STRUCTURAL, VIBRATIONAL AND CHEMICAL REACTIVITY STUDIES OF (2-(4-CHLOROPHENYL)-5-(4-METHYLPHENYL)- 1,3,4-OXADIAZOLE

Article · April 2019

Sunil L Dhonnar
Mahatma Gandhi Vidyamandirs LVH Arts Science and Commerce College Panchav…

Vishnu Adole
Mahatma Gandhi Vidyamandir's Loknete Vyankatrao Hiray Arts Science and Com…

Nutan Sadgir
MGV'S L.V.H.Arts, Science and Commerce College

Bapu Sonu Jagdale
Mahatma Gandhi Vidyamandir's Arts Science and Commerce College, Manmad

STRUCTURAL, VIBRATIONAL AND CHEMICAL REACTIVITY STUDIES OF (2-(4-CHLOROPHENYL)-5-(4-METHYLPHENYL)-1,3,4-OXADIAZOLE

Sunil L. Dhonnar [1*], Vishnu A. Adole [2], Nutan V. Sadgir [3], Bapu S. Jagdale [1]

[1] *Department of Chemistry, L.V.H. Arts, Science, and Commerce College, Panchavati, Nashik (M.S) India*

[2] *Department of Chemistry, Arts, Science, and Commerce college, Surgana , Dist.-Nashik (MS) India*

[3] *Departments of Chemistry, S.P.H. Arts, Science, and Commerce Mahila Mahavidyalaya, Malegaon, Dist.-Nashik (MS) India*

ABSTRACT:

2-(4-chlorophenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole (CPMPO**)** has been synthesized and characterized by spectroscopic techniques. The structural properties of the molecule in the ground state have been calculated using DFT employing B3LYP/6-311++G(d,p) basis set. The fundamental vibrational wavenumbers, as well as their intensities, were computed with same level of theory. The observed and scaled wavenumbers were found to be in excellent agreement. In addition, the frontier molecular (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbital were analyzed. The calculated HOMO and LUMO energies show that charge transfer occurs within the title molecule. Using Molecular electrostatic potential plot and Mulliken charges, we have investigated potential reactive sites in the title molecule. Negative electrostatic potential regions are mostly clustered over the nitrogen atoms of oxadiazole ring, and they may be candidates for an electrophilic attack.

KEYWORDS:

DFT, FT-IR, UV–Visible, HOMO-LUMO

1. INTRODUCTION

The scientific community has been drawn to 1,3,4-oxadiazole derivatives, which have special structural characteristics among the five-member heterocyclic compounds. It has been reported that 1,3,4-oxadiazole derivatives have antimicrobial [1,2], anti-inflammatory [3-4], antitubercular [5], antidiabetic [6], analgesic [3,7], anticonvulsant [8] and anticancer activities [9]. In addition, they have attracted significant interest in polymer science and pesticide chemistry [10].In the fields of chemical, biological, and material sciences, computational chemistry is becoming increasingly importance. Recently, the dentistry functional theory (DFT) has made considerable advances in organic synthesis and is used for computing the electronic and geometrical properties. Density functional theory is now widely used to estimate molecular properties such as molecular structures, spectral bands, dipole moment, etc. The B3LYP functional have been found to be the most typically used level of theory for DFT simulations in order to analyze various optical, spectral, and charge density properties of large and small molecules [11-14]. In present study, we wish to report, synthesis and theoretical study of 2-(4-chlorophenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole. For theoretical study, the DFT method with the B3LYP functional and 6-311++G (d,p) basis set have been used. The ground state optimized geometries, vibrational wave numbers and molecular reactivity parameters of title molecule investigated and studied.

2. EXPERIMENTAL DETAILS

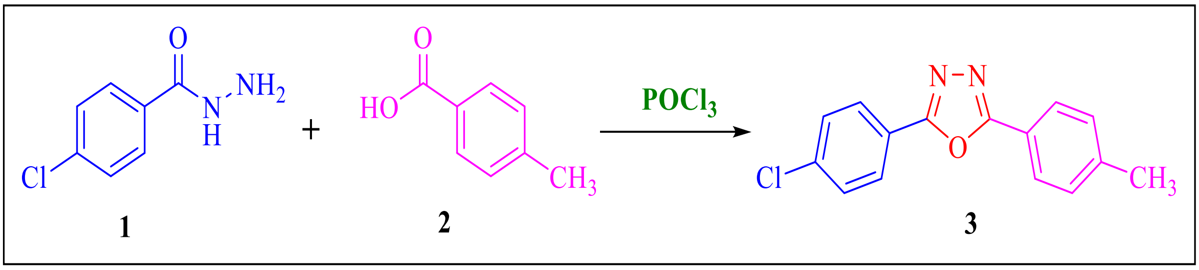
2.1. Physical Measurements

Melting point was measured by using open capillary method and uncorrected. The ^1H nuclear magnetic resonance spectra were recorded on a Bruker 500 MHz spectrometer, where TMS as an internal standard and $CDCl_3$ as solvent were used. The FT-IR spectrum was measured at room temperature on Schimadzu spectrometer in the region of 4000-400 cm^{-1}. All chemicals were purchased from commercial suppliers.

