Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 15 (3, 4) 115-125: Fall 2018 & Winter 2019
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Theoretical Studies of Solvent Effects on the Electronic Properties of 1, 3-Bis [(Furan-2-yl) Methylene] Urea and Thiourea

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Received February 2019; Accepted August 2019

ABSTRACT

The synthesis and characterization of 1, 3-bis [(furan-2-yl) methylene] urea (BFMU) and 1, 3-bis [furan-2-yl) methylene] thiourea (BFMT) have been reported by our research team. The effects of solvents polarity on their electronic transition energies (HOMO-LUMO) and associated qualitative structure activity relationship parameters (i.e. log P, ionization energies and global hardness) were investigated in this study. The lower HOMO-LUMO energy gap values of BFMT (3.42 - 3.76 eV) in the solvents of choice (water, ethanol, toluene and dimethylsulphoxide) is an indication of higher distribution of charges and probability of higher activities of BFMT relative to BFMU with energy gap in the range: 4.27 - 4.54 eV. From the frontier molecular orbital study of BFMU, the HOMO centers over the entire molecule. However, the π- electrons of the LUMO are also over the entire molecule except one of the furan rings. Similar trends was observed for the HOMO of BFMT with electron delocalization excluding one of the furan ring, while the LUMO π- electrons system are more localized on the C=N, C=O and C-S bonds than the furan rings. These attest to the charge transfer (CT) characteristic properties of the compounds in the studied solvents. The $\log P_{octanol/water}$ values for the studied compounds which are less than 3, pointed to their usefulness in industrial development especially for agrochemical products.

Keywords: Urea; thiourea; frontier molecular orbital; logP and electron delocalization

1. INTRODUCTION

Solvation is an interaction of a solute with the solvent, which leads to stabilization of the solute species in the solution [1]. In the solvated state, an ion in a solution is surrounded or complexed by solvent molecules. Solvated species can be described by coordination number and the complex stability constants. The variation in solvent polarity and the type of solute-solvent interactions can affect the geometry, dipole moment, polarizability, hyper polarizability and other molecular properties [2, 3]. This is due to their variable interaction with the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO energy respectively), and hence influencing the stability and reactivity of the molecules.

Quantum chemical computational methods have proven to be an essential tool for interpreting and predicting the vibrational spectra. These are used to determine which of the terms will give a

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dominant contribution to the total spectra shift [4]. A significant advancement in this area was made by combining semi-empirical quantum mechanical method; ab-initio quantum mechanical method and density functional theory (DFT) [5].

DFT method has however been widely used for computation of molecular and vibrational frequencies, due to efficiency which leads to high accuracy as compared to other sophisticated methods [6]. Bands that are due to local transitions are solvent insensitive, whereas the charge transfer bands are sensitive to environmental changes. To understand the behaviour of a solvent in a process, it is of paramount importance to understand the solute-solvent interactions from liquids. The effects of the solvent dipolarity/ polarizability (non-specific interactions) and hydrogen bonding (specific solvent interaction) on the electronic absorption spectra can be interpreted using the Linear Solvation Energy Relationship (LSER) [7].

For many years the *n*-octanol/water partition coefficient (log P) has been used as a measure of lipophilicity/ hydrophobicity, where hydrophobicity describes the ability of organic compounds to aggregate in water, the lipophilicity is related to intermolecular combination of organic substance and solvent, as well as, the bioavailability, permeability and toxicity of drugs [8]. The coefficient obtained is usually quantified as log P, and is crucial to the molecular property determination in medicinal chemistry.

The aim of this study was to investigate the effects of solvents' polarities on the two compounds (BFMT and BFMU) in order to determine the activities of molecules experimentally and theoretically.

