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MOLECULAR STRUCTURE, NBO ANALYSIS, REACTIVITY DESCRIPTORS, ELECTRONIC AND THERMODYNAMIC PROPERTIES OF LAMBDA CYHALOTHRIN PYRETHROID USING DENSITY FUNCTIONAL THEORY

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ABSTRACT : Lambda cyhalothrin is an important pesticide, which is widely used for the pest management. Density functional theory (DFT) has been widely used for predicting various types of molecular properties. In the present study, NBO analysis has been performed for understanding the intra-molecular charge transfer of the molecule. Molecular electrostatic potential energy surfaces and molecular orbitals (HOMO and LUMO) were plotted. Global as well as local reactivity descriptors were determined and used to identify the sites of nucleophilic and electrophilic attack. Some important thermodynamical parameters have been also computed.

Key words : Lambda cyhalothrin, DFT, NBO, reactivity, descriptors.

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INTRODUCTION

Pyrethroids are synthetic chemical analogues of pyrethrins, which are naturally occurring insecticidal compounds produced in the flowers of Chrysanthemum (*Chrysanthemum cinerariaefolium*). Synthetic pyrethroids are more toxic than pyrethrins and exist for longer time in the environment as they are more photostable. These pesticides have injurious effects, including damage to the lungs and dysfunctioning of the immune and endocrine systems (Muhammad *et al*, 2009). Pyrethroids with cyclopropane carboxylic ester structure are known as type I pyrethroids, while the addition of a cyano group at the benzylic carbon atom gives type II pyrethroids (Vijayan *et al*, 2004). The addition of cyano group increases insecticidal activity many times as compared to type-I pyrethroids. They show a pattern of toxic action typical of a strongly excitant effect on the nervous system in a variety of species. The molecular aspects of pyrethroids action are not fully understood but the electrophysiological investigations strongly suggest that the voltage dependent sodium channel in the nerve membrane is the common target in both insects and mammals (Casida, 1983; Vijverberg and Van der Bercken, 1990).

Lambda-cyhalothrin $C_{23}H_{19}ClF_3NO_3$ is a synthetic pyrethroid insecticide, which contains 1:1 mixture of two stereoisomers, (S)-α-cyano-3phenoxybenzyl-(Z)-(1R,3R)-3-(2-chloro-3,3,3- trifluoroprop-1-enyl)-2,2 dimethyl cyclopropane carboxylate and (R)-α-cyano-3-phenoxybenzyl-(Z)-(1S,3S)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2dimethyl cyclopropane carboxylate (Fig. 1). It is an insecticide that represents a good compromise between efficacy and toxicity and has found extensive uses in public and animal health applications where it effectively controls a broad spectrum of insects and ectoparasites, including cockroaches, flies, lices, mosquito and ticks (Davies *et al*, 2000). Lambda-cyhalothrin residues dissolved in water decrease rapidly if suspended solids and aquatic organisms are present because lambda-cyhalothrin molecules are strongly adsorbed by particulates, thus posing a low risk to ground water contamination (Lu, 2010). Adsorbed lambda-cyhalothrin molecules show decreased degradation rates because they are less accessible to breakdown than free molecules in the water column (He *et al*, 2000).

There is a lot of experimental work on the toxic behavior of lambda cyhalothrin on mammals and non-mammals but the exact nature of mode of action is still not known. Today quantum chemical calculations are extensively used for understanding the mechanisms at the molecular level. The present work was undertaken for electronic property evaluation, NBO analysis, HOMO-LOMO study and hence understanding the molecular basis of toxic behavior of this molecule. Computational work was done using density functional theory (DFT) method using Gaussian 09 program (Frisch *et al*, 2000) package employing 6-311g (d,p) basis set. HOMO-LUMO analysis helps to elucidate charge transfer occurring in the molecule. Molecular electrostatic potential (MEP) mapping is widely used in the study of hydrogen bonding, and reactivity of molecules (Kumar *et al*, 1996 and Yadav *et al*, 2014). Global as well as local reactivity descriptors and some important thermal properties were also calculated for the titled molecule.

Computational Details

The electronic structure and optimized geometry of the molecule were computed by the DFT (Hohenberg and Kohn, 1964) method using the Gaussian 09 program package employing 6-311G(d,p) basis set and Becke's three parameter (local, nonlocal, Hartree–Fock) hybrid exchange functional with Lee–Yang–Parr correlation functional (B3LYP) (Lee *et al,* 1988; Parr and Yang, 1989; Becke, 1993).