2.2. Synthesis 2-(4-chlorophenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole

4-Chlorobenzohydrazide (0.001 mole) with 4-Methylbenzoic acid (0.001 mole) were dissolved in phosphorous oxychloride (10 ml) and refluxed for 3 h. Reaction mixture was concentrated using a rotor evaporator, the residue was quenched with ice water and the solid separated was filtered off, washed with water and further purified by recrystallization with isopropanol to afford pure 2-(4-chlorophenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole moiety as white crystalline solid. The synthetic method and structures of the **CPMPO** used in the present work are shown in **Scheme 1.**

Yield: 88 %, FT-IR (KBr, in cm^{-1}): 2918,2947 (CH_3 str.), 1602(C=C), 1548 (C=N), 732 (C-Cl). ^1H NMR (500 MHz, $CDCl_3$, in δ) δ 8.10 -8.07 (m, 2H), 8.03 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.1, 2H), 7.35 (m, 2H), 2.45 (s, 3H).



Scheme 1: Synthesis of 2-(4-chlorophenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole (CPMPO)

2.3. Computational details

The software packages Gaussian 03W [15] and Gauss view 4.2 [16] were used to optimize the structure of CPMPO molecule. We use the DFT/B3LYP [17, 18] method with the 6-311++G (d, p) basis functional set for all these calculations. A frequency assessment was conducted at the same theory level to validate the stability of the reliable and able with the optimized geometries. The scale factors 0.9613 [19] are being used to achieve harmony between empirical values and theoretical harmonic frequencies. Mulliken charges, dipole moment, energy optimization, HOMO-LUMO analysis, Global chemical reactivity descriptor, and molecular electrostatic potential map (MESP) for **CPMPO** molecule were evaluated and recorded using the same theory.

3. Result and discussion

3.1. Optimized Molecular geometry

The molecular structure formed after optimization is shown **Fig.1**. The selected geometric parameters of molecules in the gas phase are included in **Table 1**. The Optimized structure consists of oxadiazole and two phenyl rings (Ph1: C12, C13, C14, C15, C17, C19; Ph2: C1, C2, C3, C4, C5, C24). The optimized structure is found to be with C1 point group symmetry having its ground state energy of -1223.360699 a.u. with dipole moment of 3.985345 Debye. The C-C bond lengths in phenyl rings constituting the molecule vary between 1.3879 and 1.4027 in PhI ring; 1.3912 and 1.4031 in PhII ring. If the dihedral angles between three rings are analyzed, we can conclude and say, that they are on the same plane. The C-Cl bond lengths are found within the expected range. The Bond lengths of C11-N23 (1.2996 Å) and C9-N22 (1.2988 Å) bonds in the oxadiazole ring show a double bond character. The ring C-H bond distance lies in the range of 1.0955-1.0823 Å.

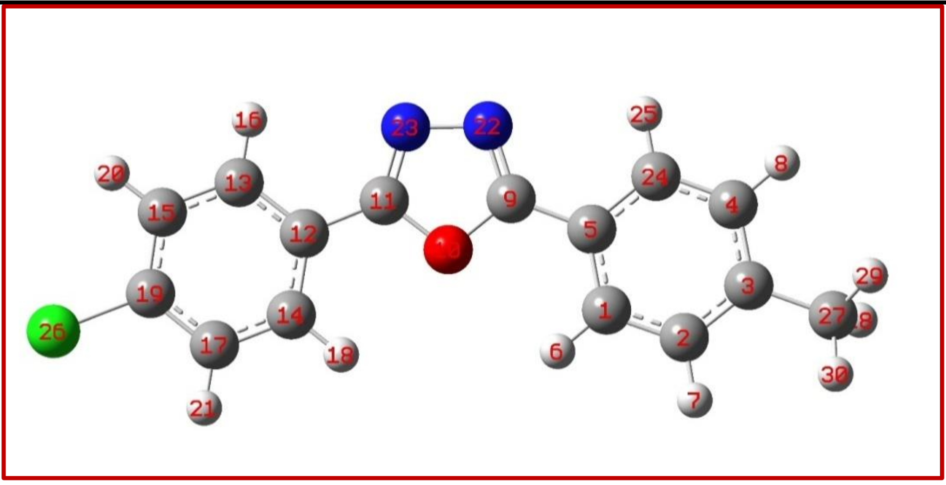


Fig. 1: The molecular structures of CPMPO molecule obtained by DFT/B3LYP/6-311G++ (d, p) method.