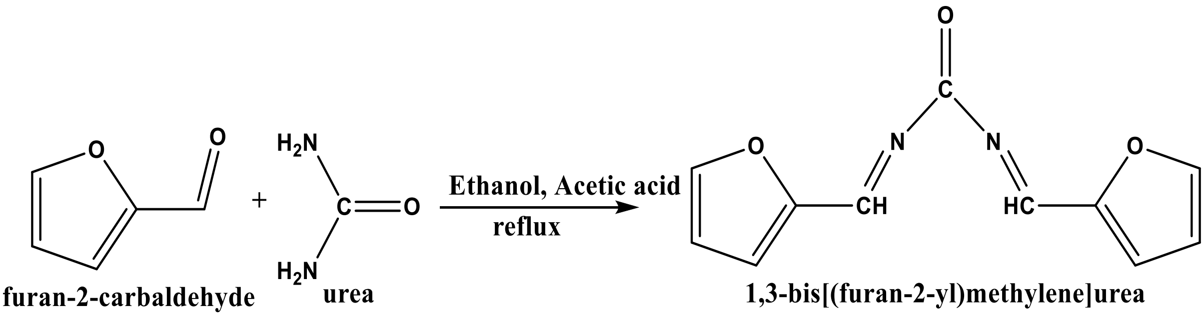
2. THEORETICAL METHOD

2.1 Materials and Methods

Furan-2-carbaldehyde, urea and thiourea were purchased from Aldrich. Other analytical grade reagents were used as received. Distilled water was used for the preparation of their aqueous solutions. The UV-Visible spectrophotometer (JENWAY 6300) available at Instrumentation room of Industrial and Environmental Chemistry Laboratory of Fountain University, Osogbo was used for the spectral studies. Formation of new functional groups was monitored with Fourier Transform Infra-red (FT-IR) Spectrophotometer produced by Shimadzu.

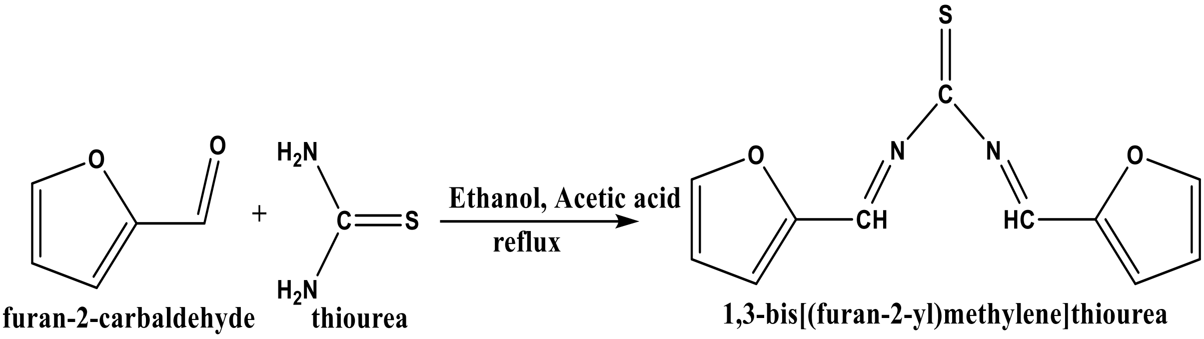
2.2 Preparation of 1, 3-bis [(furan-2-yl) methylene] urea

The studied compounds were synthesized and characterized following the standard methods as reported in one of our works [9, 10].



Scheme 1. Synthesis of 1, 3-bis [(furan-2-yl) methylene] urea.

Preparation of 1, 3-bis [(furan-2-yl) methylene] thiourea



Scheme 2. Synthesis of 1, 3-bis [(furan-2-yl) methylene] thiourea.

2.3 Determination of logP value by the shake – flask method

The octanol/water partition coefficient of the two compounds was measured using the traditional shake flask techniques at 25.0±0.1°C. The organic and the aqueous phases were mutually saturated before the experiments. The samples were dissolved in aqueous Briton- Robinson buffer solution (stock solution 1-6 mg/100 ml). Aliquots of the stock solution were equilibrated with n-octanol for 1 hr in the temperature-regulated water bath (thermostat) with intermittent shaking. After separation of the equilibrated phases by centrifugation, the concentrations of the solutes were determined in the phases by UV spectrophotometer (Spectrometer 2000- 721 model) at the λ_{max} of the compounds in *n*-octanol and water [11].

2. 4 Computational details

The equilibrium geometries and vibrational frequencies for the two synthesized compounds were fully optimized at Density Functional Theory with Becke's three parameter hybrid functional employing the Lee-Yang-Parr correlation function at 6-31G* (DFT/B3LYP/6-31G*) in solvents of different polarities (toluene, ethanol, DMSO and water). This method was used to determine and analyze the Fourier Transform- Infrared Spectrometer (FTIR) spectra shifts and UV-Visible absorbance measurements of the compounds using the in-built spectra matching computerized software. The electronic transitions, absorption wavelength, HOMO-LUMO energies and the associated parameters were calculated, as specified by Obi-Egbedi and Adeoye, (2017) using the equations below:

$$\text{Қ} = \frac{1}{2}\left(E_{HOMO} + E_{LUMO}\right) \qquad \text{(i)}$$

$$\eta = \frac{1-EA}{2} = \frac{1}{2}\left(E_{LUMO} - E_{HOMO}\right) \qquad \text{(ii)}$$

