Original Research Article

THEORETICAL STUDY OF SOLVENT EFFECTS ON THE ELECTRONIC AND THERMODYNAMIC PROPERTIES OF TETRATHIAFULVALENE (TTF) MOLECULE BASED ON DFT

ABSTRACT

Tetrathiafulvalene ($C_6H_4S_4$) is an organosulfur compound used in the production of molecular devices such as switches, sensors, nonlinear optical devices and rectifiers. In this work, a theoretical study on the effects of solvent on TTF molecule was investigated and reported based on Density Functional Theory (DFT) as implemented in Gaussian 03 package using B3LYP/6-31++G(d,p) basis set. Different solvents were introduced as a bridge to investigate their effects on the electronic structure. The HUMO, LUMO, energy gap, global chemical index, thermodynamic properties, NLO and DOS analysis of the TTF molecule in order to determine the reactivity and stability of the molecule were obtained. The results obtained showed that the solvents have effects on the electronic and non-linear-optical properties of the molecule. The optimized bond length revealed that the molecule has strong bond in gas phase with smallest bond length of about 1.0834Å than in the rest of the solvents. It was observed that the molecule is more stable in acetonitrile with HOMO-LUMO gap and chemical hardness of 3.6373eV and 1.8187eV respectively. This indicates that the energy gap and chemical hardness of TTF molecule increases with the increase in polarity and dielectric constant of the solvents. The computed results agreed with the results in the literature. The thermodynamics and NLO properties calculation also indicated that TTF molecule has highest value of specific heat capacity (Cv), total dipole moment (μ_{tot}) and first order hyperpolarizability (β_{tot}) in acetonitrile, while acetone has the highest value of entropy and toluene has a slightly higher value of zero point vibrational energy (ZPVE) than the rest of the solvents. The results show that careful selection of the solvents and basis sets can tune the frontier molecular orbital energy gap of the molecule and can be used for molecular device applications.

KEYWORDS: TTF, DFT, Chemical hardness, Thermodynamics and acetone

1.0 INTRODUCTION

The universal applications of heterocyclic materials are undeniable. Since their discovery, there is rising demand for synthesizing new heterocyclic materials and this has influenced research effort within the field. Heterocyclic compounds containing sulfur have stimulated the interest of organic researchers on decades of historical development of molecular materials. Recently, 2,5bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDTTTP) and its derivatives have attracted attention for many years as a result of their ability to donate an electron and also the electrical conductivity of their charge transfer salts. Among the wide variety of chemical modifications performed on the TTF skeleton, the introduction of aromatic rings into the TTF skeleton are known to be an attractive electron-donor molecule which may give an extremely conductive charge transfer complex owing to its highly extended π-conjugate part [1]. The synthesis of highly extended and sulfur rich materials has recently received particular attention [2]. TTFs derivatives presently play an important role as redox sites in many different areas of supramolecular materials [3].

Similarly, the improvement of organic NLO materials is of particular interest due to their applications in optical modulation, switching, and logic, frequency shifting and optical memory for the emerging technologies in areas such as signal processing, optical interconnections, and telecommunications, [4, 5, 6] etc. Since the discovery of the structural and molecular properties of Tetrathiafulvalene (TTF) [7], much effort has been devoted in the synthesis of sophisticated derivatives of this π-donor in order to improve the electro conducting properties of the corresponding charge-transfer complexes or cation radical salts [8]. It has been widely recognized that the conductive properties depend on their crystal structures and electronic states. Moreover, TTFs have been employed as a building block for molecular devices such as switches [9], sensors [10], nonlinear optical devices [11], organic field-effect transistors [12], rectifiers [13], and organic photovoltaic cells [14]. This results from their good ability to donate electron and reversible oxidation of one-electron at accessible potentials, and these properties can be finely tuned by peripheral substitution or chemical modification of the TTF framework [15]. However, interest in TTF goes beyond the area of conducting materials. In the quest to improve these systems various other interesting materials have come to light. In some years back, several kinds of theoretical and experimental work on TTF and its derivatives have been reported by a number of workers [16].

Not too long, [17] reported the investigation on the molecular structure, NBO analysis, first-hyperpolarizability, and HOMO-LUMO studies of bis(dithiolylidene)-tetrathiapentalene (BDT-TTP) by quantum computational methods. In the research, it was reported that, stability of the molecule arised from hyper-conjugative interactions and charge delocalization. Meanwhile, the intra-molecular hydrogen bond has been analyzed using natural bond orbital (NBO) and nonlinear optical (NLO) analysis. The molecule was found to be stable with HOMO-LUMO energy and chemical hardness of about 3.260eV and 1.0840eV respectively while the strongest bond was reported to have a value of bond length of about 1.0840Å [17]. In 2019, [18], reported the Structure, Electron Density and HOMO-LUMO of Tetrathiafulvalene (TTF) as Organic Superconductors. It was reported that the bond distances calculated by HF/6-311G** and B3LYP/6-311G** methods were found to be shorter than the B3LYP/aug-cc-PVDZ method. The C–H bond distances computed from both levels of calculations