Table 1: Some selected structural parameters of CPMPO molecule calculated by DFT/B3LYP/6-311++G (d, p) methods

Connectivity	Bond length [Å]	Connectivity	Bond angle	Connectivity	Dihedral angle [°]
C1-C2	1.3912	C2-C1-C5	120.16	C5-C1-C2-C3	-0.0783
C1-C5	1.3997	C2-C1-H6	119.93	C5-C1-C2-H7	179.8076
C1-H6	1.083	C5-C1-H6	119.90	H6-C1-C2-C3	-179.8957
C2-C3	1.3983	C1-C2-C3	121.25	H6-C1-C2-H7	-0.0097
C2-H7	1.0849	C1-C2-H7	119.24	C2-C1-C5-C9	-179.8642
C3-C4	1.4022	C3-C2-H7	119.49	C2-C1-C5-C24	-0.0736
C3-C27	1.5081	C2-C3-C4	118.03	H6-C1-C5-C9	-0.0467
C4-H8	1.0852	C2-C3-C27	121.19	H6-C1-C5-C24	179.7439
C4-C24	1.387	C4-C3-C27	120.77	C1-C2-C3-C4	0.2362
C5-C9	1.4552	C3-C4-H8	119.43	C1-C2-C3-C27	-179.8034
C5-C24	1.4031	C3-C4-C24	121.34	H7-C2-C3-C4	-179.6494
C9-O10	1.3676	H8-C4-C24	119.21	H7-C2-C3-C27	1.311
C9-N22	1.2988	C1-C5-C9	121.48	C2-C3-C4-H8	179.6348
O10-C11	1.3659	C1-C5-C24	119.10	C2-C3-C4-C24	-0.2491
C11-C12	1.4559	C9-C5-C24	119.41	C27-C3-C4-H8	-1.3213
C11-N23	1.2996	C5-C9-O10	119.70	C27-C3-C4-C24	178.7947
C12-C13	1.4027	C5-C9-N22	128.67	C2-C3-C27-H28	100.102
C12-C14	1.4005	O10-C9-N22	111.61	C2-C3-C27-H29	-140.5797
C13-C15	1.3879	C9-O10-C11	102.92	C2-C3-C27-H30	-19.6733
C13-H16	1.0827	O10-C11-C12	119.74	C4-C3-C27-H28	-78.9114
C14-C17	1.3907	O10-C11-N23	111.76	C4-C3-C27-H29	40.4069
C14-H18	1.0827	C12-C11-N23	128.48	C4-C3-C27-H30	161.3133
C15-C19	1.3939	C11-C12-C13	119.27	C3-C4-C24-C5	0.1034
C15-H20	1.0824	C11-C12-C14	121.363	C3-C4-C24-H25	179.9136
C17-C19	1.3914	C13-C12-C14	119.366	H8-C4-C24-C5	-179.7808

C17-H21	1.0823	C12-C13-C15	120.4316	H8-C4-C24-H25	0.0294
C19-Cl26	1.7551	C12-C13-H16	119.2628	C1-C5-C9-O10	-0.0964
N22-N23	1.3885	C15-C13-H16	120.3056	C1-C5-C9-N22	179.9221
C24-H25	1.0829	C12-C14-C17	120.4691	C9-C5-C24-C4	179.8561
C27-H28	1.0955	C12-C14-H18	119.9644	C9-C5-C24-C25	0.043
C27-H29	1.0926	C17-C14-H18	119.5666	C5-C9-O10-C11	-179.9892
C27-H30	1.0918	C13-C15-C19	119.3116	N22-C9-O10-C11	-0.0047