RESULTS AND DISCUSSION

Geometry optimization and molecular structure

All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum. The molecular structure of the compound is shown in the Fig.1. The optimized bond lengths, bond angles and dihedral angles of the compound were calculated using B3LYP method with 6-311G(d,p) basis set and are given in Table 1. As the exact crystal structure of the compound was not available till now therefore, we have compared the optimized structure with other similar systems for which crystal structure is available. The calculated geometry parameters are found to be within the range.

Natural Bond Orbital Analysis (NBO)

NBO analysis is an effective tool for the study of intra-molecular bonding and interaction among the bonds. One can investigate charge transfer or conjugative interaction in molecular systems and an electronic structure description akin to the Lewis bonding theory

Table 1 : Optimized Geometrical Parameters using B3LYP/6-311G (d,p) (bond length/ Å and angles/°).

Geometric Parameters	Optimized	Geometric Parameters	Optimized
R(C1-C2)	1.392	A(C1-C2-C3)	-0.491
R(C2-C3)	1.394	A(C2-C3-C4)	0.156
R(C3-C4)	1.394	A(C3-C4-C5)	-0.151
R(C4-C5)	1.392	A(C1-C2-H6)	-0.166
R(C1-C6)	1.392	A(C1-C2-H7)	179.829
R(C1-H7)	1.083	A(C1-C2-H8)	179.932
R(C2-H8)	1.084	A(C2-C3-H9)	-178.972
R(C3-H9)	1.083	A(C3-C4-H10)	-179.038
R(C4-H10)	1.084	A(C4-C5-H11)	-6.291
R(C5-H11)	1.082	A(C6-C1-O12)	137.719
R(C6-O12)	1.387	A(C6-O12-C13)	142.222
R(O12-C13)	1.375	A(O12-C13-C14)	177.141
R(C13-C14)	1.393	A(C13-C14-C15)	-0.181
R(C14-C15)	1.393	A(C14-C15-C16)	0.345
R(C15-C16)	1.398	A(C15-C16-C17)	-0.315
R(C16-C17)	1.391	A(C16-C17-C18)	179.968
R(C17-C18)	1.392	A(C15-C16-H19)	-179.639
R(C16-H19)	1.084	A(C16-C17-H20)	-169.63
R(C17-H20)	1.083	A(C17-C18-H21)	-3.9136
R(C18-H21)	1.083	A(C13-C14-H22)	177.863
R(C14-H22)	1.082	A(C14-C15-C23)	24.138
R(C15-C23)	1.519	A(C15-C23-C24)	-11.614
R(C23-C24)	1.469	A(C1-C2-N25)	143.153
R(C24-25N)	1.152	A(C15-C23-H26)	-105.06
R(C23-H26)	1.091	A(C15-C23-O27)	68.7394
R(C23-O27)	1.457	A(C23-O27-C28)	5.398
R(O27-C28)	1.363	A(O27-C28-O29)	-174.267
R(C28-O29)	1.206	A(O27-C28-C30)	143.0635
R(C28-C30)	1.483	A(C28-C30-C31)	112.7285
R(C30-C31)	1.549	A(C30-C31-C32)	2.191
R(C31-C32)	1.518	A(C28-C30-H33)	-140.518
R(C30-H33)	1.082	A(C30-C31-H34)	0.442
R(C31-H34)	1.083	A(C30-C31-C35)	35.782
R(C31-C35)	1.467	A(C31-C35-H36)	-142.841
R(C35-H36)	1.082	A(C31-C35-C37)	-0.031
R(C35-C37)	1.333	A(C35-C37-Cl38)	178.992
R(C37-Cl38)	1.753	A(C35-C37-C39)	123.456
R(C37-C39)	1.506	A(C37-C39-F40)	2.766
R(C39-F40)	1.345	A(C37-C39-F41)	-39.265
R(C39-F41)	1.346	A(C37-C39-F42)	-110.923
R(C39-F42)	1.355	A(C31-C32-C43)	40.471
R(C32-C43)	1.518	A(C32-C43-H44)	-81.259
R(C43-H44)	1.087	A(C32-C43-H45)	160.591
R(C43-H45)	1.094	A(C32-C43-C46)	105.806
R(C43-H46)	1.094	A(C31-C32-C47)	-33.421
R(C32-C47)	1.520	A(C32-C47-H48)	-153.892
R(C47-H48)	1.092	A(C32-C47-H49)	86.851
R(C47-H49)	1.094	A(C32-C47-H50)	-0.491
R(C47-H50)	1.094		

Note: R- Bond Length in Angstrom units, A-Bond angle in degrees.

