C-H...O hydrogen bonding indicated by dashed lines. From the above observations it is identified that the binding of protein 1DLC with MTPD is more effective and shows more insecticidal activity. The lowest value of hydrogen bonding interaction leads to the insecticidal activity of the compound (1.98 A°).

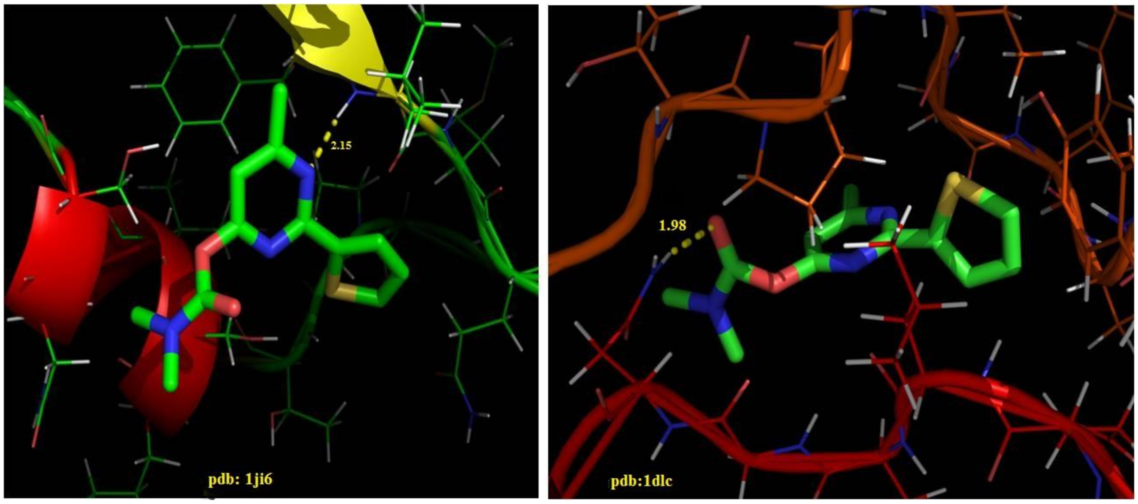

Fig. 7: Autodocked target proteins for MTPD

Table 6: Molecular docking results of MTPD with different protein targets

Protein (PDB:ID)	Binding Residue	Bond energy	H-Bond distance	Incubation constant (µm)	Binding affinity (kcal/mol)
1JI6	LEU 483	-5.29	2.15	321.69	-4.4
1DLC	ASN 618	-7.09	1.98	26.68	-6.2

4. CONCLUSION

In the present work, the optimized geometric parameters (bond lengths, bond angles and dihedral angles) were theoretically determined. The increase in wavenumber from the expected value leads to the blue shift and exhibits the possibility of intramolecular hydrogen bonding. Molecular electrostatic potential shows the carbonyl group having negative potential or donor nature. This gives the evidence for the possibility of C-H...O hydrogen bonding.

Fukui function analysis reveals that C_{13} in the pyrimidine ring shows high neucleophilic character. The lowering of HOMO-LUMO band gap supports insecticidal activity of title compound. The lowest binding energy of protein 1DLC with MTPD is more effective and shows more insecticidal activity. Thus from above studies, it can be concluded that TMPD is a good insecticidal agent and further work can be responsible for biological activity.

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Structural Analysis and Hydrogen Bonding Interactions on Pirimor and Water Mixture by Density Functional Theory

L.S. Anju, V.K. Suma, D. Aruldhas

Abstract-The geometrical parameters, different inter and intra molecular interactions of pirimor (PRM) and its water complex (PRM.$3H_2O$) have been performed using density functional theory (DFT) method with 6-31G(d) basis set. Charge analysis and Hirshfeld analysis reveals the charge transfer within the molecule. HOMO-LUMO energy gap, local softness and electrophlicity indices for selected atomic sites of the PRM and its water-complex were determined.

Key Words- Bioactivity, Hirshfeld analysis, Pirimor, Water mixture.

◆

1. INTRODUCTION

Pyrimidine ring and its derivatives are known for their biological and pharmaceutical importance. Their properties are determined by hydrogen bonding and π – bonding systems. They belong to the family of nucleic acid. Pyrimidine and its derivatives have immense importance as antibiotics, and as crucial parts of many vitamins, and coenzymes. Pyrimidine-derived biomolecules have received much attention from spectroscopists, drug, clinical, and industrial researchers because of their therapeutic importance [1]. The present work gives a detailed structural analysis on Pirimor (PRM). It is used specifically to target insects and is applied as a foliar spray to infested plant material. The mode of action of Pirimor is that it inhibits acetylcholinesterase (AChE), thereby disrupting the neutral pathways of the insect. Pirimor is also found in formulation with many other insecticides. In this study, the structures of PRM.$3H_2O$ complex formed by the hydrogen bonding interaction between PRM and three water molecules were studied. The energetic, vibrational frequencies of H-bonds were investigated. The natural bond orbital (NBO) analysis has been carried out to interpret hydrogen bonding, hyperconjugative interaction and intramolecular charge transfer (ICT). The calculated value of HOMO-LUMO energy gap is used to interpret the biological activity of the molecule [2]. Hydrogen bonding and hyperconjucative interactions have received much attention from both experimental and theoretical perspectives as they can determine the structures and biological activity of molecules.

2. COMPUTATIONAL DETAILS

The structural analysis and spectroscopic studies of PRM and PRM.$3H_2O$ were performed using Beck3-Lee-Yang-Parr (B3LYP) with 6-31G(d) basis set using GAUSSIAN 09 program package [3] without any constraint on the geometry. The optimized geometry corresponding to the minimum potential surface has been obtained by solving self-consistent field equation iteratively. The natural charges analysis interpret Atomic charges, donor-acceptor NBO hyperconjugative interactions, dipole moment, HOMO-LUMO energy gap were also computed [4]. Hirshfeld surface analysis of PRM has been constructed from CIF files in order to identify the interactions using crystal explorer 3.1[5].Gaussview.5.0.8 visualization program has been utilized to the shape of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

3. RESULT AND DISCUSSION

3.1 OPTIMIZED GEOMETRY

The optimized geometrical parameters of Pirimor (PRM) and its water complex (PRM.$3H_2O$) were calculated by B3LYP with 6-31G(d) basis set. The results of the calculated geometrical parameters (bond length, bond angle and dihedral angle) are compared with the experimental values and are