3.2. Vibrational spectra

The IR calculations of **CPMPO** molecule were performed in gas state by DFT/B3LYP/6-311++G (d,p) method. The Selected theoretical (scaled) and experimental vibrational wavenumbers (in cm^{-1}) with their assignment are given in **Table 2.** The experimental and simulated spectrums are shown in **Fig. 2.** The Gauss-view program was used to assign the calculated harmonic vibrational wavenumbers. The aromatic C-H stretching vibrations were normally seen in the region above 3100-3000 cm^{-1} [20] In the present case, the aromatic C-H stretching vibrations was observed at 3031 cm^{-1} in experimental spectra.; Theoretically, it calculated at 3041 cm^{-1}. The In-plane C-H bending vibrations for aromatic ring experimentally observe at 1267,1213,1168,1082 cm^{-1} shows good correlation with computed vibrations at 1271,1234,1161,1082 cm^{-1}. Similarly, the out of plane vibrations for aryl rings observe at 956, 829, 690 cm^{-1} agreed with computed 955,822,684 cm^{-1} infrared vibrations. Aromatic ring C-C stretching vibration generally occurs in the region 1625-1430 cm^{-1}. The C=C stretching modes experimentally observed at 1602, 1548 and 1483 cm^{-1} and by the DFT method it observed at 1589, 1548 and 1468 cm^{-1} for PhI and PhII. The bands observed at 1548 and 1483 cm^{-1} are assigned to C=N stretching vibration, however theoretically these bands are observed at 1548 and 1468 cm^{-1} shows excellent agreement with the experimental ones. The CH$_3$ group stretching vibrational mode was computed at 2957 cm^{-1} and 2906 cm$^{-1.}$ In recorded spectra, this peak was shown at 2947 and 2918 cm^{-1} respectively. The in-plane bending vibrations for the CH$_3$ group were observed in the spectrum at frequency 1413 cm^{-1} and it is lower than theoretically obtained vibration at 1430 cm^{-1}. The out plane bending vibration (rocking) for the CH$_3$ group was observed in the spectrum at frequency 1006 cm^{-1} and by theoretically obtained at 1019 cm^{-1} shows good correlation. The C-Cl stretching band normally expected around 750-580 cm^{-1}.In present study C-Cl stretching vibration observe at 732 cm^{-1} and calculated at 726 cm^{-1}.

Table 2: The observed FT-IR and calculated [B3LYP/6-311++G (d, p) level] frequencies along with their selected assignments of the CPMPO molecule

Mode	Scaled	Intensity	Experimental	Assignment
77	3041	15.17	3031	υ CH PhII
75	2957	17.05	2947	υ CH_3
74	2906	30.58	2918	υ CH_3
73	1589	35.89	1602	υ C=C PhII
70	1548	5.237	1548	υ C=N (Oxa.) + υ C=C PhI & II
67	1468	103.7	1483	υ C=N (Oxa.) + υ C=C PhII
64	1430	7.899	1413	asym. deform.CH_3
57	1271	0.756	1267	β CH PhI
55	1234	4.894	1213	υ CC + v CO + β CH PhII
53	1161	12.88	1168	β CH PhII
49	1083	12.10	1082	β CH PhI + υ N-N
46	1019	13.28	1006	γ CH_3
41	955	0.325	956	γ CH PhII
35	822	7.916	829	γ CH PhII
30	726	42.60	732	υ C-Cl
27	684	4.322	690	γ CH PhI & II

υ - stretching; asym-asymmetric; sym-symmetric; def-deformation; β-in-plane bending; γ-out of plane bending, Γ- torsion, oxa-oxadiazole ring.