are ranged 1.081–1.088Å, respectively. The C–S–C bond angles predicted from B3LYP/ 6-311G** and B3LYP/aug-cc-PVDZ methods are found to be almost equal and the average value is 94.7◦. The calculated HOMO-LUMO energy for B3LYP/6-311G** and B3LYP/aug-cc-PVDZ are 3.75eV and 3.63eV respectively [18]. In the foregoing investigations, solvent effect of the molecule was not reported. Just recently, [19] reported an investigation on the theoretical study for chemical reactivity descriptors of Tetrathiafulvalene in gas phase and solvent phase based on Density Functional Theory. The purpose of the investigation was to study the effect of solvents (water, acetone, Tetrahydrofuran (THF), Carbon tetrachloride (CCl4), and benzene) polarity on the frontier molecular orbitals energy gap and global chemical reactivity of TTF in order to understand its stability and reactivity in a different solvent medium. Density functional theory with (B3LYP/6-311++G) basis set was used to perform the work. The results obtained showed that the solvents have effect on the optimized parameters. TTF molecule was observed to have greater stability (low reactivity) in water with an $E_{HOMO} - E_{LUMO}$energy gap of 3.946 eV while it has higher reactivity (low stability) in the gas phase with $E_{HOMO} - E_{LUMO}$energy gap of 3.872eV. Moreover, Mulliken population analysis, and local reactivity as Fukui Functions (FFs) from the natural bond orbitals (NBO) charges were computed to understand the electrophile, nucleophile region, and chemical activity of the titled molecule. The dipole moment in gas phase and solvent medium was 0.00 Debye. Also, it was reported that the global chemical reactivity parameters changed depending on the molecular structure and polarity of the solvents [19]. In the work reported so far, bond lengths and bond angles, optoelectronic properties, density of states (DOS), nonlinear optical (NLO) properties and IR spectra analysis were not reported.

In the present work, we investigated the effect of solvents (toluene, acetone, acetonitrile and dichloromethane) on the structural properties, molecular geometry, thermodynamic properties, nonlinear optical (NLO) properties, and chemical reactivity such as HOMO-LUMO energy gap, chemical hardness, chemical potential, density of state (DOS) and IR spectra of the TTF molecule. Thus the purpose is to explore their electronic and spectroscopic properties on the basis of DFT for better understanding of their applications.

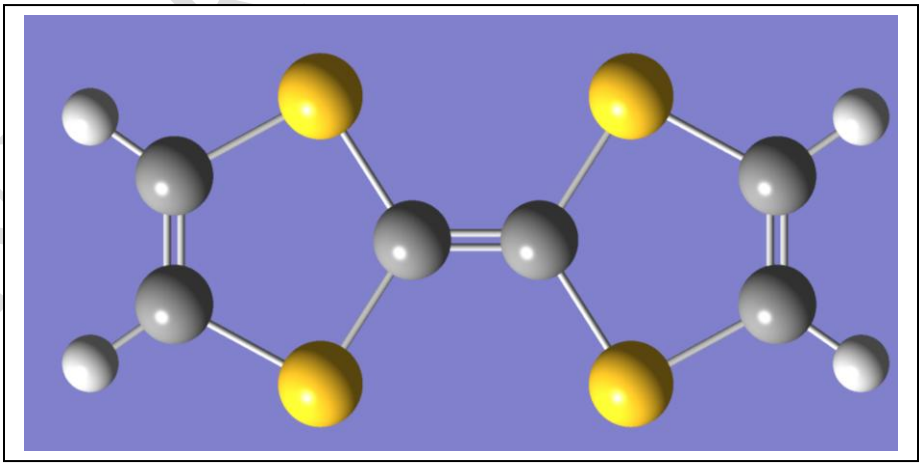


Figure 1: Optimized Structure of Tetrathiafulvalene (TTF) Molecule

2.0 THEORETICAL BACKGROUND

2.1 Global Chemical Reactivity Descriptors (GCRD)

Global reactivity descriptors such as chemical potential, chemical hardness-softness, electronegativity and electrophilicity index are useful quantities in predicting and understanding global chemical reactivity trends. The ionization potential (IP) and electron affinities (EA) of the studied molecule in gas phase and in solvents are computed by using Koopmans's as;

$$IP = -E_{HOMO} \quad (1)$$

$$EA = -E_{LUMO} \quad (2)$$

The energy gap E_g can be obtained from the relation;

$$E_g = E_{LUMO} - E_{HOMO} \approx IP - EA \quad (3)$$

The chemical hardness (η) could be expressed in terms of IP and EA as [20];

$$\eta = (E_{LUMO} - E_{HOMO})/2 \approx (IP - EA)/2 \quad (4)$$

And softness is given by [20];

$$s = \frac{1}{\eta} \quad (5)$$

The chemical potential is given by [21];

$$\mu = -(\frac{IP+EA}{2}) \quad (6)$$

The electronegativity is given by [21];

$$X = \frac{IP+EA}{2} \quad (7)$$

The electrophilictity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilictity index (ω) is expressed as [21, 22];

$$\omega = \frac{\mu^2}{2\eta} \quad (8)$$

2.2 Non-Linear Optical Properties

In order to gain an insight into the study of non-linear optical properties (NLO) of TTF molecule in solvents; the dipole moment (μ), polarizability (α), anisotropic polarizability (Δα), and hyperpolarizability (β and γ) were computed at DFT/B3LYP with 6-31++G (d, p) basis set.