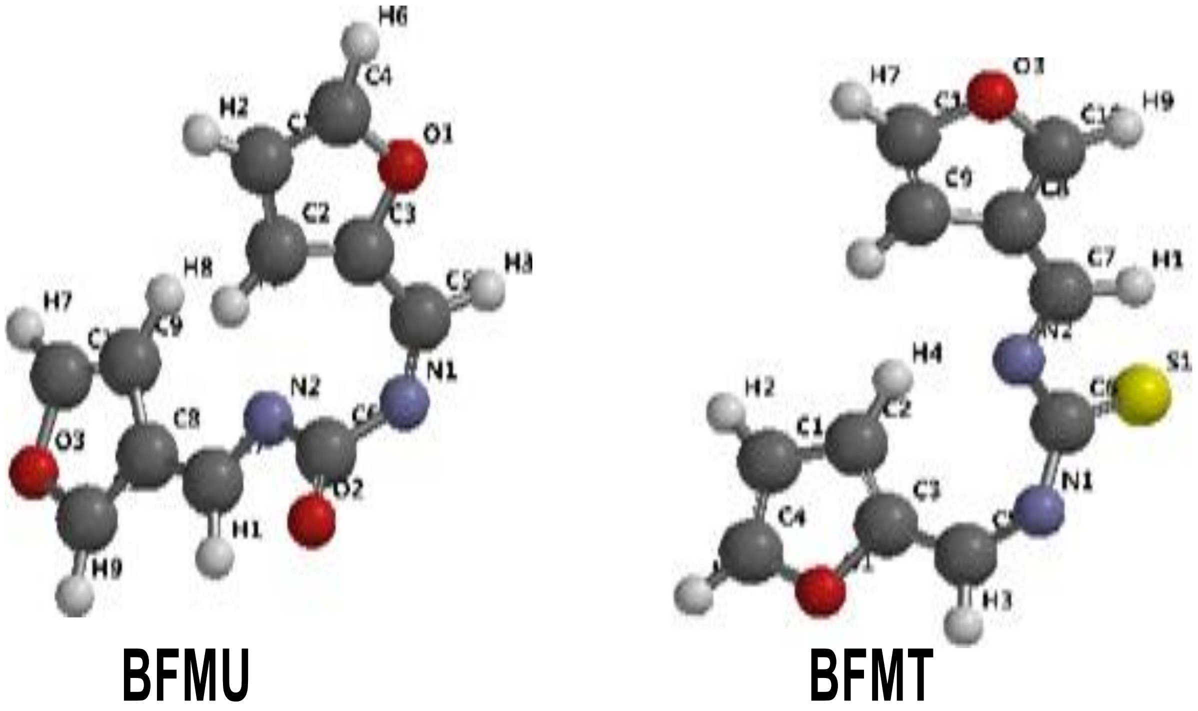
$$\omega = \frac{\text{Қ}^2}{2\eta} \qquad \text{(iii)}$$

$$EA = -E_{LUMO} = I - 2\eta \qquad \text{(iv)}$$

$$S = \frac{1}{2\eta} \qquad \text{(v)}$$

$$\chi = \frac{1+EA}{2} = -\text{Қ} \qquad \text{(vi)}$$

$$I = -E_{HOMO} = \text{Қ} + \eta \qquad \text{(vii)}$$



BFMU BFMT

Fig. 1. Optimized labelled molecular structures of BFMU and BFMT.