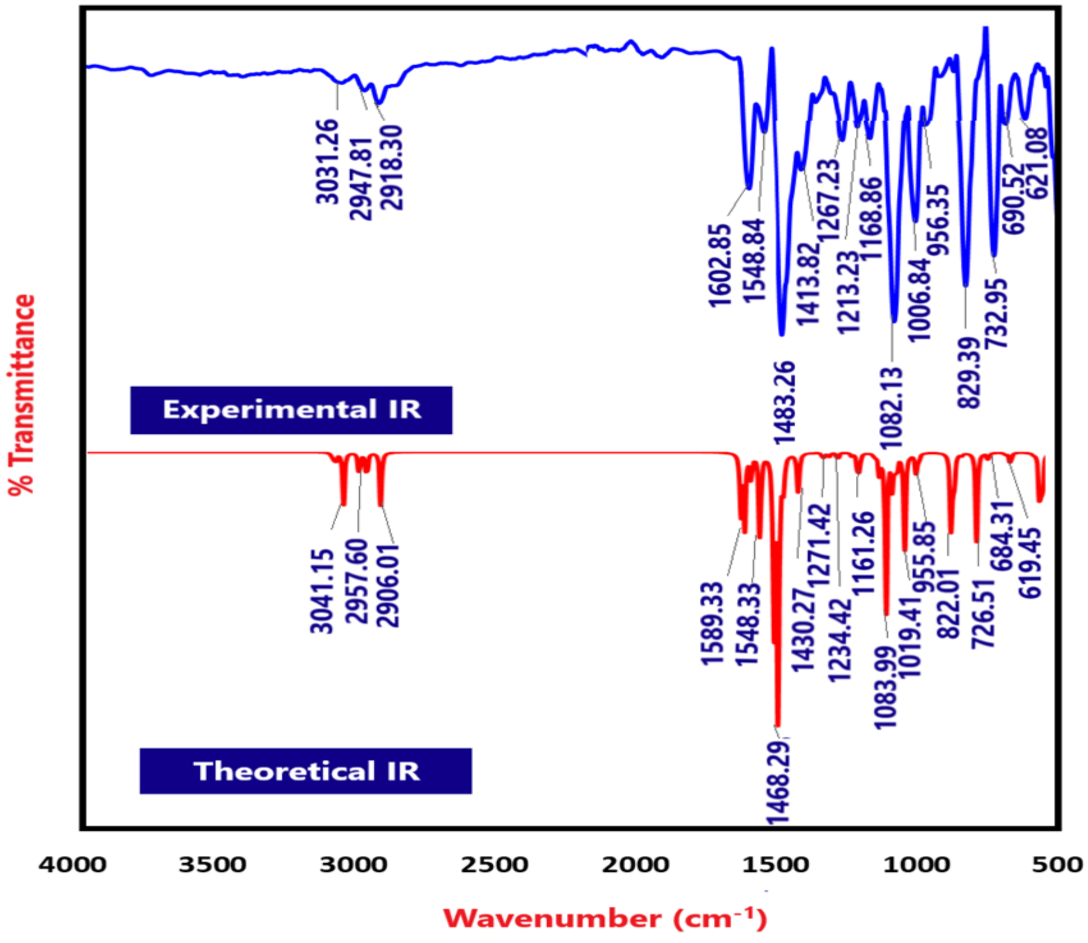


Fig. 2: Experimental & Theoretical IR spectrum of CPMPO molecule

3.3. Frontier molecular orbitals and Global Chemical Reactivity Parameters

The frontier molecular orbitals HOMO and LUMO refer to the highest occupied and lowest unoccupied molecular orbitals, respectively. The frontier molecular orbital energies have been calculated with B3LYP/6-311G++(d, p) level of theory in the gaseous phase. The pictorial representation of the HOMO and the LUMO is shown in **Fig.3.** The energies of the HOMO and the LUMO as well as the energy gap between the HOMO and the LUMO are a critical parameter in determining molecular electrical transport properties and chemical reactivity of the molecule. The energy gap values in the CPMPO molecule is 4.374 eV. From theses calculated energy gap between two orbitals, it can be decided; whether the compound is hard or soft. If energy difference is high, the molecule is hard and more stable, if difference is low; the molecule is soft and can be more polarized. By using the defined expressions and equations in the literature [21-25] the following energy parameters were calculated and are given in **Table 3.** It is seen that the chemical potential of the CPMPO molecule is negative and it means that the compound is stable.