For molecular systems, dipole moment can be obtained from [21];

$$\mu_{tot} = [\mu_x^2 + \mu_y^2 + \mu_z^2]^{1/2} \quad (9)$$

Where $\mu_x, \mu_y \; and \; \mu_z$ are the components of the dipole moment in x, y and z coordinates.

Electric dipole polarizability is given by [23];

$$\alpha = -\frac{\partial^2 E}{\partial F_a \partial F_b} \tag{10}$$

where a and b are coordinates of x, y and z.

The mean polarizability is calculated using [21];

$$< \alpha >= \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{11}$$

where $\alpha_{xx}, \; \alpha_{yy} \; and \; \alpha_{zz}$ are known as principal values of polarizability tensor.

The anisotropic polarizability is given by [21];

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2} \tag{12}$$

The first hyperpolarizability is defined as [24];

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \tag{13}$$

The second order hyperpolarizability is given by [23];

$$\gamma = \frac{1}{5}[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})] \tag{14}$$

3.0 COMPUTATIONAL METHODOLGY

Geometrical structure of TTF was optimized with no symmetry constraint using Becke's three parameter hybrid exchange combined with Lee-Yang-Parr's gradient-corrected correlation [25] functional (B3LYP) method with 6-31++G (d, p) basis set. All the parameters were fully allowed to relax and each of the calculations converged to an optimized geometry which corresponds to a true energy minimum. For the study of solvation effects, a Self Consistent Reaction Field (SCRF) approach based on Polarizable Continuum Model (PCM) was employed. The effects of four solvents (toluene, acetone, acetonitrile and dichloromethane) were investigated by means of the SCRF method based on PCM as implemented in the Gaussian 03 [26]. The optimized geometries were then used to obtain the HOMO-LUMO energy gap, chemical hardness, chemical softness, chemical potential, electronegativity, electrophilicity index, dipole moment, polarizability, anisotropic polarizability,

hyperpolarizability, entropy and the specific heat capacity of the investigated molecule at the same level of theory (B3LYP/6-31++G(d,p). All calculations were performed within the framework of Density Functional Theory (DFT) as coded in Gaussian 03 package [26].

4.0 RESULTS AND DISCUSSION

4.1 Optimized Parameters

The distance between the nuclei of two atoms bonded together is termed as bond length while bond angle is the angle between two adjacent bonds of an atom in a molecule [24]. The optimized values of bond lengths and bond angles of the studied molecule were calculated and reported in Tables 1 and 2 at DFT/B3LYP level using 6-31++G (d, p) basis set in the gas phase and in different solvents (toluene, acetone, acetonitrile and dichloromethane). From Table 1, there are little changes in the bond lengths of TTF when optimized with toluene, acetone, acetonitrile and dichloromethane compared with that in gas phase. The result shows that the lowest value obtained was 1.0834Å in gas phase. However, when compared with results of TTF molecule in gas phase with other solvents, the bond lengths tend to be a little smaller. It is worth noting that, the smaller the bond length, the higher the bond energy and stronger the bond [27]. Consequently, this has affirmed that the bond energy of TTF in gas phase is a little stronger than that in solvents. Hence, an enormous amount of energy is required to break these bonds. It was also observed that the bond length increases with a decrease in the polarity of the solvents under study. However, the longest bond length is 1.7894Å, which is almost the same in both gas phase and solvents. These are weakest bond energy of TTF in both gas phase and in solvents. Hence, a small amount of energy is required to break these bonds.

Table 1: Selected bond lengths (Å) of the optimized structure of TTF molecule in the gas phase and in different solvents

Bond Lengths (Å)	Gas Phase	Toluene	Acetone	Acetonitrile	Dichloro methane	Previous Works [18]
R(1,2)	1.7889	1.7891	1.7893	1.7893	1.7894	
R(2,5)	1.3516	1.3519	1.3526	1.3526	1.3522	1.3530
R(3,7)	1.0834	1.0853	1.0880	1.0882	1.0873	1.0880
R(8,11)	1.7611	1.7627	1.7648	1.7650	1.7643	1.7630
R(11,12)	1.3396	1.3393	1.3389	1.3389	1.3391	

Table 2: Selected bond angles (˚) of the optimized structure of TTF molecule in the gas phase and in different solvents

Bond Angles (˚)	Gas Phase	Toluene	Acetone	Acetonitrile	Dichloro methane	Previous Works [18]
A(2,1,3)	94.9157	94.9921	95.0774	95.0822	95.0514	94.7000
A(1,2,4)	113.9351	113.8609	113.7857	113.7810	113.8039	
A(4,2,5)	123.0328	123.0699	123.1074	123.1098	123.0984	123.1000
A(3,6,4)	118.1168	118.0774	118.0298	118.0273	118.0467	
A(9,12,14)	117.2287	117.1284	116.9696	116.9596	117.0442	

Similarly from Table 2, there is a slight increase in the bond angles of the studied molecule in solvents when compared with the one in gas phase. From the results, the values obtained in acetonitrile are a bit higher than the one obtained in gas phase and other solvents. This indicates that, in terms of bond angles, TTF molecule has highest stability in acetonitrile than in gas phase and other solvents. The bond angles were found to have an average value of 95.02^0 in both gas phase and solvents. The structural geometry of the studied molecule that consists of bond lengths and bond angles are found to be in good agreement with those from previous work [18].