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listed in table 1. The optimized molecular structures with atom numbering scheme adopted in the computation is shown in fig.1

TABLE 1: STRUCTURAL PARAMETERS OF HYDROGEN BONDS IN PRM.3H_2O COMPLEX

	H-bond	$R_{X\text{-}H}$	$\Delta R_{X\text{-}H}$	$R_{H...Y}$	$\delta R_{H…Y}$	<X-H…Y
PRM.3H2O	C1-H3…O42	1.089	-0.01	2.502	0.398	156.4
	C6-H8…O11	1.089	0	2.341	0.559	102.6
	C28-H31…N16	1.088	0	2.311	0.042	102.8
	C32-H33…N18	1.097	0.009	2.858	0.808	70.5
	C28-H30…N19	1.096	0	2.092	0.781	40.9
	C28-H29…N19	1.100	0.002	2.119	0.796	37.7
	C32-H34…N19	1.092	-0.009	2.104	0.821	40.7
	O36-H38…N5	0.969	0	4.032	0.743	81.5
	O39-H41…C12	0.971	0.002	2.063	0.657	165.7
	C24-H25…O39	1.098	0.006	2.545	0.355	53.2
	C6-H7…O42	1.094	-0.005	2.516	0.384	152.7
PRM	C1-H3	1.099				
	C6-H7	1.099				
	C6-H8	1.089				
	C28-H31	1.088				
	C32-H33	1.088				
	C28-H29	1.098				
	C32-H34	1.101				
	C24-H25	1.092				
H2O	O-H	0.969				

In PRM , the bond length of C_6-H_8 in methyl group 2 decreases while comparing with other methyl groups , which indicates the presence of C_6-H_8...O_{11} hydrogen bonding. Similarly, C_1-H_4 bond length in methyl group 1 is decreased due to the presence of C_1-H_4...O_{12} hydrogen bonding . The C-N bond length N_{16}-C_{17} (1.350) is increased due to the presence of weak intermolecular hydrogen bonding C_{28}-H_{31}...N_{16}. The existence of methyl group 5 and 6 provide the additional negative charge to the amino nitrogen atom resulting the contraction of bond length C_{17}-N_{19}. Comparing with other three compounds the C_{15}-C_{20} bond length increases due to steric hindrance of H_{23}…H_{26} (2.518). The bond length of C_{14}-C_{13} increases when compared with other three compounds shows the substitution of methyl group 4. The dihedral angle C_{10}-O_{12}-C_{13}-C_{14} shows the crabamate group is non-planar with the pyrimidine ring . N_{18}-C_{17}-N_{19}-C_{32} and N_{16}-C_{17}-N_{19}-C_{28} (-1.7^0 and 6.8^0) showing that the dimethyl amino group in nonplanar with the pyrimidine ring. Thus the compound pyrimidine is nonplanar in nature.

In PRM.3H_2O the C_1-H_3 bond length increased ($0.004A^0$) increased due to C_1-H_2…O_{42} hydrogen bonding interaction. In PRM.3H_2O complex C_6-H_7 bond length is increased when compared with PRM due to the influence of C_7-H_8…O_{42}^{w} hydrogen bonding interaction. Due to C_{32}-H_{34}…N_{19}^{w} hydrogen bonding interaction the C_{32}-C_{34} bond length is decreased in PRM.3H_2O complex compared with PRM.

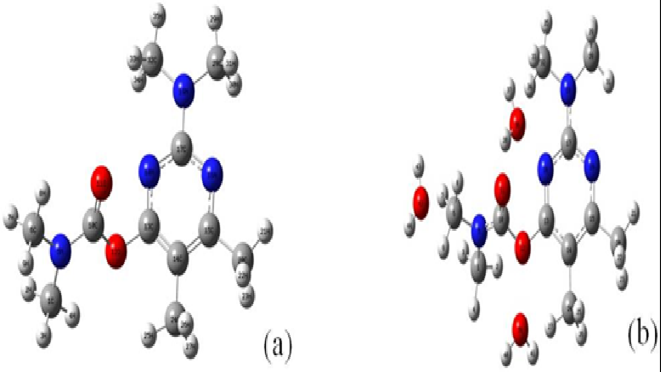

Fig1. Optimized Molecular Structure of (a)PRM and (b) PRM.3H_2O

3.2 VIBRATIONAL FREQUENCIES

The harmonic vibrational wave numbers and their shifts calculated at the B3LYP/6-31G(d) level listed in table 2. The red shift in the X-H stretching vibrational frequency has been widely used important intermolecular hydrogen bonding interaction. A shift to lower frequency relative to reference state is called a red shift. Contrarily, a shift to higher frequency is called a blue shift [6]. The larger shift value indicates the stronger H-bond interactions. The shifting of X-H stretching vibrational modes mix with other vibrational modes.

Table 2: THE VIBRATIONAL WAVE NUMBER OF PRM and PRM.3H_2O COMPLEX CORRESPONDING HYDROGEN BONDS

Compound	H-bond	υX-H	Δυ(X-H)
PRM.3H2O	C1-H3…O42^W	$3063_{(asy)}$	10
		$2939_{(sy)}$	29
	C6-H8…O11	$3073_{(asy)}$	2
		$2924_{(sy)}$	6
	C32-H33…N18	$3027_{(asy)}$	-44
		$2930_{(sy)}$	29
	C28-H29…N19	$3072_{(asy)}$	-4
		$2907_{(sy)}$	-3
	O36-H37^W…N18	$3662_{(asy)}$	-39
		$3526_{(sy)}$	-60
	O39-H41^W…C12	$3678_{(asy)}$	-23
		$3571_{(sy)}$	-15
	C24-H25…O39^W	$3052_{(asy)}$	17
		2923	4
PRM	C1-H3	$3053_{(asy)}$	
		$2910_{(sy)}$	
	C6-H8	$3071_{(asy)}$	
		$2918_{(sy)}$	
	C32-H33	$3071_{(asy)}$	
		$2901_{(sy)}$	
	C28-H29	$3076_{(asy)}$	
		$2910_{(sy)}$	
	C24-H25	$3035_{(asy)}$	
		$2919_{(sy)}$	
H2O	OH	$3701_{(asy)}$	
		$3586_{(sy)}$	

The intramolecular C_8-H_{15}…N_{18} hydrogen bonding interaction in PRM leads to the mixture of C-H stretching with pyrimidine ring stretching modes. In PRM.3H_2O complex the $\Delta\upsilon_{X\text{-}H}$ value of intermolecular hydrogen bonding interaction red shifted about 44 cm^{-1} due to the strong O_{36}-H_{37}…N^{18} intermolecular hydrogen bonding interaction. The C_1-H_3…O_{11} hydrogen bonding interaction have blue shifted about 10 cm^{-1}. In other red shifted hydrogen bonding interaction are C_{28}-H_{29}…N_{19}, O_{36}-H_{37}…N_{18} andO_{39}-H_{41}…C_{12} was supported by NBO and structural analysis.