3. RESULTS AND DISCUSSION

3.1 IR spectra analysis

The experimentally obtained and theoretically generated infrared spectra of the studied compounds are presented in Table 1, Figures 2 and 3 respectively. The peaks observed between 3304 and 3487 cm^{-1} in BFMU spectrum obtained experimentally (A_1) are assignable to water of crystallization which is absent in the theoretical spectrum (B_1). The band at 3155 cm^{-1} was assignable to C-H$_{str}$ frequency. The characteristics bands at 1595 cm^{-1} and 1600 cm^{-1} were associated with azomethine group (C=N) as appeared in Figure 2 (A_1 and B_1) below. The peaks observed at 1641 and 1700 cm^{-1} were attributable to carbonyl functional group (C=O) stretches in Figure 2 also [12]. The absorption bands at 1228 and 1200 cm^{-1}; 1008 and 1100 cm^{-1} ; 1539 and 1500 cm-^{1} were assignable to C-O, C-N and C=C respectively as in Figure 2 (A_1 and B_1). **S**imilarly the peaks observed between 3265 and 3365 cm^{-1} in BFMT spectrum are also assignable to water of crystallization. Carbon single bond hydrogen stretches (C-H$_{str}$) frequency was observed between 3093 and 3159 cm$^{-1.}$ The characteristics band observed at 1404 and 1600 cm^{-1} in both experimental and theoretical spectra were attributed to azomethine (C=N) group as shown in Figure 3 (A_2 and B_2). The band observed at 1600 and 1700 cm^{-1} were also assignable to C=S$_{str}$ frequency of the two spectra A_2 and B_2 respectively. The absorption bands at 1222 and 1200 cm^{-1} were attributable to C-O; 1078 and 1100 cm^{-1} to C-N peak while C=C absorption bands were observed at 1465 and 1500 cm^{-1} of A_2 and B_2 respectively.

Table 1. FTIR Peaks of experimentally and theoretically obtained spectra

	BFMU Experimental ($\mathbf{A_1}$)	BFMU Theoretical ($\mathbf{B_1}$)	BFMT Experimental ($\mathbf{A_2}$)	BFMT Theoretical ($\mathbf{B_2}$)
O-H	3304-3487	-	3265-3365	-
C-H	3155	-	3093-3159	-
C=N	1595	1600	1404	1600
C=S/C=O	1641	1700	1600	1700
C-O	1228	1200	1222	1200
C-N	1008	1100	1078	1100
C=C	1539	1500	1465	1500