4.2 Frontier Molecular Orbital Energies

Table 3 presents the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) and the energy gap (E_{gap}) of TTF in the gas phase and in solvents calculated at the DFT/B3LYP level using 6-31++G (d, p) basis set. The values of HOMO, LUMO and their energy gap reflect the chemical activity of the molecule. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness-softness of a molecule [28]. Compounds with large HOMO-LUMO gap value tend to have higher stability [22].

It is clear from Table 3 that the HOMO-LUMO energy gap for the TTF molecule is higher in acetonitrile with value of about 3.6373eV followed by acetone, dichloromethane, toluene and then in gas phase with values of 3.6330eV, 3.6221eV, 3.5816eV and 3.5418eV respectively. The results show that, TTF has greater band gap energy in acetonitrile (3.6373 eV) than in gas phase and the rest of the solvents. Therefore, the electron transfer from HOMO to LUMO of the molecule in acetonitrile is relatively harder than that in the gas phase. This shows that TTF molecule is having higher stability in acetonitrile than in gas phase and other solvents. However, TTF has smaller energy gap in gas phase than in solvents thus, the electron jumps from the HOMO to the LUMO energy orbital more easily (softer) in the gas phase than in the other solvents. Interestingly, the order of stability increases with an increase in polarity of the solvents under study. The HOMO-LUMO gap of TTF obtained in acetone is found to be very close to 3.6300 eV of TTF molecule reported by [18].

HOMO represents the ability to donate an electron, while LUMO represents the ability to accept an electron. The higher the HOMO energies, the easier it is for HOMO to denote electrons; the lower the LUMO energies, the easier it is for the LUMO to accept electrons [29]. Hence, the electron transfer from HOMO to LUMO of the molecule in toluene is relatively easier than that in gas phase and in the rest of the solvents. It can also be observed that the HOMO and energy gap of TTF molecule increases with increase in polarity and dielectric constant of the solvents.

Table 3: Calculated HOMO, LUMO, IP, EA, Dielectric (ε) and energy gap in (eV) of the optimized structure of TTF molecule in the gas phase and different solvents using B3LYP methods with 6-31++G(d,p) basis set

Solvents	Dielectric (ε)	E_{HOMO}(eV)	E_{LUMO}(eV)	IP(eV)	EA(eV)	E_{gap} (eV)	Previous work [18, 19]
Gas phase	---------	-4.7345	-1.1927	4.7345	1.1927	3.5418	
Toluene	2.379000	-4.7427	-1.1611	4.7427	1.1611	3.5816	
Acetone	20.700000	-4.8134	-1.1804	4.8134	1.1804	3.6330	3.6300
Acetonitrile	36.640000	-4.8191	-1.1818	4.8191	1.1818	3.6373	3.872
Dichloromethane	8.930000	-4.7936	-1.1715	4.7936	1.1715	3.6221	

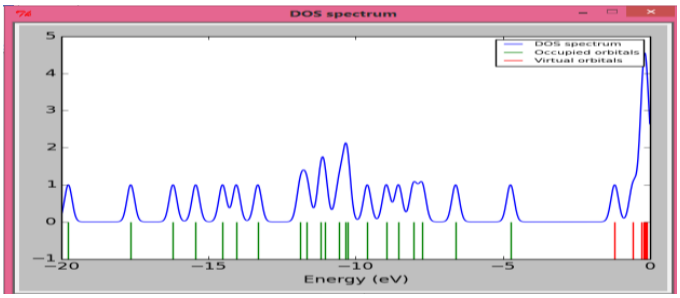
The ionization potential (IP) and electron affinity (EA) measure the tendency of compounds to lose or gain an electron [30]. The IPs and EAs are presented in Table 3. The higher the ionization potential (IP), the more difficult it is to remove an electron to form an ion. The lower the electron affinity (EA), the less easy it is to add an electron. In Table 3, it can be observed that it is more difficult to remove an electron from gas phase<toluene<dichloromethane<acetone<acetonitrile to form an ion. Similarly, it is more difficult to add an electron in terms of their EAs to the molecule in gas phase<acetonitrile<acetone<dichloromethane<toluene. It was observed that the ionization potential increases with an increase in the polarity of the solvents while the electron affinity decreases as the polarity of the solvents decreases.