3.3 NATURAL BOND ANALYSIS

The natural bond orbitals (NBO) calculations were performed using NBO 3.1 program as implemented in the Gaussian 09 package at the B3LYP 631-G(d) level in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the intramolecular delocalization or hyper conjugation.

The second-order Fock-matrix was carried out to evaluate the donor-acceptor interactions in the NBO basis . The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j) the stabilization energy $E^{(2)}$ associated with the delocalization $i \rightarrow j$ is determined as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F_{ij}^2}{(E_i - E_j)}$$

where, q_i - donor orbital occupancy

E_i, E_j - diagonal elements

F_{ij} - the off diagonal NBO Fock matrix element.

NBO analysis provides the most accurate possible 'natural Lewis structure' picture of 'j' because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interactions of both filled and virtual orbital spaces that could enhance the analysis of intra and inter molecular interactions. The electron density of conjugated single as well as double bond of pyrimidine ring about 1.976 - 1.987e clearly demonstrate strong delocalization for Pirimor. The intermolecular interaction are formed by the orbital overlap between σ(N-C)→σ*(O-C), σ(C-C)→σ*(C-C)σ(C-N)→σ*(C-N) and σ(C-N)→σ*(N-C) bond orbital which orbital which results intramolecular charge transfer (ICT) causing stabilization of the system as seen from the table 3. The stabilization energy contributions from the σ(C_{13}-C_{14})→σ*(C_{10}-O_{12}) interaction is 8.24kJ/mol. The hydrogen bonding interaction between the oxygen cone pair and (C-H) antibonding.ie, σ (O_{11})→σ*(C_6-H_8) increases the C_6-H_8 bond.

TABLE 3: SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS CORRESPONDING TO THE INTRA MOLECULAR HYDROGEN BONDS AND HYPERCONJUGATION IN PRM AND PRM.3H_2O COMPLEX INTRACTION ENERGIES (E2) IN KJ MOL^{-1} WITH HYBRID ORBITALS AND ELECTRON DENSITY(E.D)

Complex	H-bond	RX-H	ΔRX-H	RH...Y	δRH…Y
PRM. 3H2O	C1-H3…O42	1.089	-0.01	2.502	980
	C6-H8…O11	1.089	0	2.341	0.559
	C28-H31…N16	1.088	0	2.311	0.042
	C32-H33…N18	1.097	0.009	2.858	0.808
	C28-H30…N19	1.096	0	2.092	0.781
	C28-H29…N19	1.1	0.002	2.119	0.796
	C32-H34…N19	1.092	-0.009	2.104	0.821
	O36-H38…N5	0.969	0	4.032	0.743
	O39-H41…C12	0.971	0.002	2.063	0.657
	C24-H25…O39	1.098	0.006	2.545	0.355
	C6-H7…O42	1.094	-0.005	2.516	0.384
PRM	C1-H3	1.099			
	C6-H7	1.099			
	C6-H8	1.089			
	C28-H31	1.088			
	C32-H33	1.088			
	C28-H29	1.098			
	C32-H34	1.101			
	C24-H25	1.092			
H2O	O-H	0.969			

The shortening of C_6-H_8 is due to C-H…O hydrogen bonding having stabilization energy 4.184 KJ/mol. The existence of weak intermolecular C-H…O hydrogen bond due to interaction between lone pairs of σ (O_{12}) with (C_1-H_4) (26.359 kJ/mol) have confirmed. The corresponding intra-molecular H…O distance (H_8….O_{11})/ (H_4….O_{12}) is found to be 2.309 and 2.235Å. These distances are significantly shorten than that of Vander waals seperation between the oxygen atom and the hydrogen atom (2.720Å) indicating the existence of C-H...O interaction [7]. The interaction C-H...N hydrogen bonding between cone pairs (N_{16}) to antibonding σ*(C_{28}-H_{31}) (8.242 kJ/mol) have been confirmed by the results of NBO analysis.

3.4 CHARGE ANALYSIS

All hydrogen atoms have positive charge. Hydrogen in methyl group is more positive than hydrogen in ring. The largest positive charge occurs at H_{33} in PRM, which are involved in C_{32}-H_{33}…N_{18} hydrogen bonding with atomic charges of 0.263e.

TABLE 4: CHARGE ANALYSIS TABLE

Atom	Natural Charge	
	PRM	PRM.3H_2O
C1	-0.469	-0.464
H2	0.222	0.228
H3	0.219	0.229
H4	0.257	0.24
N5	-0.488	-0.489
C6	-0.469	-0.482
H7	0.22	0.222
H8	0.263	0.259
H9	0.218	0.231
C10	0.948	0.935
O11	-0.631	-0.628
O12	-0.578	-0.585
C13	0.587	0.585
C14	-0.178	-0.176
C15	0.284	0.288
N16	-0.555	-0.551
C17	0.621	0.623
N18	-0.559	-0.573
N19	-0.436	-0.434
C20	-0.706	-0.707
H21	0.255	0.256
H22	0.245	0.246
H23	0.242	0.245
C24	-0.691	-0.679
H25	0.253	0.229
H26	0.24	0.243
H27	0.237	0.251
C28	-0.469	-0.469
H29	0.218	0.22
H30	0.213	0.214

H31	0.262	0.263
C32	-0.469	-0.459
H33	0.264	0.245
H34	0.212	0.216
H35	0.22	0.226

In PRM.3H_2O largest positive charge occurs at H_{31} due to C_{28}-H_{31}…N_{16} hydrogen bonding interaction. Charge of N_{18} is decreased by the influence of C_{25}-H_{26}…N_{18} hyperconjugative interaction. It is worthy to mention that C_{10}, C_{13}, C_{17} and C_{15} atoms exhibit positive charge while other carbon atoms exhibit negative charge. The more negative values on C_{20} and C_{24} of CH_3 group leads to a redistribution of electron density and also influenced by H_{23}…H_{27} steric repulsion. The negative charges located at atoms O_{11} and O_{12} will interact with C_{10} and C_{13} atoms due to inductive effect the bond distance N_5-C_{10} (1.364A˚) increases. The presence of two large electronegative oxygn atom and one nitrogen atom impose very high charge on carbon atom (C_{10}) in the carbamate group.