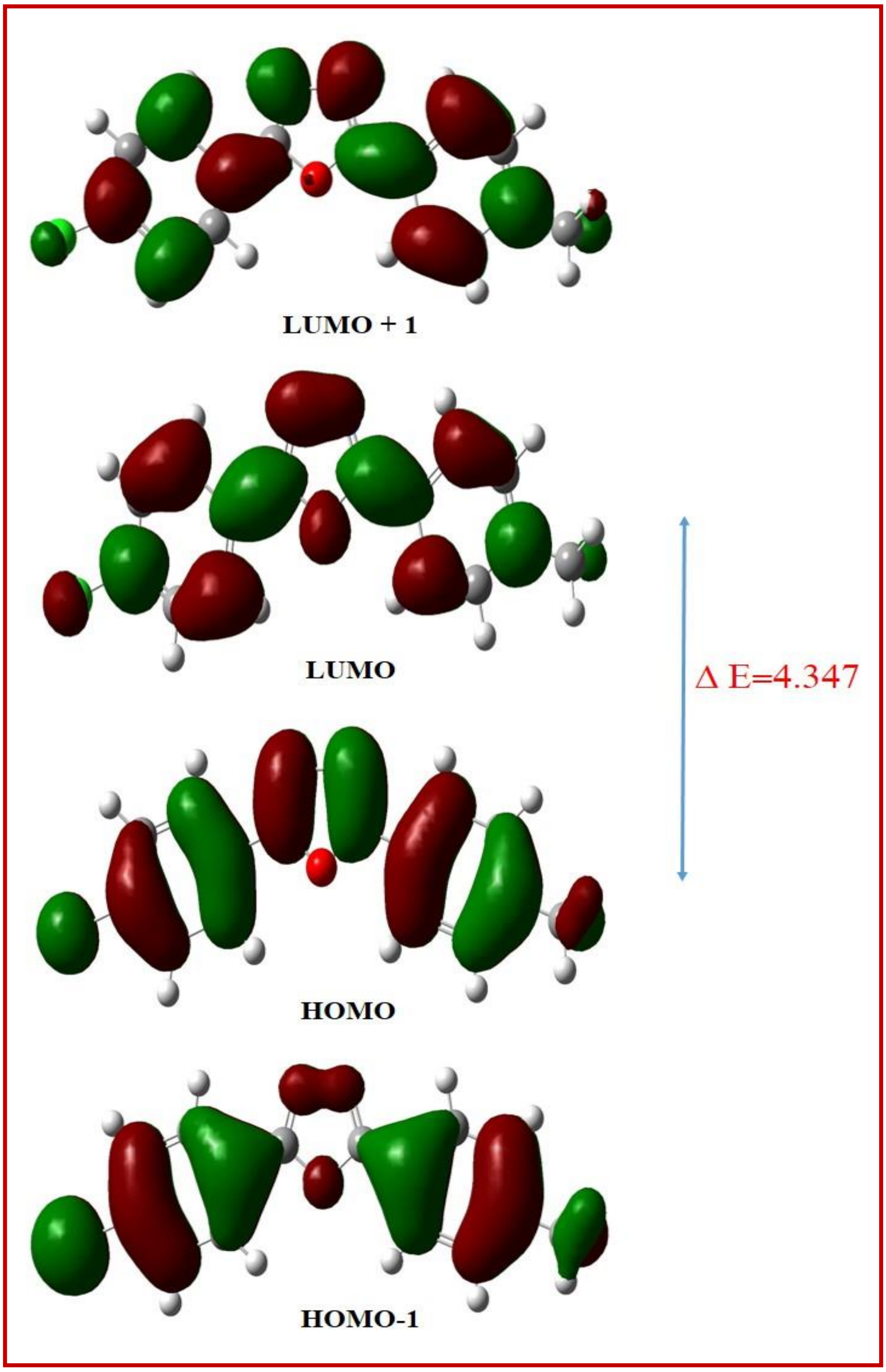


Fig. 3: Frontier molecular orbitals surface and energy gap for CPMPO Molecule

Table 3: The HOMO–LUMO energy and reactivity descriptor values of the CPMPO Molecule are calculated in the gas phase

Molecular properties	GAS
E_{LUMO} energy (eV)	-2.105
E_{HOMO} energy (eV)	-6.452
E_{LUMO+1} energy (eV)	-1.377
E_{HOMO-1} energy (eV)	-7.421
Δ E= $E_{LUMO} - E_{HOMO}$ energy gap (eV)	4.347
Electron affinity **A**	2.105
Ionization energy **I**	6.452
Chemical hardness **η** (eV)	2.173
Chemical Softness **S** $(eV)^{-1}$	0.46
Chemical potential **µ** (eV)	- 4.279
Electrophilicity index **ω** (eV)	4.211

3.4. Mullikan atomic charges and MESP surfaces

The Mulliken atomic charge calculation plays an important role in the application of Quantum theory based calculation of molecular system because it affects the properties such as dipole moment, molecular electrostatic potential surface [26]. Mulliken charge is shown in **Table 4**. In CPMPO molecule, amongst the all carbon atoms C17 bears highest negative charge (-0.784174) and C5 has highest positive charge (0.775893).The C5 and C12 atom is more positive charge due to the entire charge of the carbon is distributed in the ring as well as it is like a bridge between the phenyl ring and oxadiazole ring.