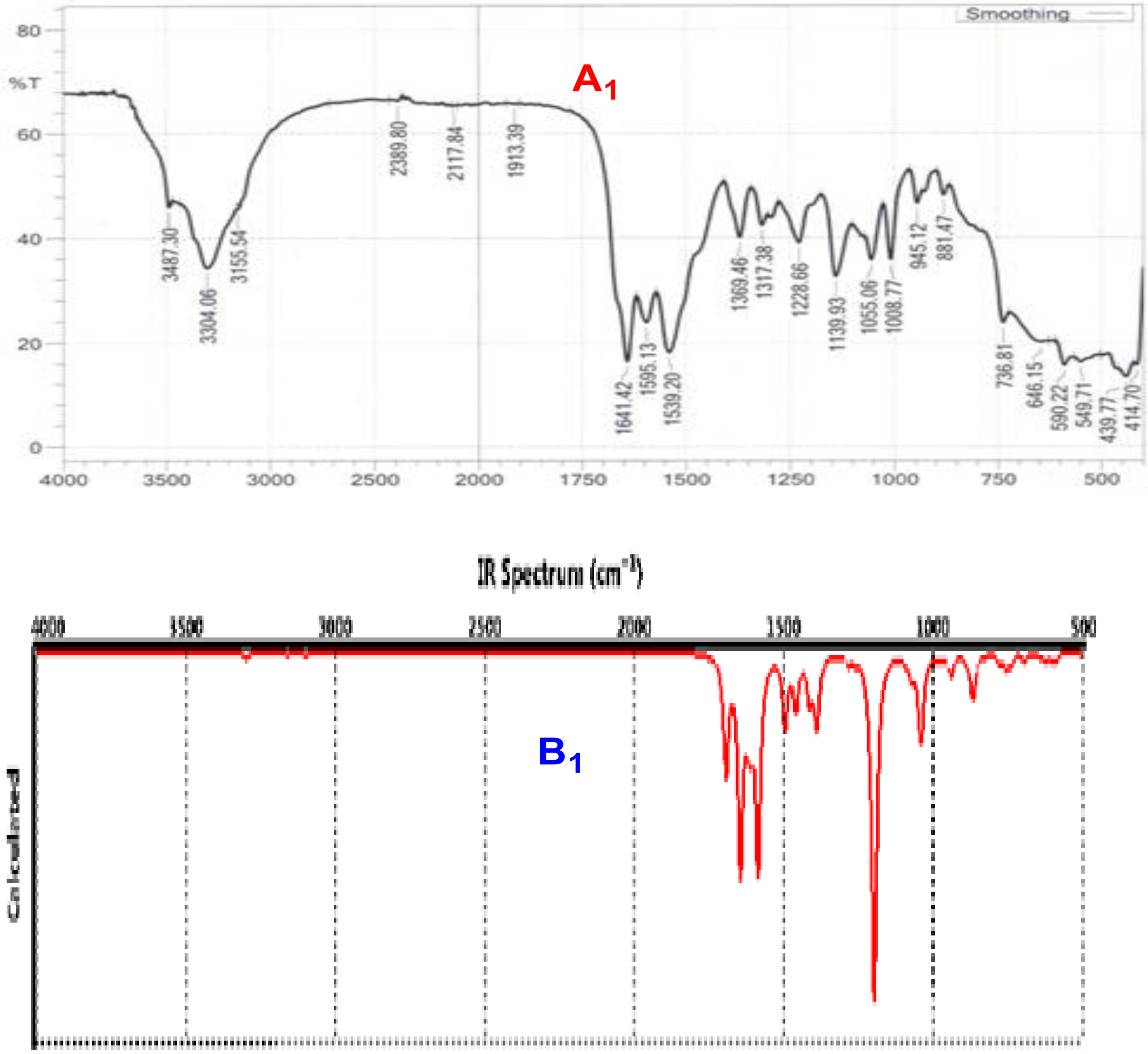


Fig. 2. IR Spectra of BFMU [experimental ($\mathbf{A_1}$) and theoretical ($\mathbf{B_1}$)].

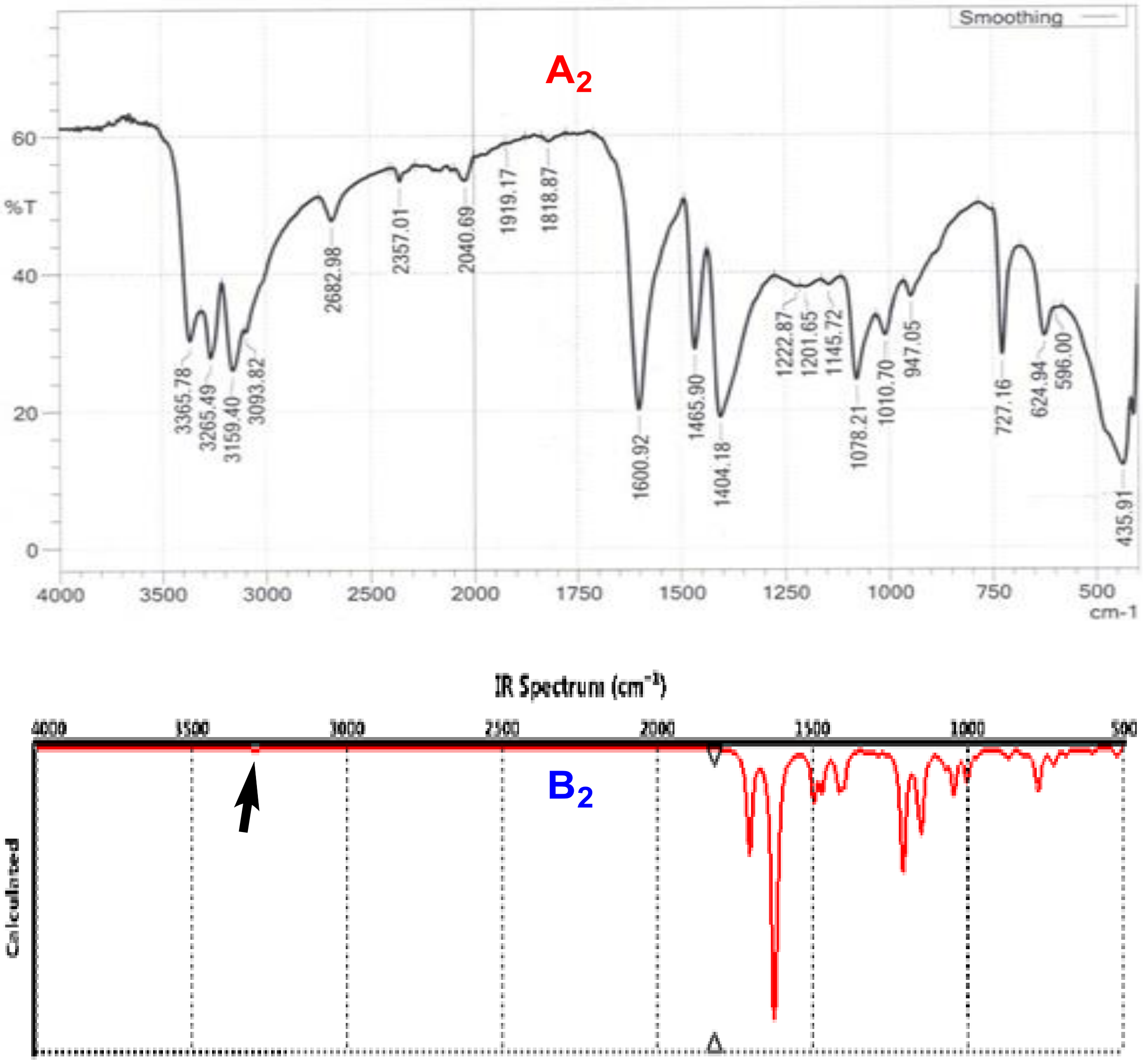


Fig. 3. IR Spectra of BFMT [experimental (**A**2) and theoretical (**B**2)].