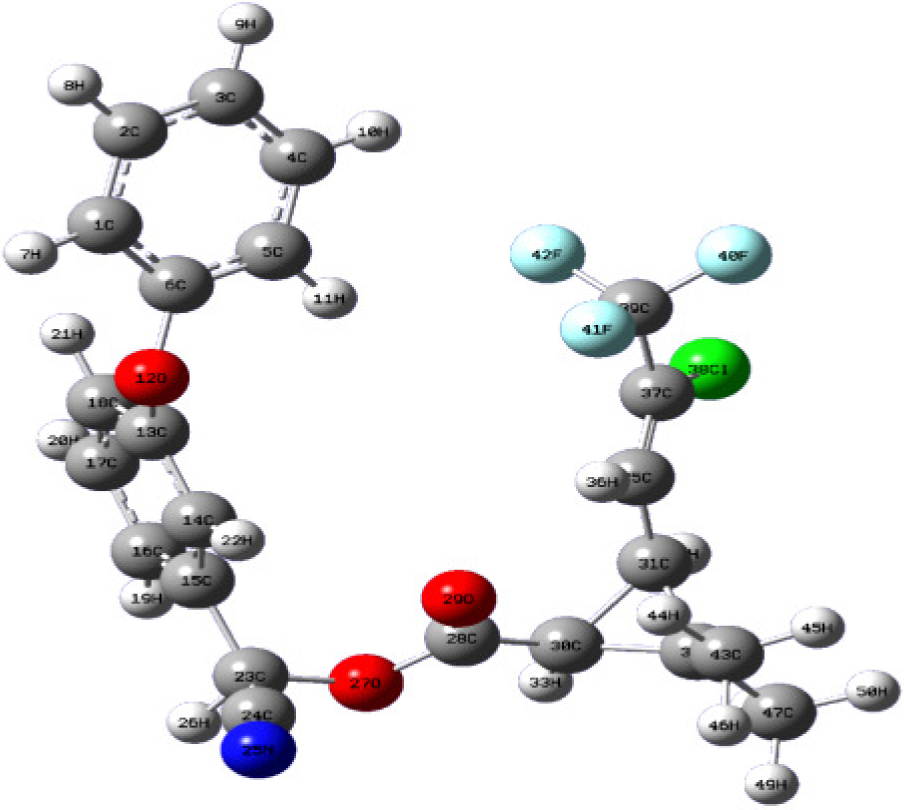

Fig. 1 : Optimized structure of lambda cyhalothrin using DFT/B3LYP/6-311G(d,p).

(Reed *et al*, 1988; Weinhold and Landis, 2001, 2005).The natural bond orbital (NBO) analysis was performed using Gaussian09 package at DFT/B3LYP/6-311G(d,p) level to observe the intra-molecular charge transfer interaction, rehybridization, and electron density delocalization within the molecule. The stabilization energies of all possible interactions between donor and acceptor orbitals in the NBO basis were evaluated by second-order perturbation theory. The off-diagonal elements of the Fock matrix in the NBO basis provide information about the delocalization effect i.e. donor-acceptor charge transfer. For each donor (i) and acceptor (j); the stabilization energy $E^{(2)}$ associated with the delocalization i to j is given by

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

Where, q_i is the donor orbitals occupancy, ε_i and ε_j are diagonal elements and $F_{(i,j)}$ is the off-diagonal NBO Fock matrix element. Larger will be the value of $E^{(2)}$, more intensive will be the interaction between electron donor and electron acceptor.

The second-order perturbation theory analysis of the Fock matrix shows strong intra-molecular hyper conjugative interactions of π electrons between π bond orbitals and anti-bonding orbitals. The intra-molecular hyper conjugative interactions are formed by the orbital overlap between π (C-C) or π^* (C-C) bond orbitals resulting in intra-molecular charge transfer (ICT) causing stabilization of the system. The larger be the value of the energy of hyper conjugative interactions $E^{(2)}$, the more intensive is the interaction between electron donors and electron acceptors i.e. more electron-donating tendency from electron donor to electron acceptor. The natural bond analysis has been performed for lambda cyhalothrin at the DFT/B3LYP/6-311G (d,p) level and prominent results are given in Table 2.