4.3 Density of State (DOS)

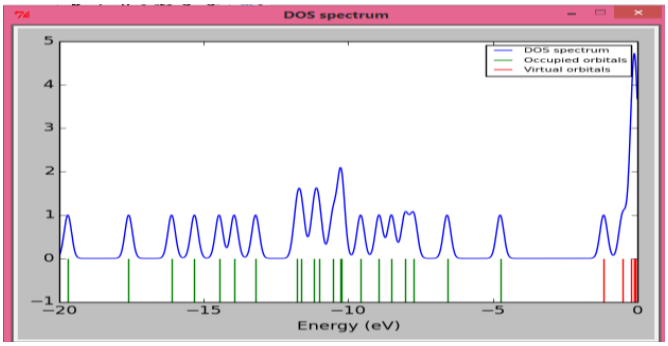
The important application of Density of State (DOS) plot is to demonstrate the molecular orbital and their contribution of chemical bonding through the Overlap Population Density of States (OPDOS) plot [31]. The DOS plot results shows overlapping population in the molecular orbital. The OPDOS result shows nonbonding, bonding and anti-bonding interactions between the two orbital atom groups. The positive value of OPDOS indicates the bonding interaction and negative value indicates the anti-bonding interactions and zero values indicate the nonbonding interactions. The DOS plot gives the

composition of group of orbital contributing to the molecular orbital. The graph exhibits the orbital characteristics of different energy range. It is the major contribution from s orbital and p orbital basic function of carbon in the frontier molecular orbital.

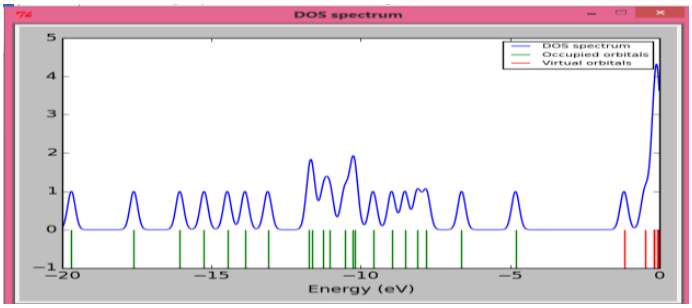
From the DOS of the TTF molecule in gas phase and in solvents, the population of charges is becoming denser in the order gas phase<toluene<dichloromethane<acetone<acetonitrile (as seen from Fig. 1). This suggests that the existence of the solvents molecule free charges and the weak intermolecular forces within acetonitrile clearly affect the charges population compared to gas phase and other solvents. As observed in the entire DOSs, the charges populations are highly concentrated in the valence region, which indicates that TTF in gas phase and in solvents possess high tendency to behave as n-type semiconductor materials. Besides, the presence of strong hybridization has elevated the charges population near the zero Fermi energy level and consequently, the valence band maxima of the molecule in acetonitrile are pushed to higher energies. Since charges population is denser near zero Fermi energy, the possibility to succeed in transmitting the charges from valence region to conduction region is increased as well. As we compared, the gaps produced in DOS are in agreement with the previously found on the HOMO–LUMO energy gaps and band gap values for all the solvents.



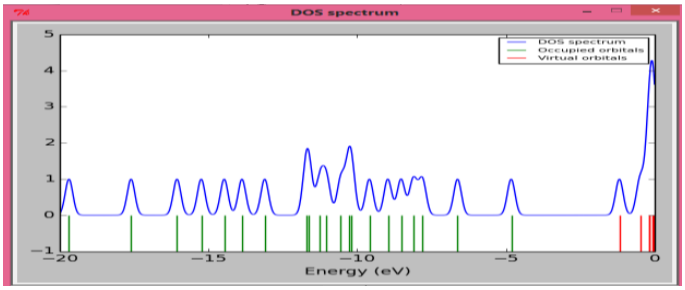
Gas Phase



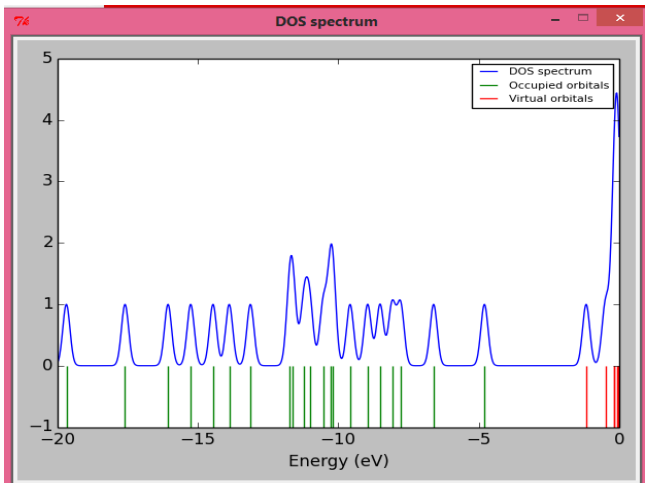
Toluene



Acetone



Acetonitrile



Dichloromethane

Figure 2: Computed density of states (DOS) of TTF molecule in gas phase and in solvents

4.4 Global Chemical Reactivity Descriptors (GCRD)

The Global Chemical Reactivity Descriptors parameters of molecules such as hardness (η), softness (ʃ), chemical potential (μ), electronegativity (χ) and electrophilictity index (ω) of TTF molecule in gas phase and in solvents are reported in Table 4 using frontier molecular orbital energy. Chemical hardness is proportional to the HOMO-LUMO energy gap. An increase in the chemical hardness makes the molecule more stable and less reactive. As seen in Table 4, TTF molecule in acetonitrile with slightly higher value of chemical hardness of 1.8187eV is considered to be harder and more stable than in gas phase and the rest of the solvents, followed by acetone, dichloromethane and toluene with chemical hardness of 1.1.8165eV, 1.8111eV and 1.7908eV respectively. This indicates that TTF in acetonitrile solvent is more stable.

