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Quantum Computational on Structural and Electronic Properties of Quinoxaline Derivative

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ABSTRACT

In this work, we conducted a comparative analysis among toluene, chloroform and pentanol through theoretical analysis of 2-chloro-5,6-dimethyl-3-(methylsulfanyl) quinoxaline (2Cl5,6Dm3MsQ) molecule with the help of Gaussian 09 software, the geometry of the molecule is optimized and studied the geometric properties using density functional theory (DFT) method. By using DFT method the Mulliken charge distribution of 2Cl5,6Dm3MsQ molecule, highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) analysis of the molecule in different solvent atmosphere which are used to establish the energy band gap and the stability of the molecule are analysed. Potential distribution and density distribution of the titled molecule is analysed by the surface mapping to understand the reactivity of the molecule. From all the findings we observed that, the 2Cl5,6Dm3MsQ molecule has good kinetic stability, by the optical property study we can also ensure that, the molecule may have good biological properties and may also use in optoelectronic devices.

1. Introduction

The fluorescent organic molecule has been intensively used in the biochemical, medicinal, and synthetic organic chemistry areas [1, 2]. They are frequently employed in medicines, food, fragrances and optical brighteners used as fluorescent laser dyes. Organic molecules with good physicochemical properties also have good antibiotic properties. The molecule with nitrogen group is having the ability to treat the cancer cells.

The study of molecular stability and reactivity are important elements in drug design which is supported by density functional theory (DFT) and it also predicts structural aspects in an affordable manner with experimental data [3].DFT analysis of the probe produced fruitful development for optoelectronic applications. This research primarily focuses on the theoretical analysis for molecular optical parameters to understand, how the structure affects the interactions between solutes and solvents [4]. We can observe the progression of an electron from the HOMO to LUMO, leading to frontier molecular orbital (FMO) study. Additional medical uses for this organic molecule include their ability to serve as antidepressants, antimicrobials, anti-oxidants and anti-inflammatory agents [5].

2. Computational details

The Gaussian 09 software package has been used for all computational research [6] using the DFT approach, the molecule's geometry was optimized during the vacuum phase. Becke's 3 functional exchange factor (B3) and non-local correlation functional are combined in the well-known functional Becke's 3 Lee, Yang, and Parr (B3LYP) [7]. B3LYP is implemented in combination with the triple zeta set together with the 6-311+G (d,p) diffuse and polarization parameters to examine structural characteristics. The Mulliken charge distribution, FMO analysis and molecular electrostatic potential studied cases [8-11].

3. Results and analysis

Geometry of the molecule has been confirmed by optimizing the structure and analysing the bond length, bond angle and dihedral angle of the molecule, charge and potential distribution of the molecule and also explained the inter molecular interactions and electrophilic and nucliophilic sites. Frontier molecular orbital studies help to know the kinetic stability of the molecule and energy band gap. In these studies we have chosen toluene, chloroform and pentanol solvents because of similar refractive index (≈1.4) with increase in polarity.

3.1 Structural properties

The structure of 2Cl5,6Dm3MsQ molecule was drawn using Gauss view 5.0 for the molecule (2Cl5,6Dm3MsQ) was obtained and compared with standard parameters [12-14]. Then decreased the energy to a minimum in the gas phase by density functional theory with B3LYP/6-311+G(d,p) level by Gaussian 09. The optimized geometry of the molecule is shown in Figure 1.

The bond length of C-S (13S-10C and 15C-13S) bonding shows the highest value of 1.79 Å and 1.83 Å, the 9C-14Cl shows a bond length of 1.76 Å. Between carbon and hydrogen the bond length is less compared to C-C, C-N, C-Cl and C-S. The bond angle of the atoms of methyl group shows the values between 110.6 ºC to 111.46 ºC. The 2Cl5,6Dm3MsQ molecule has two methyl (CH3) groups

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got high polarity in pentanol than other solvents and the number of cycles taken to optimize the structure is comparatively more in pentanol than other solvents due to its more atomic sites. Bond angle between the atoms which are joined with methylsulfanyl group shows less value compared with other atoms. Dihedral angle is observed to be less inside the benzene rings due to boat like structure [15-16].