3.1.1 *Frontier molecular orbital analysis and partition coefficient, logP values of the studied compounds*

The frontier orbital electron densities of atoms in a molecule can be used for analysis of their donor-acceptor interaction [13]. The optimized labelled structures for the studied compounds are shown on Plates 1 and 2. Their HOMO-LUMO energy gaps and associated molecular properties are presented in Tables 2 and 3, while their molecular orbital (HOMO and LUMO) structures are as shown in Figure 4. The energy gaps reflect the chemical activity of the molecules. As observed from the results, the HOMO and LUMO π-electrons of BFMU are delocalized all over the entire molecules. The HOMO π-electrons of BFMT also extended all over the entire molecule except one of the furan rings while the LUMO are more localized on the C=N, C=O and C-S of BFMT structure than the furan rings. This is attesting to the charge transfer characteristic properties of the synthesized compounds in the studied solvents.

The results from the partition coefficient experiment shown in Table 2 revealed that BFMU gave higher concentration in the organic layer, while higher concentration was obtained for BFMT in the aqueous layer leading to negative value for BFMU and positive value for BFMT. From Table 2, the LogP values were found theoretically and experimentally to be -1.01 and -1.07 respectively for compounds BFMU and 0.45 and 0.51 for BFMT.

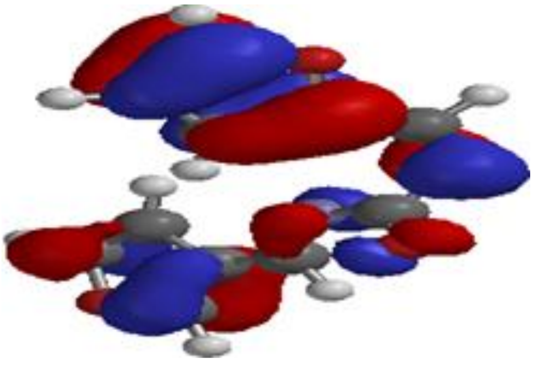
LogP or lipophilicity is the main physicochemical determinant influencing the bioavailability, permeability and toxicity of a compound [14]. The negative LogP values obtained for BFMU is an indication that the studied molecules will have higher affinity for the aqueous phase, with less affinity for organic phase and is therefore more hydrophilic while positive values for BFMT denotes a higher concentration in the lipid phase relative to the aqueous phase which is a pointer to the fact the compound (BFMT) will be more lipophilic in nature. The magnitude of the LogP values is used as determinants in some industrial processes such as in agro-chemistry, drug formulation and flavouring of finished products [14].

For a compound to be bioavailable as agrochemical, it should have among other parameters, LogP value of < 3 (Brigg's rule 3). The values obtained for the two compounds were within this range and therefore could be useful chemical as agrochemicals. The compounds will however not be useful in drug formulation targeted at central nervous system (CNS) and oral and intestinal absorption (LogP = 1.35 - 1.8) [15]. The LogP value is also important to industries and researchers in determining how to deliver chemical substances to specific sites or eliminate chemicals from others as well as limiting unwanted dispersal of chemicals through the environment and water ways. The close agreement between the experimental and theoretical values obtained differently (-1.01 and -1.07; 0.45 and 0.51) indicate they are true representations of the studied compounds.