Electronegativity and chemical potential are important parameters in the quantum chemical reaction. The higher the value of electronegativity, the greater the ability of the atoms or molecules to attract electrons, whereas the greater the value of chemical potential, the more the reactivity and less stability of the molecules [19]. TTF molecule in acetonitrile has a higher electronegativity than other solvents as reported in Table 4. Also, it has maximum chemical potential in the gas phase and acetonitrile. As a result, this molecule is more reactive and less stable in both gas phase and acetonitrile. The electrophilicity index value is used for the determination of chemical reactivity of molecules. Higher reactive nucleophile is considered to have a lower value of (ω) than a strong electrophile with a high value of (ω). TTF in gas phase is considered to be more reactive nucleophile, indicating that this molecule is a good electrophile in gas phase when compared to solvents. Electrofugality and nucleofugality are important concepts to explain the chemical reaction. Due to the greater polarity of acetonitrile

compared to the gas phase and the other solvents, TTF in acetonitrile has the highest electrofugality and nucleofugality. The results obtained in Table 4, shows that, the global chemical indices parameters of TTF increases with the increases in polarity of the solvents.

Table 4: Global Chemical Indices of the optimized structure of TTF molecule in the gas phase and different solvents

Molecules	η(eV)	∫(eV)	χ (eV)	μ (eV)	ω(eV)
Gas Phase	1.7709	0.5647	2.9636	-2,9636	2.4798
Toluene	1.7908	0.5584	2.9519	-2.9519	2.4329
Acetone	1.8165	0.5505	2.9969	-2.9969	2.4722
Acetonitrile	1.8187	0.5498	3.0005	-3.0005	2.4751
Dichloromethane	1.8111	0.5522	2.9826	-2.9826	2.4559

4.5 Thermodynamic properties

Table 5 presents the components and total contribution of the electronic, translational, rotational and vibrational energies to the entropy (S) and heat capacity (Cv) as well as the rotational constants and zero-point vibrational energies (ZPVE) of TTF in the gas phase and in different solvents. The results obtained shows that, acetonitrile have higher value of specific heat capacity and entropy, while, gas phase has higher value of ZPVE. It can be observed that the specific heat capacity of TTF is found to increase with an increase in the polarity of the solvents, while the entropy decreases as the dielectric constant increases. The zero-point vibrational energy (ZPVE) also decreases with an increase in the polarity of the solvents. The variation of thermodynamic properties changes slightly due to the effect of the solvents. Therefore, we conclude that the solvents have influence on the thermodynamic properties of the molecule. The results affirm that the molecule has higher chemical reactivity and thermal resistivity in solvents than in gas phase due to the increase in their kinetic energy.

Table 5: Thermodynamics properties of the optimized structure of TTF molecule in the gas phase and different solvents

Solvents	Gas Phase		Toluene		Acetone		Acetonitrile		Dichloromethane	
Positions	Cv (Kcal/ Mol)	S (Kcal/ Mol)	Cv (Kcal/ Mol)	S (Kcal/ Mol)	Cv (Kcal/ Mol)	S (Kcal/ Mol)	Cv (Kcal/ Mol)	S (Kcal/ Mol)	Cv (Kcal/ Mol)	S (Kcal/ Mol)
Electronic	0	0	0	0	0	0	0	0	0	0
Translational	2.981	41.842	2.981	41.842	2.981	41.842	2.981	41.842	2.981	41.842
Rotational	2.981	29.793	2.981	29.795	2.981	29.798	2.981	29.799	2.981	29.978
Vibrational	28.316	23.512	28.398	23.519	28.521	23.532	28.531	23.524	28.492	23.516
Total	34.278	95.146	34.359	95.156	34.482	95.172	34.492	95.164	34.453	95.155

Rotational Constants (GHz)	1.60012 0.54935 0.40895	1.60082 0.54838 0.40846	1.60160 0.54721 0.40786	1.60160 0.54712 0.40781	1.60111 0.54749 0.40798
ZPVE (Kcal/Mol)	51.23578	50.96078	50.55899	50.52542	50.65384

4.6 Non-Linear Optical Properties

Nonlinear optical (NLO) effect arises from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude and other propagation characteristics from the incident fields [32]. Also, dipole moment in a molecule is an important electronic property which results from non-uniform distribution of charges on the various atoms in the molecule [28]. It is worth l noting that, the molecule with higher dipole moment tends to be a polar material. Our investigation highlighted the effects of solvents on the nonlinear optical properties of TTF molecule. This is necessary for sufficient understanding of the nonlinear optical response of the molecule.