The most important interaction (n-π*) related to the resonance in the molecules is electron donation from the n2(O27) (electron donating group) to the anti-bonding acceptor π*(C28-O29). This shows the conjugation between electron donating group and the π electron of the carbonyl (C=O) group which corresponds to the stabilization energy 42.54 kcal/mol. The other important interaction is electron donation from the n2(O29) (electron-donating groups) to the antibonding acceptor σ*(027-C28) and σ*(028-C30) with stabilization energies 32.65 kcal/mol and 17.41 kcal/mol, respectively. There occurs a strong intramolecular interaction of π electrons for π(C1-C6), π(C4-C5) bonds to the π*(C2-C3) corresponding to the stabilization energies 21.06 and 18.93 kcal/mol, respectively. Similarly,the electron donation from the σ(C35-H36), σ(C23-H26) bonds to anti bonding

Table 2 : Second order perturbation theory analysis of Fock matrix in NBO basis for lambda cyhalothrin.

Donor NBO(i)	ED(i)/e	Acceptor NBO(j)	^{a}ED (j)/e	^{b}E(2) k cal/mol	^{c}E(j)-E(i) (a.u.)	^{d}F(i,j) (a.u.)
π (C1 – C6)	1.660	π*(C2 - C3)	0.03279	21.06	0.29	0.07
		π *(C4 - C5)	0.03209	18.91	0.29	0.067
π (C2 – C3)	1.66914	π *(C1 - C6)	0.02591	19.71	0.28	0.067
		π* (C4 - C5)	0.03209	22.03	0.28	0.07
π * (C4 – C5)	1.67704	π*(C2 - C3)	0.03279	18.93	0.28	0.066
π (C13 - C14)	1.6243	π * (C15 -C16)	0.01599	22.58	0.28	0.072
		π *(C17 - C18)	0.01886	19.54	0.29	0.068
π (C15 - C16)	1.6731	π *(C13 - C14)	0.01928	19.66	0.29	0.068
		π *(C17 - C18)	0.01886	20.72	0.29	0.069
		σ*(C23 - O27)	0.20975	7.05	0.48	0.056
π (C17 - C18)	1.6717	π*(C13 - C14)	0.01928	21.54	0.28	0.07
		π*(C15 - C16)	0.01599	19.72	0.28	0.068
σ(C23 - C24)	1.98469	σ*(C24 - N25)	0.90672	6.98	1.64	0.096
σ(C23 - H26)	1.9534	π *(C24 - N25)	0.09264	6.03	0.64	0.055
σ (C24 - N25)	1.99591	σ*(C23 - C24)	0.40662	6.26	1.48	0.087
BD (3)C24-N 25	1.97569	σ*(C23 - O27)	0.20975	6.01	0.57	0.053
σ (C30 - C31)	1.88527	σ*(C30 - C32)	0.31306	7.21	0.85	0.071
		σ*(C31 - C32)	0.32436	6.22	0.86	0.066
σ (C30 - C32)	1.91151	σ*(C30 - C31)	0.27113	6.25	0.84	0.065
σ (C31 - C32)	1.91604	σ*(C30 - C31)	0.27113	5.07	0.84	0.059
σ (C35 - C36)	1.95654	σ*(C37 - C38)	0.1153	11.42	0.65	0.077
σ (C35 - C37)	1.93393	σ*(C39 – F40)	0.21843	5.34	0.54	0.048
		σ*(C39 - F42)	0.20656	6.19	0.53	0.052
σ(C43 - H45)	1.98186	σ*(C30 - C32)	0.31306	5.74	0.82	0.062
σ(C43 - H46)	1.9831	σ*(C31 - C32)	0.32436	5.65	0.83	0.062
LP (1) O 12	1.93712	σ*C 13 - C 18	0.55028	5.02	1.09	0.066
LP (2) O 12	1.85301	π *C 1 - C 6	0.02591	11.52	0.35	0.06
		π *C 13 - C 14	0.01928	16.04	0.34	0.07
LP (1) N 25	1.96818	σ*C 23 - C 24	0.40662	11.86	0.92	0.093
LP (1) O 27	1.96236	σ*C 28 - O 29	0.58764	6.2	1.18	0.077
LP (2) O 27	1.80306	π *C 28 - O 29	-0.01249	42.54	0.34	0.109
LP (2) O 29	1.83828	σ*O 27 - C 28	0.32324	32.65	0.62	0.128
		σ*C 28 - C 30	0.3936	17.41	0.69	0.1
LP (2)Cl 38	1.96065	σ*C 37 - C 39	0.31992	5.93	0.66	0.056
LP (3)Cl 38	1.92749	π *C 35 - C 37	0.00771	14.53	0.35	0.065

Table 2 continued....