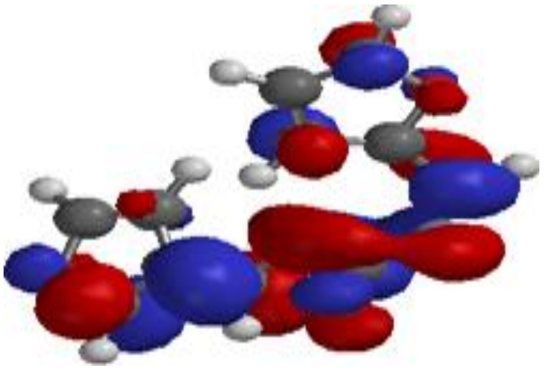
Table 2. LogP values for the compounds using the shake-flask method

Sample	Log P_{cal}	Log P_{exp}
BFMU	-1.01	-1.07
BFMT	0.45	0.51

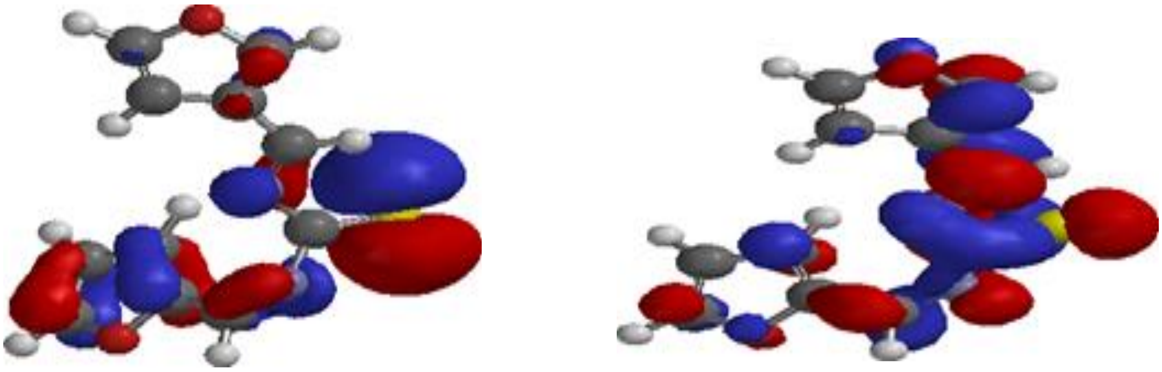
Note; Log P_{cal} = theoretical value and Log P_{expt} = experimental value



HOMO of BFMU



LUMO of BFMU



HOMO of BFMT **LUMO of BFMT**

Fig. 4. HOMO and LUMO structures of BFMU and BFMT.

3.1.2 Reactivity descriptors of BFMU and BFMT in different media

The results obtained for the theoretical calculated molecular descriptors and structure activity relationship properties of BFMU and BFMT compounds in different media (vacuum, ethanol, water, DMSO and toluene) are presented in tables 3 and 4. The dipole moment, polarizability, area and volume values obtained followed the trend: DMSO > Water > Ethanol > Toluene for the studied compounds, attesting to the influence of solvent polarities as earlier reported.. The chemical potential (μ) values of the compounds were found to increase with increasing solvent polarities except in water where low values were obtained compared to other polar solvents. The higher values obtained for the molecules in polar solvents is an indication of their lesser activities in polar solvents relative to non-polar. A high μ value is a pointer to a strong tendency of a molecule to hold electrons firmly which leads to increasing chemical hardness.

The results also revealed that polarizability (α) values obtained for compound B were found to be slightly higher than compound A. Polarizability is a measure of distortion of a molecule in an electric field, which is used to determine the strength of molecular interactions and optical properties of a system [16]. Polarizability values for the two compounds were found to increase slightly with increased solvent polarities and dielectric constant values except for water. HOMO is the ability of a molecule to give out electrons while LUMO denotes accepting electrons and therefore E_{L-H} accounts for the distribution of electrons to or from the aromatic part of the molecule to the substituents on the ring system [17]. The E_{L-H} energy gap for BFMT decreases with increasing dielectric constant values of the solvents making the molecules to be more reactive in solvent of higher polarity. Also the lower E_{L-H} energy gap values indicate a higher distribution of charges and probability of high interaction of BFMT relative to BFMU.

The magnitude of the energy gap between HOMO and LUMO is a good determinant of the softness (s) or hardness (η) nature of a molecule. The trends observed for the global softness values for the studied compounds are BFMU: Water > Ethanol > Toluene > DMSO and BFMT: Toluene > Ethanol > DMSO > Water.

These variations indicate that BFMU is less stable in water and more stable in DMSO while BFMT is less stable in toluene and more stable in water. This was also affirmed by the solubility of the compounds when dissolved in solvents experimentally. The observation can also be explained in terms of the H-bonding ability of BFMU with water and ethanol (polar-protic solvents). From the results, lowest HOMO-LUMO energy gaps were obtained for BFMU and BFMT in DMSO and water respectively, which can be linked to the different degrees of interactions of solvents with the HOMO and LUMO orbitals of the compounds.