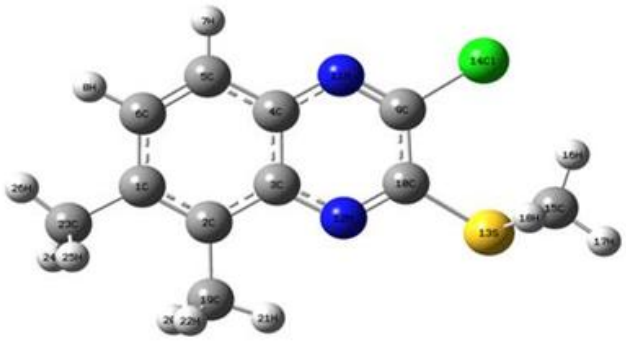

Figure 1. Optimized geometry of 2Cl5,6Dm3MsQ molecule.

3.2 Mulliken atomic charge distribution

The atomic charge distributions are useful for knowing the stability of the probe, atomic charge effect, polarizability of the molecule and also give us the knowledge of acceptor and donor atoms [17]. Mulliken atomic charge at each atomic site of 2Cl5,6Dm3MsQ by using DFT method and B3LYP functional with 6-311+G(d, p) basis set, which calculated in toluene, chloroform and pentanol solvents. Molecular charge distribution in different solvent atmosphere data listed in Table 1. From these studies, it was observed that all the hydrogen and sulphur (13S) atoms were acts as acceptors, nitrogen (11N, 12N) and chlorine (14Cl) acts as donor atoms. The carbon atoms which are in bonding with nitrogen but not sulphur (3C, 4C, 9C) are acts as donor and carbon atoms which share the bond with hydrogen and sulphur (1C, 2C, 5C, 6C,11C, 12C, 14C, 15C, 19C, 23C and 10C) acts as acceptors. It is observed that atomic charges of C, H, N and Cl atoms were increases with solvent polarity for 2Cl5,6Dm3MsQ and the similar trends are observed in 2-(3-oxo- 3H-benzo[f]chromen-1-ylmethoxy)-benzoic acid methyl ester (2BME) and 6-amino-3-methyl-4-(4-nitrophenyl)-1,4-dihydropyrano [2,3-c]pyrazole-5-carbonitrile (NDPPC) molecules [18-19]. Mulliken atomic charge of all the atoms shows less value in Toluene medium compared to Chloroform and Pentanol, it is found that, the charge increses with solvent polarity.

3.3 FMO and Optoelectronic Properties

The detailed information on transition states, energy values, and structural representations are analysed by the Frontier molecular orbital (FMO) study using DFT. The electrons occupied and unoccupied (electron affinity and donating) sites are obtained by using the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The compression between the HOMO and LUMO energies of the corresponding medium determines the energy band gap (E_g) [20].

Energy band gap of 2Cl5,6Dm3MsQ molecule in toluene, chloroform and pentanol solvents were studied and presented in Figure 2. Molecule in toluene shows lowest energy gap than the other solvents (6.3244 eV) compared to E_g in chloroform is 6.3445 eV and pentanol is 6.3595 eV.

Table 1: Mulliken atomic charges of 2Cl5,6Dm3MsQ by DFT method in different solvents.

Atoms	Mulliken atomic charge		
	Toluene	Chloroform	1-Pentanol
1C	-0.12031	-0.12111	-0.12160
2C	-0.07309	-0.07381	-0.07431
3C	0.10481	0.10645	0.10754
4C	0.13016	0.13273	0.13450
5C	-0.05321	-0.05683	-0.05947
6C	-0.05645	-0.05754	-0.05797
7H	0.11032	0.11198	0.11313
8H	0.10435	0.10916	0.11275
9C	0.08413	0.08642	0.08791
10C	-0.00651	-0.00176	0.00155
11N	-0.28321	-0.28963	-0.29431
12N	-0.29795	-0.30271	-0.30620
13S	0.12007	0.10855	0.09979
14Cl	-0.06229	-0.06597	-0.06872
15C	-0.45223	-0.45154	-0.45093
16H	0.16531	0.16680	0.16794
17H	0.15903	0.16253	0.16511
18H	0.15690	0.15976	0.16191
19C	-0.24344	-0.24361	-0.24369
20H	0.12703	0.12966	0.13164
21H	0.13389	0.12953	0.12611
22H	0.12490	0.12785	0.13012
23C	-0.25107	-0.25177	-0.25216
24H	0.13163	0.13333	0.13460
25H	0.13204	0.13393	0.13536
26H	0.11514	0.11753	0.11933

The 2Cl5, 6Dm3MsQmolecule in different medium shows, the different ionization potential (I), electron affinity (E), chemical hardness (η), chemical potential (μ), chemical softness (s), global electrophilicity(ω) according to its solvent polarity [21]. These optoelectronic parameters of 2Cl5,6Dm3MsQ molecule given in the Table 2. The molecule with higher bond gap shows the highest chemical hardness, all the studied properties were directly proportional to the polarity of the medium and molecule in pentanol solvent shows higher bond gap.