Table 2 continued....

LP (2) F 40	1.95018	σ*C 37 - C 39	0.31992	6.38	0.77	0.063
LP (3) F 40	1.93471	σ*C 39 - F 42	0.21188	10.81	0.65	0.076
		σ*C 39 - F 42	0.075	10.6	0.65	0.075
LP (2) F 41	1.94948	σ*C 37 - C 39	0.31992	6.4	0.77	0.063
LP (3) F 41	1.93883	σ*C 39 - F 40	0.21843	9.99	0.67	0.074
		σ*C 39 - F 42	0.075	10.86	0.66	0.076
LP (2) F 42	1.95214	σ*C 37 - C 39	0.31992	5.97	0.77	0.061
LP (3) F 42	1.93815	σ*C 39 - F 40	0.21843	9.25	0.66	0.071
		σ*C 39 - F 41	0.21188	10.92	0.66	0.076
π * C 15 - C 16	0.39055	σ*C 23 - O 27	0.20975	5.07	0.19	0.059

[a] ED: electron density

[b] E(2): energy of hyper-conjugative interactions (stabilization energy)

[c] Energy difference between donor and acceptor i and j NBO orbitals

[d] F(i,j) is the Fock matrix element between i and j NBO orbitals.

acceptors σ*(C37-Cl38) and π*(C24-N25) has stabilization energy equal to 11.42 kcal/mol and 6.03 kcal/mol, respectively. All these intra-molecular charge transfers (π-π*, n-σ*, n-π* and π*-π*) are responsible for polarization of molecule and may produce nonlinearity in the molecule.

Molecular Electrostatic Potential

The net electrostatic effect, produced by the total charge distribution (electrons + nuclei) of a molecule at a point in space around it, is known as molecular electrostatic potential (ESP). The ESP correlates the total charge distribution with dipole moments, partial charges, electro-negativity and site of chemical reactivity of a molecule. It provides a visual method to understand the relative polarity of a molecule and serves as a useful quantity to explain hydrogen bonding, reactivity and structure–activity relationship of molecules including biomolecules and drugs (Politzer *et al,* 1985; Casida and Chong, 1995; Munoz-Caro *et al*, 2000; Srivastava *et al*, 2011). The different values of the electrostatic potential at the MEP surface are represented by different colors; red, blue and green represent the regions of most negative, most positive and zero electrostatic potential, respectively. The negative electrostatic potential corresponds to an attraction of the proton by the aggregate electron density in the molecule (shades of red), while the positive electrostatic potential corresponds to the repulsion of the proton by the atomic nuclei (shades of blue). The negative (red color) regions of ESP were related to electrophilic reactivity and the positive (blue color) ones to nucleophilic reactivity (Yadav *et al*, 2019). The molecular electrostatic potential map of the title molecule has been generated (Fig. 2) at B3LYP/6-311G(d,p) optimized geometry using the Gaussview 5.0 program. From the inspection of 3D maps of lambda cyhalothrin, it is observed that the negative regions are associated with oxygen and fluorine atoms. All these atoms have large negative MEP values. Thus, it is evident that all oxygen, nitrogen and fluorineatoms will be preferred sites for electrophilic attack. A positive region is localized on many CH bonds which indicate possible sites for nucleophilic attack. The three fluorine atoms in lambda cyhalothrin show negative MEP values which indicate that this region has more active sites spread in large surface area. Therefore, this region contains three sites of electrophilic attack resulting in more toxicity as compared to others pyrethroids where a hydrogen atom is attached with carbon instead of CF3 group.

HOMO-LUMO Analysis

The energies of the frontier molecular orbitals e.g., the highest occupied molecular orbital (HOMO) has the ability to donate an electron and the lowest unoccupied molecular orbital (LUMO), as an electron acceptor, shows the ability to obtain an electron. HOMO and LUMO energies are calculated using B3LYP/6-31G (d,p) level of theory. Reactivity between the electrophile and a nucleophile increase when the E-LUMO is decreased (Zhao *et al*, 2000). From HOMO and LUMO plots (Fig. 3) it is clear that HOMO is mainly localized in acidic moiety while LUMO is shifted from acidic moiety to alcohol moiety. HOMO and LUMO energies in the ground state using B3LYP/6-311G (d,p) level of theory are calculated as