From Table 4, the BFMT compound with lower E_{L-H} gap values would be softer in nature and is expected to be more polarizable, possessing high chemical reactivity, higher charge transfer (CT) characteristic and planarity [4]. This may be responsible for the increased electronic properties noticed for the compound. Electronegativity (χ) values as obtained showed a gradual decrease with increase in ε and solvent polarity indicating the solvent dependent nature of χ. This also describes how much an atom holds its electrons tightly. A compound in solvent that gave less electronegative value will have the likelihood of giving up its electrons and will be more reactive [17].

The ionization energies (I) for the two compounds in the solvents followed the same trend as observed for electronegativity values. The knowledge of the ionization energy and other parameters such as electron affinity of organic molecules is necessary for quantitative interpretation of intermolecular resonance, reactivity and their semi-conductance properties. The hydrophilicity index (ω) value for the two compounds in DMSO was found to have higher value than other solvents. This is a better parameter to describe molecules in terms of their reactivity and site selectivity [18]. The high value in DMSO implies that the compounds will have high interaction with DMSO and will enhance their better adhesiveness and higher surface energy than in other solvents.

Table 3. Computational studies of BFMU and BFMT

Parameter	Vacuum	Water	Ethanol	DMSO	Toluene
		BFMU			
E_{HOMO} (eV)	-6.65	-6.39	-6.65	-6.65	-6.65
E_{LUMO} (eV)	-2.11	-2.02	-1.98	-2.04	-1.86
Dipole moment (Debye)	5.07	5.15	5.08	5.99	4.44
Area (Å^2)	237.01	239.32	239.20	239.67	238.93
Volume (Å^3)	211.99	213.12	213.03	213.25	212.86
log P	-1.01	-1.01	-1.01	-1.01	-1.01
Polarizability (Å^3)	57.59	57.63	57.62	57.66	57.59
		BFMT			
E_{HOMO} (eV)	-5.48	-6.11	-6.06	-5.94	-5.77
E_{LUMO} (eV)	-2.06	-2.35	-2.33	-2.34	-2.22
Dipole moment (Debye)	6.04	7.75	7.68	7.89	6.23
Area (Å^2)	251.40	251.36	251.33	251.33	250.99
Volume (Å^3)	223.18	223.44	223.36	223.46	223.16
log P	0.45	0.45	0.45	0.45	0.45

Polarizability (cm^3)	58.67	58.63	58.61	58.65	57.64

Table 4. Frontier orbital energy related molecular parameters of BFMU and BFMT

Parameter	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{L-H} (eV)	χ (eV)	ω (eV)	I (eV)	EA (eV)	η (eV)	S (eV)	μ (D)	α ($Å^3$)
BFMU											
Toluene	-6.39	-2.02	4.37	4.21	4.05	6.40	2.02	2.19	0.23	4.44	57.59
Ethanol	-6.39	-1.98	4.39	4.15	3.91	6.35	1.98	2.20	0.23	5.08	57.62
DMSO	-6.31	-2.04	4.27	4.18	4.08	6.32	2.04	2.14	0.23	5.99	57.66
Water	-6.31	-1.86	4.45	4.09	3.75	6.32	1.86	2.23	0.22	5.15	57.63
BFMT											
Toluene	-6.11	-2.35	3.76	4.23	4.76	6.11	2.35	1.88	0.27	6.23	58.64
Ethanol	-6.06	-2.33	3.73	4.20	4.72	6.07	2.33	1.87	0.27	7.75	58.61
DMSO	-5.94	-2.34	3.60	4.14	4.76	5.94	2.34	1.80	0.28	7.89	58.65
Water	-5.77	-2.22	3.55	4.00	4.49	5.78	2.22	1.78	0.29	7.68	58.61

ΔE_{H-L}: $E_{HOMO-LUMO}$ (eV), χ: Electronegativity, ω: Electrophilicity index, I: Ionization energy
EA: Electron affinity, η: Hardness, S: Softness, μ: Chemical potential (D), α: Polarizability (A^2)

CONCLUSIONS

This research has successfully investigated the effects of solvent polarity on the activities of the synthesized compounds both experimentally and theoretically. The FT-IR spectra obtained theoretically are in good agreement with the experimental values. There is probability of higher charge distribution, indicating a strong tendency of higher chemical activity for BFMT than BFMU. Their chemical activities were also found to decrease with increasing solvent polarities and highest in dimethyl sulfoxide. The log P values (< 3) for the compounds pointed to their usefulness in agrochemicals.

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