3.5 HIRSHFELD SURFACE ANALYSIS

The Hirshfeld surface analysis, a unique new method of visualizing the intra molecular interaction, was performed in order to explore the properties of all inter contacts within the crystal structure of PRM. Additionally corresponding two-dimensional (2-D) fingerprint plots [8] provide rapid quantitative summary of them (the percentage of each contact), which is important for understanding of the contribution of intra molecular interactions to the crystal packing. This plot provides information not only about close contacts, but also about more distant contacts and areas where the interactions are the weakest. Hirshfeld surface display all of the inter contacts within the crystal at once and are therefore ideal for analyzing the crystal packing. The molecular Hirshfeld surface were constructed on both d_e (external distance that is the distance between the Hirshfeld Surface and the nearest atom of an adjacent molecule.), d_i (internal distance that is the distance from the nearest nucleus internal to the calculated Hirshfeld surface and the vanderWaals radii of the atom, enabling identification based on the electron distribution calculated as the sum of spherical atom electron densities [9].The Hirshfeld surfaces of PRM crystal structure have been mapped over. The d_e 1.000 to 2.650 A^0, the d_i is 0.961 to 2.650 A^0, d_{norm} is -0.271 to 1.226 A^0 for PRM. Fig represents the $d_{norm,}$ d_i, d_e, shape index and curvedness of PRM. The shape index and curvedness surfaces have been shown to give the information about each donor-acceptor pair and to measure how much effectively divides the surfaces into set of patches respectively.is shown in fig 2. Fingerprint plots give an idea about interactions with in the molecule.

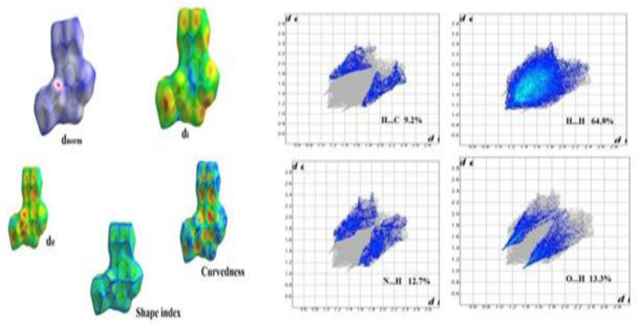

Fig2: Hirshfeld surface analysis and fingerprint plots

3.6 HOMO LUMO ANALYSIS

According to the frontier molecular orbital theory (FMO) of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species [10]. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [11].

The molecule interacts with other species; hence, they are called the Frontier molecular orbitals (FMO's). HOMO, which can be thought the outermost orbital containing electrons, tends to act as electron donor. On the other hand, LUMO can be thought the innermost orbital containing free places to accept electrons. To explain several types of reactions and for predicting the most reactive position in conjugated systems, molecular orbital and their properties are used. A molecule having a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [12]

The plots of MO’s (HOMO and LUMO) are shown in fig.3 and its energy values are given in table 5. All the HOMO and LUMO have nodes. The nodes in each HOMO and LUMO are placed symmetrically. The positive phase is red and the negative is green. In the title compound, the HOMO is delocalized over the carbamate group. By contrast, the LUMO is located over the dimethyl amino pyrimidine.

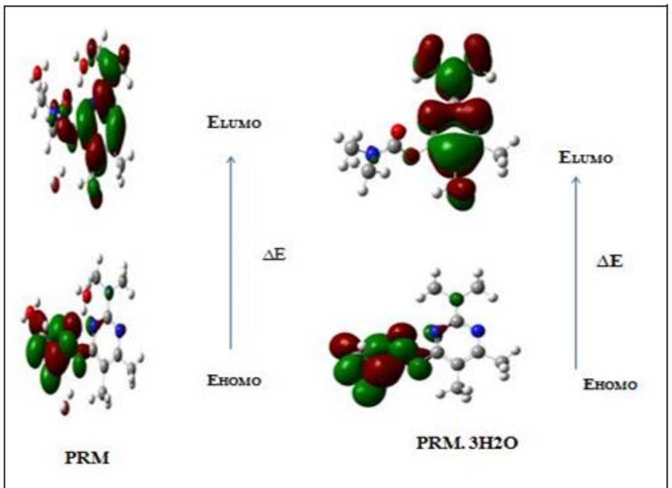

Fig3: HOMO LUMO Plots of PRM and PRM.H_2O

Global Reactivity Descriptors

By using HOMO and LUMO energy values of a molecule, the global chemical reactivity descriptor of molecules such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined [13]. The HOMO and LUMO energies, the energy gap (E), ionization potential (I), electron affinity (A), absolute electronegativity (χ) absolute hardness (η),and softness of title compound and its related compounds computed by DFT/B3LYP/6-31G(d) level.

The chemical potential provide a global reactivity index and related to charge transfer from a system of higher chemical potential to lower chemical potential. The reactivity index is the measure of stabilization in energy when the system acquires an additional electronic charge (N). A molecule or atom that has a positive electron affinity is often called an electron acceptor and may undergo charge transfer reactions. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital. The overall energy balance (ΔE), i.e., energy gained or lost, in an electron donor acceptor transfer is determined by the difference between the acceptor's electron affinity (EA) and the ionization potential (IP) as ΔE=EA-IP. Electronegativity is a chemical property that describes the ability of an atom or a functional group to attract electrons or electron density towards itself. Parr et al. have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor [14]. The usefulness of this new reactivity quantity has been recently demonstrated understanding the toxicity of various pollutants in terms of their reactivity and site selectivity. The electrophilicity index is positive, definite quantity and direction of the charge transfer is fully determined by the chemical potential (V) of the molecule. Because an electrophile is a chemical species, it has an electron accepting capability from the environment and its energy must decrease upon accepting electronic charge, therefore, its electronic chemical potential must be negative. Using Koopman’s theorem for closed shell compounds the electronegativity and chemical hardness can be calculated as follows:

$$\text{Electronegativity}\ ,\chi = -\frac{1}{2}(E_{LUMO} + E_{HOMO})$$

$$\text{Chemical reactivity,}\ \boldsymbol{\eta} = \frac{1}{2}(E_{LUMO} - E_{HOMO})$$

Softness, $\sigma = 1/\eta$

Electrophilicity index, $\omega = \mu^2 / 2\eta$

where I and A are Ionisation Potential and Electron Affinity. Large HOMO-LUMO gap means a hard molecule and small HOMO-LUMO gap means a soft molecule. One can also relate the stability of the molecule to hardness, which means that the molecule with least HOMO-LUMO gap means it is more reactive.