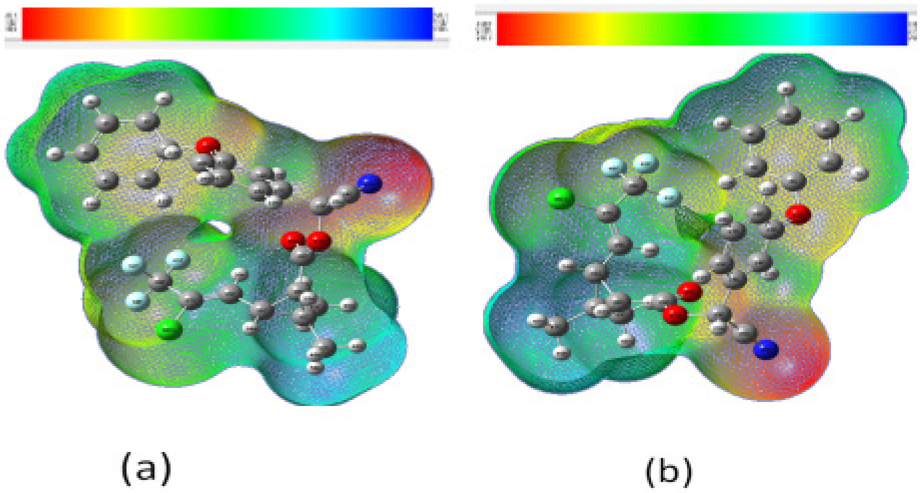

Fig. 2 : The molecular electrostatic potential maps of lambda cyhalothrin in two different orientations.

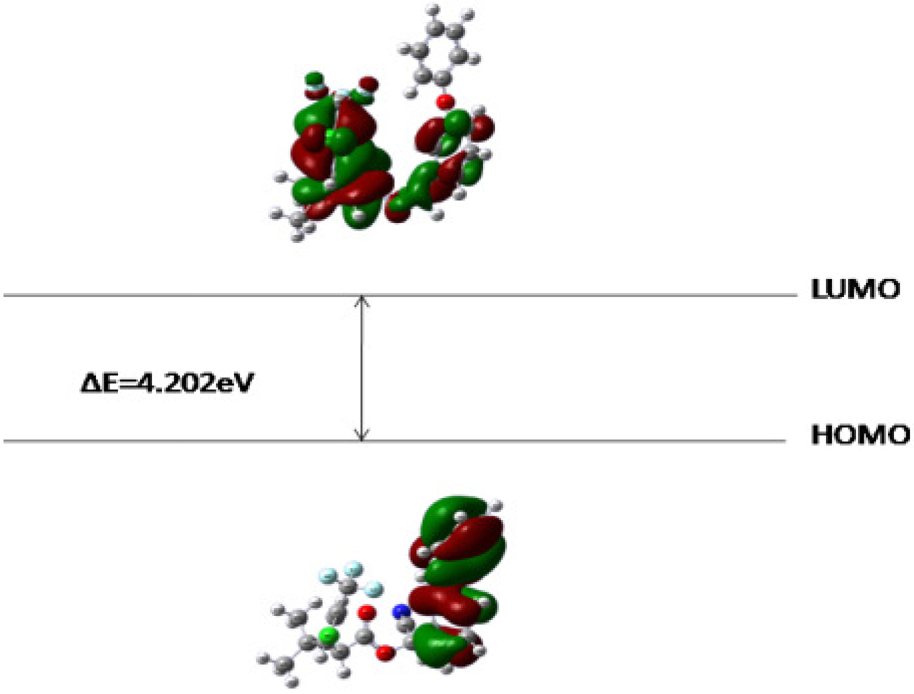

Fig. 3 : The ground state isodensity surface plots for the HOMO and LUMO orbitals of lambda cyhalothrin.

HOMO Energy = -0.24174a.u = -6.578eV

LUMO Energy = -0.08731a.u = -2.375eV

The calculated value of HOMO–LUMO energy gap is found to be 4.2eV, which reveals that significant degree of possibly reactive nature of the titled molecule.

Global and Local Reactivity Descriptors

Global reactivity descriptors of lambda cyhalothrin molecule have been calculated using HOMO and LUMO energies. From HOMO–LUMO energies, global reactivity descriptors such as the energies of frontier molecular orbitals (E_{HOMO}, E_{LUMO}), energy band gap (E_{HOMO} - E_{LUMO}), electronegativity (χ), chemical potential(μ), global hardness(η), global softness (S) and global electrophilicity index (ω) were calculated using quantum calculations. These descriptors describe the electrophilic nature of the molecule (Ganapayya *et al*, 2012; Yadav and Singh, 2017).