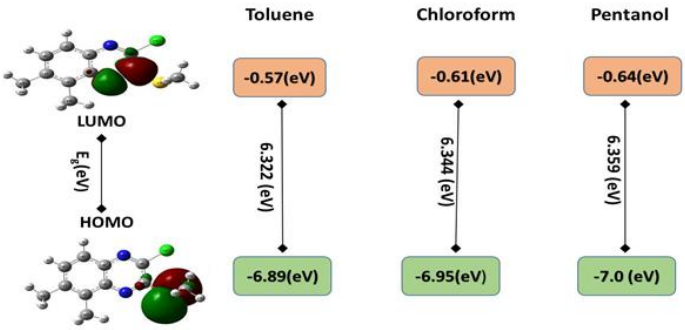

Figure 2: Energy band gap of 2Cl5,6Dm3MsQ molecule in different solvents.

The optoelectronic properties of this molecule give us the parameters in different solvents [22] (Table 2). It is observed that, the lower value are found in toluene and higher results are observed in case of pentanol solvent, which are helpful for optoelectronic applications. Electrostatic potential (ESP), total electron density (TED) and molecular electrostatic potential (MEP) studies of the quinoxaline derivative [23].

3.4 Density and molecular potential distribution mapping

The surface mapping of the 2Cl5,6Dm3MsQ molecule is presented in Figure 3. Total Electron Density (TED) of molecule represents the density distribution of the molecule, which shows uniformity on the entire structure and density distribution mapping illustrates the homogeneity of the compound's surface (Figure 3(a)), which shows that, the total electron density distribution all over the molecular surface uniformly which also shows the solvent accessibility mapping. The Molecular Electrostatic Potential (MEP) of 2Cl5,6Dm3MsQ molecule in toluene, chloroform and pentanol were shown in Figure 3(b), red colour surrounds the nitrogen atoms were represents the minimum potential region, green colour inside the benzene rings represents the zero potential region and blue colour near the hydrogen atoms shows the maximum potential regions. The electrostatic potential map (ESP) of the molecule with energy range is shown in Figure 3(c), the colour of the potential mapping surface varies from red to blue the energy values of molecule in toluene ranges from -4.052 eV to 4.052 eV, for chloroform –4.067eV to 4.067eV and for pentanol the energy values starts with -4.063 eV to 4.063 eV. The positive values in ESP indicate the nucliophilic attack regions and negative areas which were electrophilic attack regions [24]. From the potential surface mapping, we observed that, the atomic site of nitrogen shows the electron rich position with highest negative charge the atomic sites of hydrogen atoms. It indicates that, the highest positive charge position with blue colour, by studying surface mapping, we can clearly understand the intermolecular interactions.

4. Conclusion

The theoretical studies of quinoxaline derivative (2Cl5,6Dm3MsQ) and its geometric properties of the synthesized molecules, Mulliken atomic charge distribution, frontier molecular orbital study with optoelectronic properties by using Kooper's theorem and molecular electrostatic potential by surface mapping. From the optimized geometry of this quinoxaline derivative, we observed that, the bond length between C-H is less than all other bonds like C-C, C-N, C-Cl, C-O and C-S.

We observed that, the slight increase in Mulliken atomic charge of hydrogen atoms, carbon atoms, nitrogen and chlorine atoms for all the studied molecules from alkanes (toluene and chloroform) to alcohol (pentanol) solvent with increases in solvent polarity. The molecule 2Cl5,6Dm3MsQ has highest energy, nuclear repulsion, zero point vibrational energy and heat capacity. From molecular orbital study of 2Cl5,6Dm3MsQ quinoxaline derivative in different mediums (toluene chloroform and pentanol) shows that, the band gap between different molecular orbital (HOMO to LUMO) is increases with solvent polarity. The optoelectronic properties like ionization potential (I), electron affinity (E), chemical hardness (η), chemical potential (μ), chemical softness (s), global electrophilicity (ω) were also directly affected by the solvent polarity (increases with increase in polarity of the medium). The total electron density of the molecule showed the uniform distribution throughout the surface of molecules. MEP helps in understanding of molecular parameters like charge density, polarity of the molecule, electrophilic and nucliophilic atomic positions of 2Cl5,6Dm3MsQ molecule by using the colour code. The molecule showing a good kinetic stability with effective optical property hence it may be used for optical property studies.