The usefulness of this new reactivity quantitivity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [15]. The calculated parameters are shown in Table.5. Global softness 0.271 shows more chemical active nature of PRM, and electrophilicity index 11.744, which shows more bio active nature of PRM.3H_2O complex while comparing with PRM while comparing with PRM.3H_2O.

TABLE 5: CALCULATED GLOBAL PARAMETERS

	PRM	PRM.3H_2O
Ionization Potential (I)	8.453	8.42
Electron Affinity (A)	4.705	4.736
Electro negativity (χ)	-6.579	-6.578
Chemical potential (η)	6.579	6.578
Hardness	1.874	1.842
Softness	0.267	0.271
electrophilicity index (ω)	11.547	11.744

CONCLUSION

The present study has been performed on Pirimor its water complex (PRM.3H_2O) to investigate the intermolecular hydrogen bonding interaction to show the insecticidal activity. The theoretically predicted optimized geometry of Pirimor and its related compounds by DFT method suggests the possibility of intermolecular C-H...O and C-H...N hydrogen bonding. The stretching vibration of dimethyl amino group shows a blue shift due to the C-H...N hydrogen bonding. The lowering of Homo-Lumo energy gap of Pirimor while compairing with PRM.3H_2O indicate the charge transfer. The carbon atom in carbamate group (C_{10}) shows more positive charge which shows charge transfer from carbamate to dimethyl amino pyrimidine group. NBO analysis confirms the possibility of C-H...O and C-H...N hydrogen bonding. The experimental and theoretical vibarational, NBO, HOMO-LUMO energy gap, global softness and electrophilicity index shows more insecticidal activity of PRM.3H2O in comparison with Pirimor compound.

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Poyikayil Yohannan and His Attempts in Organizing the Non Caste Christians of Kerala

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Abstract:

Due to the existence of caste system the non caste people were marginalized in the society. The caste system is characterized by a hierarchical arrangement which implies that, there are some castes, which are considered superior to the others and enjoying privileges. With the advent of Christianity in Kerala, large number of non caste people embraced Christianity because it was a casteless religion. Non castes Christians are Scheduled Caste people converted to Christianity and are excluded from the Scheduled Caste list by the Presidential order of 1950. But conversion to Christianity does not change the caste identities of the non caste people. Separate churches were constructed for the non caste people because the Syrian Christians of Kerala considered them as untouchables. The non caste Christians are economically impoverished, socially out caste, politically powerless and educationally backward. Lack of integration between the Syrian Christians and the converted Christians are revealed both at the social as well as at the denominational levels. This discriminative attitude of upper caste Christians hurts the minds of the non caste Christians. Poyikayil Yohannan, a non caste Christian began to criticize the caste discrimination within the church. The movement started by Poyikayil Yohannan came to be known as Prathyaksha Raksha Daiva Sabha (PRDS). According to him Bible was meant only for the Jews and not for Harijans. He was also against the superiority of upper class in church and the introduction of separate churches for the depressed classes. His dynamic and magnetic personality, his deep and divine speech and his timely composed a song, his genuine and affectionate generosity etc., were the most important causes for the rapid spread of his faith and his teachings, throughout the length and breadth of Kerala. The spiritual and material dimensions of life of the non caste Christians was an important aspect in which PRDS gave more emphasize.

Key Words: Non caste Christians, Prathyaksha Raksha Daiva Sabha, identity, conversion, Syrian Christian, equality, Paraya.

The substantial social groups generally termed as Dalits or Non caste were subjected to different types of discrimination due to caste system. Under colonialism these marginalized groups began to achieve the social transformation and tried to crossroad the disabilities imposed upon them. So the Non caste people have been engaged in struggles and protest movements. In Kerala this spirit first manifested itself more in religious and social ideas leading to an unprecedented awakening in the socio – religious life of the community. There was a social and political awakening among the Non caste converts as well as their Hindu counterparts. The Non caste Christians began to protest against the caste discrimination within and outside the church with the assistance of social space created by colonial modernity. Protest movements were the authentic vehicles through which the backward caste in Kerala attempted social mobility in the pre independent period (Prabash, 2000, p. 43). Their protest ideology involves resistance, opposition, confrontation and conflict with the dominant group's inorder to achieve their desired goal of social equality, social dignity and the organized social identity. The protest movements of Dalits asserted the demand for self respect social dignity and equality and gave them direction in liberation struggles in their respective societies (Singh, 1999, p. 149).

The non castes Christians are people converted to Christianity and are excluded from the Scheduled Cast list by the Presidential order of 1950. They are socially and economically backward, educationally and occupationally low, politically and religiously powerless. Above all they are assigned the lowest nature in society. But their kith and kin, who belonging to Scheduled Castes are entitled to enjoy more benefits to improve their socio economic conditions. The non caste Christians or Dalit Christians in Kerala are also known as Puthukristhianikal or Neo Christians.

The mid nineteenth century witnessed the beginning of protestant missionary work among the non castes and in the subsequent decades, thousands of them joined missionary church. But in the church also they had to experience the bitterness of caste discrimination. One of the peculiarities of the protest movements of the Non caste Christians was it originated within the frame work of missionary Christianity but moved beyond the limits of missionary project and eventually offered a critique of it (Sanal, 2005, p. 155). Apart from the socio economic aspirations the non caste people emblazed Christianity as part of a religious quest. In Kerala one of the realms of conflict between non caste and caste Hindus in this period was religion. In this context, new movements originated in Kerala inorder to organize the people. The emergence of social reformers accelerated the process of social change and created a most conducive climate for the protest struggles. Pratyaksha Raksha Daiva Sabha (PRDS) movements started by Poyikayil Yohannan worked for the liberation of the non caste Christians.