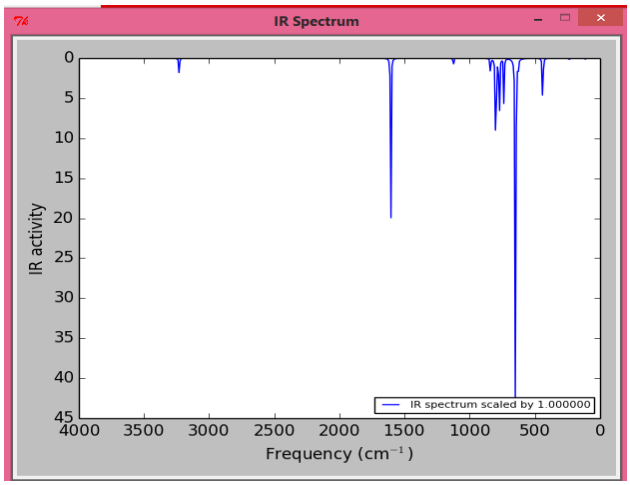
Table 6 shows the non-linear optical properties, in atomic unit (a.u), of TTF molecule in the gas phase and in solvents. It can observed from that there is an increase in values of total dipole moments ($\boldsymbol{\mu_{tot}}$), anisotropy of polarizability $\langle \boldsymbol{\Delta\alpha} \rangle$, first-order hyperpolarizability ($\boldsymbol{\beta_{tot}}$), and second-order hyperpolarizability ($\boldsymbol{\gamma_{tot}}$), while the mean polarizability $\langle \boldsymbol{\alpha} \rangle$ decreases due to the effects of the solvents. From the results obtained, acetonitrile has the highest values of dipole moment with value of 0.0053 Debye. The increase in the dipole moments of TTF in solvents leads to our belief that the molecule may behave as polar material in solvents. Our finding reveals that TTF molecule in gas phase has slightly higher value of mean polarizability when compared with the results obtained in solvents. However, the results obtained for total anisotropic polarizability shows that TTF in dichloromethane has slightly higher value (151.9769 au) when compared with the results obtained in gas phase and other solvents. Therefore, the polarizability of TTF molecule increases as the polarity of the solvents decreases whereas the anisotropic polarizability increases with an increase in the polarity of the solvents. Also, from the result in Table 6, TTF molecule in acetonitrile has slightly higher value of first order hyperpolarizability (0.1325au), followed by acetone, dichloromethane, toluene and then in gas phase with values 0.1299au, 0.1325au, 0.1151au and 0.1035au respectively. This shows that, there is an increase in the value of the first order hyperpolarizability in the order gas-phase<toluene<dichloromethane<acetone <acetonitrile. Therefore, the result indicates that the first order hyperpolarizability of TTF increases with an increase in the polarity of the solvents. Given the foregoing, we conclude that the presence of the solvents actually improved the NLO properties of the studied molecule.

Table 6: Non-linear optical properties (in atomic mass unit, au) and dipole moment (DEBYE) in of the optimized TTF Molecule in the gas phase and different solvents

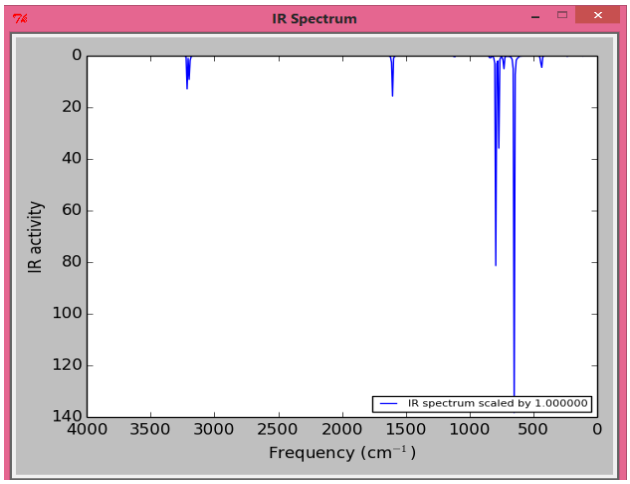
Molecules	μ_{tot}	$\langle\alpha\rangle$	$\langle\Delta\alpha\rangle$	β_{tot}	γ_{tot}
Gas Phase	0.0040	-81.2875	152.2049	0.1035	-1087.5936
Toluene	0.0045	-80.2293	153.0263	0.1151	-1070.6069
Acetone	0.0052	-78.8535	153.9108	0.1299	-1048.9696
Acetonitrile	0.0053	-78.7487	153.9736	0.1325	-1047.3424
Dichloromethane	0.0050	-78.8370	151.9769	0.1233	-1055.0988