Table 2. Optoelectronic properties of 2Cl5, 6Dm3MsQ molecule in vacuum and different solvents.

Optoelectronic Parameters	Toluene	Chloroform	Pentanol
HOMO (eV)	-6.8950	-6.9581	-7.0076
LUMO (eV)	-0.5706	-0.6136	-0.6478
Energy band gap (E_g)	6.3244	6.3445	6.3597
Ionization potential (I)	6.8950	6.9581	7.0076
Electron affinity (A)	0.5706	0.6136	0.6478
Electronegativity (χ)	3.7328	3.7859	3.8277
Chemical hardness (η)	3.1622	3.1723	3.1798
Chemical potential (μ)	-3.7328	-3.7859	-3.827
Chemical Softness (s)	1.5811	1.5861	1.5899
Global electrophilicity (ω)	22.030	22.733	23.295

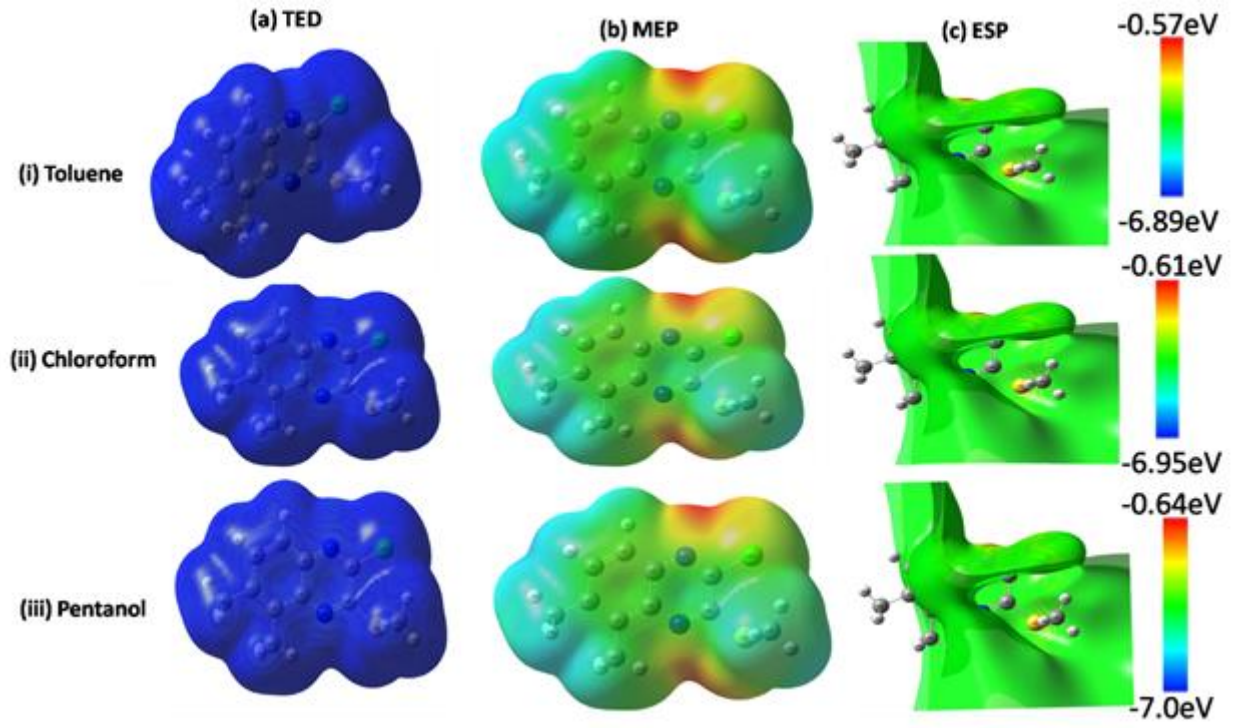

Figure 3. Surface mapping (a) Total electron density, (b) Molecular electrostatic potential map and (c) Electrostatic potential of 2Cl5,6Dm3MsQ Molecule in different solvents.

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