The low caste people in pre independent Kerala as elsewhere in India were a highly differentiated lot. According to Dick Koiman for the non caste people conversion itself was the product of a search for identity outside Hinduisam (Koiman, 1989, p. 44). Kumara Guru popularly known as Poyikayil Yohannan started a movement in 1910 came to be known as PRDS that tried to erase the previous caste identities and tried to create a new one. He was born on 17th February 1879 in a poor illiterate and untouchable Paraya family called Manakkal Poyikayil in Eraviperur, a village in the central Travancore in the Pathanamthitta district of modern Kerala, as the son of Kandan and Lechi (Joseph, 1994, p. 46). Since the members of the slave community were prohibited from selecting good and fair names for their children, his parents named him Kumaran. His parents were laborers attached to a Syrian Christian family.

In the religious matter too, the non caste people were forbidden to select a religion as they wish to join instead they had to accept the religion of their masters. Here Kumaran's masters were the followers of Marthomite Christians and became the member of Marthoma church. His new baptism renamed Kumaran as Yohannan as a part of the forcible conversion to Christianity (Chentharasserry, 1983, pp. 14-15). As a child he never bothered to observe caste rules and mingled freely with children of other untouchables. As a boy Yohannan had learnt to read and write and when they went to herd cattle he used to read from the Bible for his friends. This early interaction with the written word and the word of the Lord influenced him greatly (Vijayan , 1978, pp. 10-11).

Yohannan led an ordinary life of an agricultural laborer. As he grew up he began to attend the conventions of the missionaries. He was influenced by the Christian message and became a devoted follower of the Marthoma Church. He was however highly critical of its discrimination against non caste Christians arguing on theological grounds that after baptism, followers become one in Christ and thus there was no justification for referring to them as Pulaya / Paraya Christian (Sanal, 2005, p. 156). When he was 18 years old an event occurred in his life. The place at Pullad in Pularikkadu when a Christian from backward community died and the dead body was buried in the church cemetery. But due to the opposition of the upper caste Christians they dug the grave and took the dead body outside and buried in some other place. This incident which was an unexpected one forced him to join the Bretheren Mission (Joseph, 1994, p. 18). When he was in Bretheren mission another incident took place. There he planned marriage between Mariyamma of Syrian Christian to Daniel, who belonged to the non caste Christian community. But it proved to be a failure one. Then he joined the Verpadu Mission (ibid., p. 22).

The Syrian Christians wanted to continue their domination within the church over the non caste Christians who were formerly their slaves. Ultimately Yohannan decided to gave up the different Christian denominations because of the existence of caste system in the churches and he became a independent preacher. He has attracted a number of followers. The non caste people followed him wherever he went and they made up their mind to become his followers, after attending special functions. He put an end to their sin and pardoned them mentally. They had changed and they had become his followers (Rejikumar, 2005, pp. 29-30). He thus feels the necessary to start from the very beginning itself from the imagining of a historical point to the construction of a new self. Yohannan's emphasis on history and the proclamation of divine love for the oppressed brought together many people belonging to the oppressed castes in Central Travancore under his leadership.

His dynamic and magnetic personality, his deep and divine speech and his timely composed a song, his genuine and affectionate generosity etc., were the most important causes for the rapid spread of his faith and his teachings, throughout the length and breadth of Kerala (Rejikumar, 2005, p. 35). Among his followers Yohannan was evolving as a divine power to the community of his followers he was the one who had come with divine revelation to the untouchables of Travancore and his message were touched in subversive argument. Contrary to the usual practice of celebrating the Bible, Yohannan initiating a critique of the Bible even when he was working with the missionaries. According to him Bible was meant only for the Jews and not for Harijans. He was also against the superiority of upper class in church and the introduction of separate churches for the depressed classes.

Yohannan began to criticize the caste differences among the Christians, through his speeches and tried together the untouchables into one group for their emancipation. He observed, In the New Testaments are certain epistles by St. Paul and others. To whom did St. Paul write these epistles to the Romans, Corinthians etc... There was not one written to the Pulayas of Travancore Therefore there is no revelation in these Epistles for you but only for the Romans Corinthians etc... The revelation to you Pulayas of Travancore is through me (Sanal, 2005, p. 159). The clam of personal revelation immediately raised Yohannan's status. In challenging the power of the church hierarchy on the basis of esoteric knowledge on social and spiritual questions, he not only put himself at odds with the missionaries, but asserted a claim to precedence over them (Sanal., p. 161).

Yohannan decided to establish an independent religion for the non caste people, who combined the ideas of salvation and spiritual progress along with notions of social and economic development. In 1910, PRDS was formed by Poyikayil Yohannan who mobilized the Parayas Pulayas and similar Dalit communities to establish an independent religion of their own. His use of prophetic techniques was powerful was enough to earn him new adherents who were assured of salvation. A little more understanding of the nature of his congregation and meeting would provide us more insights into the character of the movement. It was a sort of esoteric system which is unfolded midnight gathering at lonely jungles (Sanal., p. 158). The spiritual and material dimension of life of the Dalit Christians was an important aspect in which PRDS gave more emphasize. Yohannan imaginatively created a by brad religion by combining several elements of Christian discourses and practices with elements down from the Dalit life world (Sanal, p. 182). The PRDS movement tried to engage with problems of caste hierarchy and exploitation and strove to achieve social equality along with material and spiritual progress.

Those people who believed in Yohannan had expected a transformation of their lives and social equality. He won large number of followers and they lovably called him Appachan (Chentharasserry, 1983, p. 60). Before the organization of the formal structure of the PRDS there did not exist any institutional space to bind the people together and it remained mostly as an amorphous gatherings or conventions of people. The formal institutional structure becomes necessary to contest the Christian denominations and to acquire their social demands. It is in this context that the institutional structure of the PRDS movement was formed (Baby and Baburajan, 1994, pp. 132-46).

Initially people were approached on the basis of Kinship ties and wherever they went Yohannan discussed with the people his theme subjects and won their hearts. These deliberations of Yohannan were an irritant to the upper caste particularly Syrian Christians and they were waiting for an opportunity to finish him. As a result of the opposition it became difficult for Yohannan and his followers to propagate the PRDS message. In several places the opposition led to open confrontation and are treated in the history of experience in their quest for liberation. While Yohannan gave a public speech at Mundakkayam in 1908, he was attacked by the Syrian Christians. This struggle came to be known in history as Mundakkayam struggle (Chentharasserry, 1983, pp. 28-32). In 1908, there was a open confrontation at Vakathanam and Vellinadu, in 1912 at Kuzhikuchi and in 1913 at Mangalam. All these were planned by the locally dominant people inorder to suppress the movement. For the next couple of decades Yohannan and his associates concentrated more on the organizational details of the new congregation and nurturing it (Vijayan Kangazha, 1978, pp. 17-18). In addition to the material aspect the PRDS movement gave priority to the spiritual realm also. Sanal Mohan observes, its great achievement was to coalesce elements of modernity with certain notions of the traditional, shared life would of Dalit by which means the Dalit experience of slavery, their 'Adi Dravida' past and the religious notion of prathyakshata (revelation) were made part of modernity (Sanal, 2005, p. 166).