The reactivity descriptors in terms of molecular orbital energies are given as

$\chi = -(E_{LUMO} + E_{HOMO})/2 = 0.164$ a.u = 4.477eV

$\mu = -$Ç$= (E_{LUMO} + E_{HOMO})/2 = -0.164$ a.u = -4.477eV

$\eta = (E_{LUMO} - E_{HOMO})/2 = 0.077$ a.u = 2.101eV

$S = 1/2\ \eta = 6.475$ a.u = 0.238eV

$\omega = \mu^2/2\ \eta = 0.175$ a.u = 4.77eV

Higher the value of ω results strong electrophilicity and measures the stabilization in energy when the system

Table 3 : Values of Fukui Functions sing Hirshfeld charges.

Atoms	**q_k^+**	**q_k^-**	**q_k^0**	**f_k^+**	**f_k^-**	**f_k^0**
C 1	-0.015112	-0.068983	-0.056493	0.041381	0.01249	0.0269355
C 2	0.001261	-0.064728	-0.043183	0.044444	0.021545	0.0329945
C 3	0.022579	-0.07163	-0.053513	0.076092	0.018117	0.0471045
C 4	-0.007139	-0.050473	-0.041362	0.034223	0.009111	0.021667
C 5	-0.01911	-0.057462	-0.05882	0.03971	-0.001358	0.019176
C 6	0.114825	0.076333	0.074164	0.040661	-0.002169	0.019246
H 7	0.079038	0.044452	0.054121	0.024917	0.009669	0.017293
H 8	0.078596	0.035902	0.050369	0.028227	0.014467	0.021347
H 9	0.081607	0.035447	0.048352	0.033255	0.012905	0.02308
H 10	0.074276	0.04476	0.050418	0.023858	0.005658	0.014758
H 11	0.062458	0.051109	0.045813	0.016645	-0.005296	0.0056745
O 12	-0.044745	-0.136608	-0.127026	0.082281	0.009582	0.0459315
C 13	0.111392	0.059918	0.083694	0.027698	0.023776	0.025737
C 14	-0.01603	-0.071612	-0.046898	0.030868	0.024714	0.027791
C 15	0.016822	-0.040914	-0.011636	0.028458	0.029278	0.028868
C 16	0.008336	-0.081778	-0.054605	0.062941	0.027173	0.045057
C 17	-0.00982	-0.068582	-0.03947	0.02965	0.029112	0.029381
C 18	-0.016625	-0.100688	-0.050718	0.034093	0.04997	0.0420315
H 19	0.077247	0.031395	0.049601	0.027646	0.018206	0.022926
H 20	0.076697	0.034094	0.054219	0.022478	0.020125	0.0213015
H 21	0.069665	0.030198	0.054362	0.015303	0.024164	0.0197335
H 22	0.0755	0.045635	0.058526	0.016974	0.012891	0.0149325
C 23	0.096211	0.067051	0.090685	0.005526	0.023634	0.01458
C 24	0.086383	0.078122	0.087932	-0.001549	0.00981	0.0041305
N 25	-0.180619	-0.265576	-0.21174	0.031121	0.053836	0.0424785
H 26	0.082604	0.049987	0.071922	0.010682	0.021935	0.0163085
O 27	-0.121079	-0.156264	-0.130059	0.00898	0.026205	0.0175925
C 28	0.230022	0.195052	0.22814	0.001882	0.033088	0.017485
O 29	-0.246474	-0.27211	-0.244852	-0.001622	0.027258	0.012818
C 30	-0.033887	-0.056141	-0.038395	0.004508	0.017746	0.011127
C 31	-0.019374	-0.042399	-0.026457	0.007083	0.015942	0.0115125
C 32	0.033232	0.007805	0.024217	0.009015	0.016412	0.0127135
H 33	0.05994	0.036509	0.053267	0.006673	0.016758	0.0117155
H 34	0.052481	0.031796	0.045854	0.006627	0.014058	0.0103425
C 35	-0.016439	-0.083122	-0.02732	0.010881	0.055802	0.0333415
H 36	0.055082	0.038614	0.054127	0.000955	0.015513	0.008234
C 37	0.01094	-0.059851	-0.003306	0.014246	0.056545	0.0353955
Cl 38	-0.007029	-0.127044	-0.053186	0.046157	0.073858	0.0600075
C 39	0.234143	0.215919	0.232489	0.001654	0.01657	0.009112
F 40	-0.080558	-0.118005	-0.092844	0.012286	0.025161	0.0187235
F 41	-0.075413	-0.085829	-0.073992	-0.001421	0.011837	0.005208
F 42	-0.096318	-0.114334	-0.094399	-0.001919	0.019935	0.009008
C43	-0.093167	-0.10354	-0.096934	0.003767	0.006606	0.0051865
H 44	0.038663	0.038321	0.039825	-0.001162	0.001504	0.000171
H 45	0.049808	0.027948	0.042209	0.007599	0.014261	0.01093
H 46	0.051902	0.029638	0.04366	0.008242	0.014022	0.011132
C47	-0.084084	-0.099988	-0.090134	0.00605	0.009854	0.007952
H48	0.046543	0.03328	0.041786	0.004757	0.008506	0.0066315
H49	0.052422	0.02824	0.043379	0.009043	0.015139	0.012091
H50	0.052371	0.03017	0.044236	0.008135	0.014066	0.0111005