Table 4: Mullikan Atomic Charges

Atom	Charge	Atom	Charge
1 C	-0.497638	16 H	0.224851
2 C	-0.617882	17 C	-0.784174
3 C	0.596587	18 H	0.142074
4 C	-0.603449	19 C	0.535170
5 C	0.775893	20 H	0.189168
6 H	0.123142	21 H	0.201046
7 H	0.169990	22 N	-0.079266
8 H	0.169653	23 N	0.031154
9 C	0.425548	24 C	-0.407208
10 O	-0.005078	25 H	0.204750
11 C	-0.167903	26 Cl	0.465897
12 C	0.534931	27 C	-0.547472
13 C	-0.607228	28 H	0.171171
14 C	-0.629101	29 H	0.146626
15 C	-0.629101	30 H	0.148806

The molecular electrostatic potential (MESP) is a plot of electrostatic potential mapped on constant electron density surface. The MESP is very important in the study of molecular interactions, hydrogen bonding interactions prediction of relative sites for nucleophilic and electrophilic attack. [27, 28]. In **Fig. 4**, the molecular electrostatic potential map (MESP) is given framed on the structure optimized at DFT/B3LYP/6-

311++G (d, p) theory level in the gas phase. The electrostatic potentials at the surface are represented by different colors; red, blue and green represent the regions of negative, positive and zero electrostatic potential respectively. The negative regions V(r) were related to electrophilic reactivity (H acceptor) and the positive ones to nucleophilic reactivity (H donor). As the MESP is analyzed which shows three dimensional charge distribution of the molecule, it can be seen that negative regions are located on N-N bond of oxadiazole ring. On the other hand, positive region represented by blue is mainly located on all hydrogen atoms.

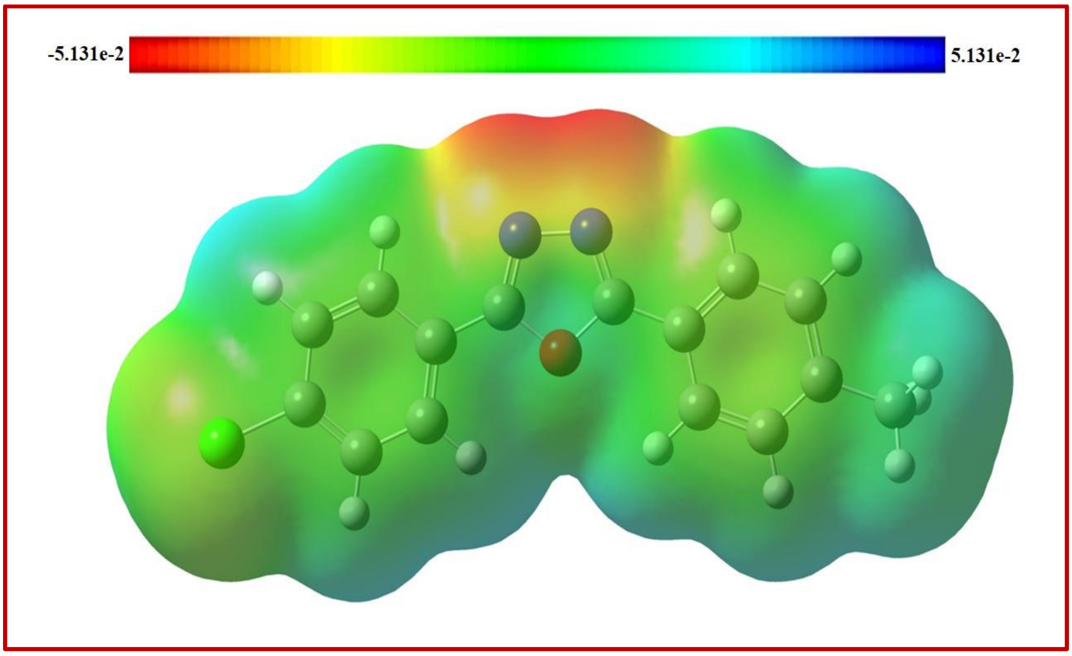


Fig. 4: The MESP map of the CPMPO Molecule.

CONCLUSION

In conclusion, 2-(4-chlorophenyl)-5-(4-methylphenyl)-1, 3, 4-oxadiazole was synthesized and analyzed by using experimental and computational chemistry approach. The DFT/B3LYP method with a 6-311++G (d, p) basis set in the gas phase was used to measure the structural, vibrational, molecular electrostatic potential and reactivity parameters. With ground state energy of -1223.360699 a.u. and a dipole moment of 3.985345 Debye, the optimized structure is found to have C1 point group symmetry. A very good correlation has been obtained between the scaled and experimental vibrational data at DFT/B3LYP method with a 6-311++G (d,p) basis set. Frontier molecular orbital and global chemical reactivity parameters have also been reported in the gas phase. It indicates that the title molecule possesses good strength and stability. From FMO energy data, it has been revealed that the title molecule has an energy gap of 4.374 eV. As shown in the molecular electrostatic potential diagram, the negative electrostatic potential regions are primarily distributed over the nitrogen atoms of the oxadiazole ring and are site for an electrophilic attack. All theoretical findings, in general, indicate strong agreement with experimental evidence.