PRDS movement also gave emphasize to education. The pastors were well versed in the Bible and have a critical reading. These Biblical interpretations were the source of knowledge that shaped the worldview of the non caste people. Considering the various activities in the field of social life Yohannan was twice nominated in the Sreemulam poplar Assembly in the year 1921 and 1931. In the assembly he spoke for all marginalized groups irrespective of their caste, reed and community. His speeches in the assembly were convincing and authoritative (Vijayan, 1978, pp. 24-29).

Another peculiarity of the PRDS movement was the presence of non caste women in it and gave them an entry into the public sphere that was created by the movement (Sanal, 2005, p. 165). Some of the Dalit women had been working as Bible women, visiting houses and propagating the message of the Bible by distributing pamphlets and flysheets. The female disciples of Yohannan gave the new sect access to a broader constituency through their interaction with Dalit families who professed other religions especially christianity (Sanal, 2005, p. 165). Yohannan had been noted for his excellent compositions for his oration eve when he was working with the missionaries. The oral tradition of the movement comprises mostly of the songs sung during various ritual occasions of the PRDS and other everyday situations in the families of his followers. He articulated the concerns of the non caste in the established church. He vehemently questions the presence of casteism in the church. The multiplication of the churches on the basis of caste distinctions and individual predictions has not produced any positive result.

The Parayas have a church, the Pulaya have another church
A church for the Fisherman
Members of the household have separate churches
The master have a church, the serf has another church
Church after church has come up in line
But I find distinction still not removed (Joseph, 1994, p. 58).

Yohannan reminded that non caste people in India were the inheritors of a rich ancient culture. Yet conventional historiography had conveniently forgotten the non caste and the great contributions they had made for mankind. The song titled 'Kanunnilorakshravum'. I do not see any word was said to have sung by Yohannan is an attempt of searching non caste people's roots and identity. The most significant aspect of the notions of history that Yohannan articulated was the lack of an authentic history of Kerala's slave caste (Sanal, 2005, p. 271). Yohannan introduced the nation of history in his discourses to emphasize the argument that the slave castes were heir to a historical past that was destroyed by the conquering races and that the retrieval of that past was the way to salvation (Sanal, 2005, p. 271). His followers he had descended on earth to redeem the non caste from their sufferings. This particular argument was emphasized inorder to contest the claims of the upper caste on the labour power of the slave caste and the systematic subjection (Sanal, 2005, p. 273).

Yohannan continued the struggles for land to the landless and economic assistance for their material benefits. He also worked for their educational progress and job opportunities. To sum up his evangelism and his contributions as a member of the legislature could established a sense of oneness among his followers and to build up a separate identity for the Dalits. Though the instrumentality of history he tried to make his people feel the pinch of their current deprivation. Based on the sermon, Adi Dravida he visualized the constitution of a new social self and visualized an identity based on the unity of non caste people.

Historical knowledge plays a pivotal role in the process of identity formation and the consciousness that evolves out of it. Historical knowledge is perceived sometimes as embodiment of true knowledge of the past, without considering the process by which a particular knowledge of the past is created Yohannan through his efforts and initiated such a search for history of the non caste people (Sanal, 2005, p. 272). To conclude the significance of PRDS lies in the fact that the demand for eradication of untouchability was taken up more seriously by the Kerala society. The movement led by PRDS was instrumental in effecting unprecedentedly impact on the society which finally culminated in the genesis and triumph of innumerable anti caste movement Yohannan laminated the lack of written history for the non castes in Kerala whom he referred as the original inhabitants of the land.

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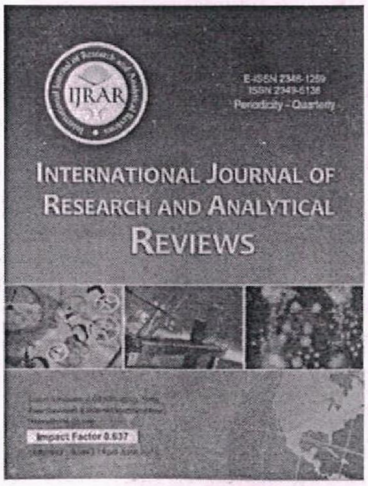

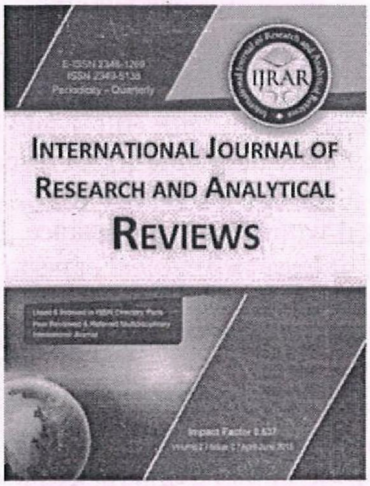

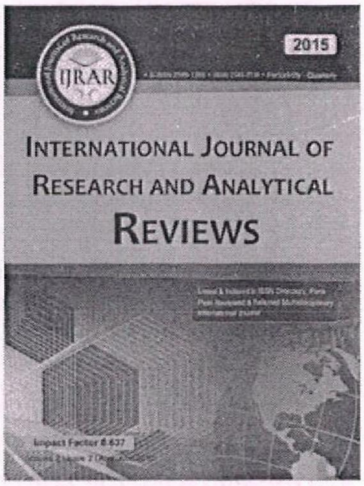

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THE ROLE OF PAMPADY JOHN JOSEPH IN ORGANIZING THE NON CASTE CHRISTIANS OF KERALA

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ABSTRACT *Due to caste system the substantial social groups generally known as non caste people in Kerala, were subjected to different types of disabilities. Non caste Christians are scheduled caste people converted to Christianity and were excluded from the Scheduled Caste list, by the Presidential order of 1950. They are socially and economically backward educationally low, politically and religiously powerless. Such socio, economic environment of these people is not conducive to achieve a better standard of living and subsequently they enjoy a very low position in the society. But after conversion the caste discrimination existed within the church also. In this context Pampady John Joseph, a non caste Christian took efforts to organize the low caste Christians. For this purpose he established an organization called "Cheramar Mahasabha". Through this organization he fight against the caste inequalities which prevailed in the Christian church.*

Keywords: *Concept of divorce , Divorce with mutual consent, grounds.*

The substantial social group generally termed as, Dalits or Non castes were subjected to different types of discrimination due to caste system. Under colonialism these marginalized groups began to achieve the social transformation and tried to crossroad the disabilities imposed upon them. There was a social and political awakening among the Non caste converts as well as their Hindu counterparts. The Non caste Christians began to protest against the caste discrimination within and outside the church with the assistance of social space created by colonial modernity.