4.7 IR Intensities

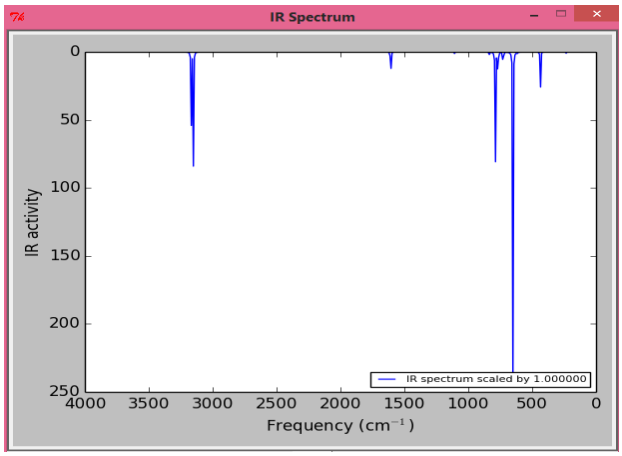
The main idea of frequencies analysis is to get vibrational modes connected with precise molecular structures of the measured compound [33]. Figure 2 shows the graphical representations of the calculated vibrational frequencies and intensities of TTF molecule in solvents and in gas phase. The representation shows that there is slight increase in the peak values of frequencies for the titled molecule in solvents when compared with gas phase. From the graphs, TTF in acetonitrile has the most intense frequency with value of 649.0267cm^{-1} with corresponding intensities of 256.6201 km/mol followed by acetone, dichloromethane, toluene and then gas phase with values of frequencies at 649.1057cm^{-1}, 648.9736cm^{-1}, 648.5214cm^{-1} and 647.0979cm^{-1} with corresponding intensities of 248.9105km/mol, 229.4762km/mol, 175.3651km/mol and 134.7277km/mol respectively. From the results obtained, the frequency of TTF molecule in gas phase and in solvents are in the order of acetonitrile>acetone>dichloromethane>toluene>gas phase. For all the solvents and gas phase under investigation, the frequency ranges between 647.09cm^{-1} and 649.03cm^{-1} with corresponding intensities between 134.73 km/mol and 256.62 km/mol. At these frequencies, s-#C-H band and s-C-Br stretch were observed. Infra-red pal (IRPAL) was used to interpret these frequencies. Comparing the graphs presented, TTF in acetonitrile has slightly higher peak values of frequencies with corresponding intensities than in gas phase and the rest of the solvents.



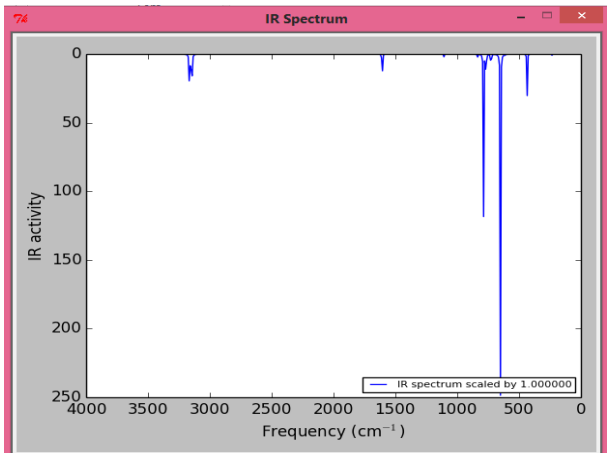
Gas Phase



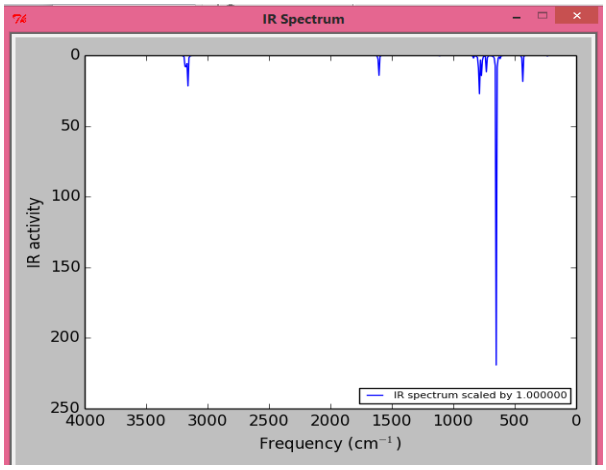
Toluene



Acetone



Acetonitrile



Dichloromethane

Figure 3: Computed IR Spectra of TTF molecule in gas phase and in solvents

CONCLUSION

In this work, the optimized parameters, electronic properties, density of state, thermodynamic parameters, non-linear optical properties, and vibrational frequencies of TTF in solvents and in gas phase have been investigated. It was revealed that the decrease in dielectric constant and polarity of the solvents increases the bond energy of the titled molecule. The average bond angles of the molecule in all the solvents used is 95.02˚. The global and local descriptors have been used to investigate the reactivity of different solvents and the influence of these on the molecular interaction was shown in a qualitative and quantitative way. The descriptors obtained could also provide more information and may contribute to a better understanding of the electronic structure of this compound. The HOMO-LUMO gap shows that the title compound is more stable in acetonitrile than in the rest of the solvents. In addition, theoretical results from reactivity descriptors and NLO studies for title compounds affirmed the stability of the titled molecule in acetonitrile than in the rest of the solvents. This indicates that the TTF molecule is more stable in solvent with higher dielectric constant. Finally we hope that this investigation will be of assistance in the quest of ionic and charge distribution for the title compound in the future.

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