ACKNOWLEDGEMENT

The authors acknowledge the central instrumentation facility (CIF), Savitribai Phule Pune University, Pune and KTHM College Nashik for spectral analysis. The authors are also grateful to Ex-Professor Dr. A. B. Sawant for the Gaussian study. Dr. Apoorva P. Hiray, Coordinator, M. G. Vidyamandir institute, is gratefully acknowledged for the Gaussian package.

CONFLICT OF INTEREST:

The authors declare that they have no conflict of interests.

REFERENCES:

1) Kagthara PR, Shah NS, Doshi RK, Parekh HH. *Indian J. Chem.*, 1999; **38B**:572-576.
2) Kumar VL, Naik PJ, Naveen M, Chandrasekhar T, Reddy AB. *Indian J. Chem.*, 2014; **53B**:208-211.
3) Amir M, Saifillah K, Akhter W. *Indian J. Chem.*, 2011; **50B**:1107-1111.
4) Singh A, Lohani M, Parthsarthy R. *Iranian J. Pharma. Res.*, 2013; **12 (2)**:319-323.
5) Pattan SR, Rabara PA, Pattan JS, Bukitagar AA, Wakale VS, Musmade DS. *Indian J. Chem.*, 2009; **48B**: 1453-1456.
6) Husain MI, Kumar A, Srivastava RC. *Current Sci.*, 1986; **55**:644–646.
7) Husain A, Ahmad A, Alam M, Ajmal M, Ahuja P. *Eur. J. Med. Chem.* 2009; **44**:3798-3804.
8) Almasirad A, Tabatabai SA, Faizi M, Kebriaeezadeh A. *Bioorg. Med. Chem. Lett.*, 2004; **14(24)**:6057-6059.
9) Sengupta P, Dash D, Yeliger CY, Myrugesh K. *Indian J. Chem.*,2008;**47B**:460-462.
10) Xiumian Z, Zhong L, Yanli W, Weidong C,Qingchun H, Chuanxiang L, Gonghua S. *J. Fluor. Chem.*, 2003; **123:163**–169.
11) Dhonnar SL, Jagdale BS, Sawant AB, Pawar TB, Chobe SS. *Der Pharma Chemica*, 2016; **8 (17):**119-128.
12) Sawant AB, Nirvan R.S. *Ind. J. Pure & Applied Physics*, 2012; **50:**308-313.
13) Patel UH, Gandhi SA, Patel BD,Yadav J, Desai KR. *Ind.J.Pure & Applied Physics*, 2013; **51:**819-826.
14) Sundaraganesan N, Meganathan C, Joshua BD, Mani P, Jayaprakash A. *Spectrochim. Acta Part A.* 2008, **71**, 1134-1139.
15) Frisch, M. J. et al. Gaussian 03, Revision E.01, Gaussian, Inc. Wallingford CT, 2004.
16) Dennington R, Keith T, Millam J. Gauss View, Version 4.1.2. Semichem Inc. Shawnee Mission, KS, 2007.
17) Becke AD. *J. Chem. Phy.*, 1993; **98(7)**:5648-5652.
18) Lee C, Yang W, Parr RG. *Phy.Review B*.1988; **37**:785-789.
19) Foresman JB, Frisch AE. Exploring chemistry with electronic structure methods (2nd Edn. Gaussian, Inc. Pittsburgh; PA), 1996.
20) Roeges NPG. A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures. New York: Wiley; 1994.
21) Koopmans TA. *Physica*., 1934; **1:104**-133.
22) Pearson RG. *J. Org. Chem*., 1989; **54:1423**-1430.
23) Parr RG, Sznetpaly LV, Liu SJ. *J. Am. Chem. Soc.*, 1999; **121(9)**:1922-1924..
24) Chattaraj PK, Giri S. *J. Phy. Chem. A.*, 2007;**111**:11116-11126.
25) Chattaraj PK, Maiti SU, *J. Phy. Chem. A.*,2003;**107(25)**:1089-5639.
26) Gunasekaran S,Kumaresan S, Arunbalaji R, Anand G, Srinivasan S. *J.Chem.Sci.*,2008; **120 (3)**:315-324.
27) Murray JS, Sen K. Molecular Electrostatic, Potentials Concepts and Applications, Amsterdam:Elsevier;1996.
28) Scrocco E, Tomasi. *Adv. Quantum Chem.*,1978;**11**:115-193.