Table 4 : Theoretical Computed Thermodynamical Papameters of Lambda Cyhalothrin.

	Thermal Energy (E)Kcal/mole	**Heat Capacity (Cv) Cal/Mol-Kelvin**	**Entropy(S) Cal/Mol-Kelvin**
Total	251.784	108.157	199.049
Vibrational	250.007	102.196	118.045
Rotational	.889	2.981	36.808
Translational	.889	2.981	44.195
Zero Point Vibration Energy (Kcal/Mole)	233.65676		
Rotational constants	0.14864 0.11161 0.07439		

requires an additional charge from the environment whereas μ predicts the direction of charge transfer because an electrophile is capable of accepting electron from environment and its energy decreases when accepting electronic charge.

Local Reactivity Descriptors

Fukui function predicts the information of the most electrophilic and nucleophilic sites and it is widely used to the local descriptors of reactivity of different atoms in the whole molecule. Fukui functions for electrophilic, nucleophilic and free radical attacks have been calculated with the basis ofB3LYP/6-311G (d,p) level of theory with following equations:

$f_k^+ = [q_k(N+1) - q_k(N)]$ for nucleophilic attack

$f_k^- = [q_k(N) - q_k(N-1)]$ for electrophilic attack

$f_k^0 = \frac{1}{2}[q_k(N+1) - q_k(N-1)]$ for radical attack

Where, q_k is atomic charge (Mulliken, Hirshfeld or NBO etc.) at the kth atomic site in the anionic (N+1), cationic (N-1) or neutral (N) molecule. Parr and Yang suggest that the sites in molecular systems having the largest values of Fukui function (f_k) show high reactivity for corresponding attacks (Parr and Yang, 1984; Lee *et al*, 1988).

The calculated values of Fukui functions using Hirshfeld charges are shown in Table 3. From this table, it is observed that the reactivity order of first six atoms for nucleophilic activity is O12>C3>C16>C2>C1 and the electrophilic reactivity order is C35>N25>C28>C17>C16, while the order of reactivity for the sites of free radicals attack is C3>O12>C16>N25>C18.

Thermodynamic Properties

Thermodynamic properties provide useful information about the molecular system. These are essential to understand the chemical reactions of the molecule and can be obtained by the DFT method. Some standard thermodynamic functions such as thermal energy, heat capacity, entropy, zero-point energy, and rotational constants have been obtained at room temperature (300 K) from the output of structure optimization calculations and are listed in Table 4. Contributions of translational, rotational, and vibrational components in thermal energy, heat capacity, and entropy are also given. It is clear from the data that contribution due to vibrational motion is greater than the other two motions.

CONCLUSION

In the present study, quantum chemical investigation of lambda cyhalothrin molecule has been carried out. The molecular geometry, NBO analysis and other electronic properties and thermodynamic parameters of the molecule have been calculated using DFT (B3LYP/6-311G(d,p)) method. The NBO analysis revealed the occurance of intramolecular charge transfer within the molecule. MEP map provided the visual representation of the active sites of electrophilic and nucleophilic attack. HOMO and LUMO energies were used to obtain the global reactivity descriptors. Local reactivity descriptors provided the information of reactivity of atomic sites which indicates that most electrophilic site is on C35, whereas most nucleophilic site is on O12. Calculated various thermodynamic parameters for the molecule reveal that the contribution due to vibrational motion is greater than translational and rotational motions.

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