The mid nineteenth century witnessed the beginning of protestant missionary work among the Non caste and in the subsequent decades, thousands of them joined missionary church. But in the church also they had to experience the bitterness of caste discriminations. Apart from the socio economic aspirations the non caste people embraced Christianity as part of a religious quest. In Kerala one of the realms of conflict between non caste and caste Hindus in this period was religion[1]. In this context, new movements originated in Kerala inorder to organize the people. The emergence of social reformers accelerated the process of social change and created a most conducive climate for the protest struggles.

Non castes Christians are scheduled caste people converted to Christianity and were excluded from the Scheduled Caste list, by the Presidential order of 1950. Large numbers of Dalits were converted to Christianity because it was a casteless religion. But the non caste people were subjected to caste discrimination within the church. Conversion to Christianity really affected a perceptible change in the daily life, the customs and cultures of the Indian adherents. Yet conversion did not virtually encourage the development of the identity of the non caste Christians. The social difference between the non caste Christians and the Syrian Christians date back from the days when the former group joined the mission in the mid nineteenth century and it continued to post colonial period Pampady John Joseph who belonged to the non caste Christian community realize the inequalities existed in the church on the basis of caste. In this context John Joseph fight against the difference between non caste and caste Christians and efforts were taken to organize them inorder to acquire the identity.

John Joseph noted in history through his actions which oriented for the liberation of the non caste Christian community especially the Cheramar Christians. He was born in a Pulaya family at Manjoor, north of Kottayam in 1887. Under the influence f the CMS missionaries John Joseph's family members were converted to Christianity. This was happened when they settled down at Pampady, near Kottayam and joined the Catholic Church. Though he was a Christian, others treated him as untouchable since he was originally a Pulaya. He was educated up to sixth standard at Thrikkakara Mission School. In 1910 he came to Kottayam and then in Travancore in 1918. During his life time he engaged in different types of profession. He had worked as a teacher in Mission school at Pampady, as a military man during the First World War, who travelled widely in different nations of the world and as a zealous missionary engaged in evangelical and other medical mission services[2].

John Joseph belonged to the Pulaya community and fought for the achievement of their liberation in different levels of life. At the same tome he took efforts to generate the awareness about the rights and privileges in the minds of the people of his community. He got an opportunity to work with various Christian missionaries. From this experience he felt that he had to work within the Christian religion. Through conversion they changed from tribal traditions to organized practices and worship such a change was the first that they had to undergo. But the egalitarian concept of Christianity did not produce any result regarding the case of non caste Christians. Because after conversion they were also treated as untouchables in the church and this attitude towards his brethren hurts the mind of John Joseph consequently there arose a crisis regarding their identity. It was the context of the identity crisis and the growing discontentment among the non caste Christians prompted him to launch a new movement against the inequalities that suffered by his community.

John Joseph had a deep sense of history and realized its importance in identity formation. He tried to construct the history of the polluted castes based on their ancient heritage and glorious memories of the past. The turning point in the life of John Joseph was his association with Jhana Joshua. As the chief Accounts Officer of Travancore state, Joshua had in his custody a rich collection of government records[3]. From the source provided by Joshua, John Joseph learned that the Pulaya lineage was linked with the ancient Chera dynasty of Kerala. The ancient name of Kerala was Cheranadu and its first inhabitants were a tribe called Cheramar who were also known as Cheramans, Cheramakkal or Cheras. In the earlier period they were the rulers, landlords, agriculturalists poets and educated people of the land. He even located a family called 'Aykara Yajamanans' then living in a village called Kunnathunadu in central Travancore belonging to this lineage[4]. Thus he developed a view that the Cheramar were the original inhabitants of Kerala and hence they should not be suppressed in their homeland. This created a feeling of pride in the minds of the people of the Pulaya community. On this basis he even changed his caste name from Pulaya to Cheramar which means son of the soil[5].

John Joseph made an attempt to organize the non caste Christians under a banner and decided to acquire their rights and liberties. In 1921 John Joseph organized a grand meeting of the Christian converts to launch a movement by the name Cheramar Mahajan Sabha, Pampady John Joseph and Parody Abraham Isac were elected as the General Secretary and President of the Sabha respectively. A large number of Pulayas both Hindus and Christians of Changanassery and Kottayam became the members of this organization. The slogan of this organization was "to organize through lineage and not through religion". A section of the Pulayas joined the Cheramar Sabha were attracted by the slogan.

Soon the movement established by John Joseph flourished in Thiruvalla and spread to other places like Changanassery and Kottayam. He articulated that the Cheramar, Pulayas, Parayas and Kuravas, all belong to the Adi Dravida race. In fact it was a new attempt in constructing a separate identity and providing self confidence and pride among the marginalized section. In order to popularize his critical views on the existing social situations and to awaken his fellowmen, he started a magazine called Sadujana Doodan in 1914 and wrote many articles which awakened the minds of the people. John Joseph was elected as a member of Sree Moolam Popular Sabha in 1931. He submitted a memorandum to the British Parliament on April 24, 1935 requesting to accord all the civil rights to the entire subaltern section which enjoyed by the elite section of the society. He actively associated with Ayyankali, the pioneer of Dalit liberation movement in Kerala[6]. He passed away in 1940 at the age of 53. The intervention of Ayyankali, were brave and dynamic but the problem of the non caste Christians was not directly connected with Ayyankali movement. Here John Joseph viewed the problem of the converted Christians as an important issue. He advocated identity politics on the basis of historical facts and sense of identity. The contribution of John Joseph was remarkable in awakening the consciousness and identity of the non caste Christians during the first half of the 20th century.

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