Electronic Structure and IR Spectra Analysis of Tetrathiafulvelene (TTF) Using RHF and DFT Quantum Mechanical Methods

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Tetrathiafulvalene ($C_6H_4S_4$) is an organosulfur compound used in the manufacture of organic optoelectronic materials. Restricted Hartree-Fock (RHF) and Density Functional Theory (DFT) were employed for the study of the optimized molecular structure of TTF using different basis sets. All computations were performed using Gaussian 03 package. Parameters such as minimum energy, bond lengths and bond angles, HOMO-LUMO energy gap, chemical reactivity descriptors, Non-linear optical properties (such as isotropic polarizability (α), anisotropy of polarizability (∆∝), and total first hyper-polarizability (β_{tot})), density of states, vibrational frequencies, and intensities were computed and reported in order to determine the relative stability as well as chemical reactivity of the molecule. The results obtained show that RHF has the lowest average value of bond length of 1.0729Å while that obtained using DFT has the lowest average value of 1.0812Å using the same basis set 6-311++G (d, p). This shows that the value is a bit higher using DFT than RHF which implies that the bonds of TTF molecule will be slightly stronger when optimized using RHF than DFT. The bond angles were found to be slightly higher by using DFT than RHF. The calculated HOMO-LUMO energy gap shows that the molecule will be slightly more stable in chemical reaction using RHF than DFT. The DFT values, 3.59 eV and 3.60 eV obtained for the energy gap are closer to the reported value of 3.63eV compared to those obtained by RHF. From the results obtained for

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vibrational frequencies using both methods, TTF is stable due to the absence of imaginary frequencies. This confirms the stability of the molecule as stated in the results of HOMO-LUMO energy gap. The calculated vibrational frequencies show that the most intense frequency was obtained to be $752.6293 cm^{-1}$ at corresponding intensity of 145.9063KM/mole by RHF/6-31++G (d, p) while at B3LYP/6-31+G(d), the most intense frequency is about $635.0243\ cm^{-1}$ with corresponding intensity of 138.5738MK/mole. By and large, the studyunveil the potential of Tetrathiafulvalene for optoelectronic applications.

1. INTRODUCTION

Energy shortage has become a worldwide issue in the 21st century [1]. The urge to look for renewable energy to replace fossil fuel has driven substantial research effort into the energy sector [2]. Many research efforts were made in order to study the properties of other materials to solve the problem of this energy shortage, heterocyclic compounds included. Heterocyclic compounds are commonly distributed in nature and are essential to life in various ways [3]. Since the emergence of organic metals, a large amount of research work has been carried out in order to improve the conductivities of salts and charge transfer complexes (CT) of TTF derivatives. Tetrathiafulvalene ($C_6H_4S_4$) is an organosulfur compound used in the manufacture of organic electronic materials. However, interest in TTF molecules goes beyond the area of conducting materials. To investigate its role as an important building block in supramolecular conductivity, various categories of organic conductors have now been described [4-5]. These include systems based upon molecular charge-transfer complexes, conjugated polymers, and stacked organometallic species, where the metal atoms play no active role in the conduction. Tetrathiafulvalene (TTF) and its derivatives [6] are very versatile electro-active molecules commonly used as building blocks to prepare

organic metals for supramolecular functions [7] and in molecular electronics [8]. Donor–acceptor type dyads using a Tetrathiafulvalene (TTF) framework have received considerable interest as materials for fluorescence switches, chemical sensors, molecular rectification, photovoltaic, and NLO applications [9-14].

Quantum mechanical calculation is one of the emerging methods in analyzing the physical and chemical properties of these molecules. Density Functional Theory (DFT) has emerged as a powerful method for the study of electronic properties of polyatomic molecules. The application of DFT to chemical molecular systems has received much attention because of its faster convergence in time than traditional quantum mechanical correlation methods [15]. Theoretical computational method such as geometry optimization is very important for understanding and predicting the pathways of electron and energy transfer processes in photoactive assemblies [16]. As a result, a set of global and local descriptors parameters to measure the reactivity of the molecule have been investigated. However [17] reported the investigation of the molecular structure, HOMO-LUMO, MEP and Fukui Function analysis of some TTF-donor Substituted Molecules using DFT (B3LYP).
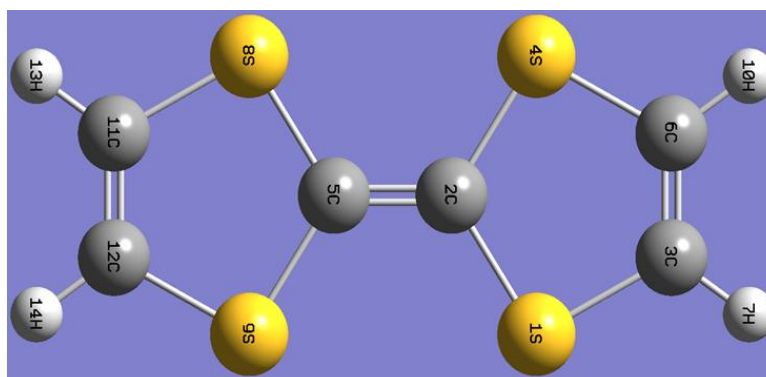

Fig. 1. optimized structure of TTF

The presence of the donor substituted molecules showed a significant increase in the HOMO-LUMO energy gap of the neutral TTF molecule. Similarly, [18] carried out a theoretical study of the molecular structure, NBO analysis, first-hyperpolarizability, and HOMO-LUMO studies of bis(dithiolylidene)-tetrathiapentalene (BDT-TTP) by quantum computational methods. The molecule was revealed 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. In another report by [19], they authors explored the structure, electron Density and HOMO-LUMO Studies of Tetrathiafulvalene (TTF) as organic semiconductor. It was found that the bond distance calculated by HF/6-311G** and B3LYP/6-311G** methods were shorter than the B3LYP/aug-cc-PVDZ method. The C–S–C bond angles predicted from B3LYP/ 6-311G** and B3LYP/aug-cc-PVDZ methods were found to be almost equal and the average value was 94.7∘. The calculated HOMO-LUMO energy for B3LYP/6-311G** and B3LYP/aug-cc-PVDZ were obtained to be 3.75eV and 3.63eV respectively. Recently [20] reported on the theoretical study of chemical reactivity descriptors of Tetrathiafulvalene in gas phase and in solvents based on DFT. TTF molecule was observed to have greater stability (low reactivity) in the 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 [20]. In the results, bond lengths and bond angles, optoelectronic properties, density of states (DOS), nonlinear optical (NLO) properties and IR spectra analysis were not reported. Just recently, [21] reported a theoretical study of solvent effects on the electronic and thermodynamic properties of Tetrathiafulvalene (TTF) based on DFT. The results revealed that the molecule has strong bond in gas phase with smallest bond length of about 1.0834Å. It was also observed that the molecule was more stable in acetonitrile with HOMO-LUMO gap and chemical hardness of 3.6373eV and 1.8187eV respectively. The thermodynamics and NLO properties calculation also indicated that TTF molecule has the highest value of specific heat capacity (Cv), total dipole moment (μ_{tot}) and first order hyperpolarizability (βtot) in acetonitrile, while acetone has the highest value of entropy and toluene has a slightly higher value of zero point vibrational energy (ZPVE) . In all the results reported in the literatures so far, RHF quantum mechanical method has not been adequately used to report the properties of parent TTF such as thermodynamic properties and IR spectra. Thus, the purpose of the work is to investigate the effect of different quantum methods on the electronic, non-linear optical, thermodynamic properties and IR frequencies of the molecule using the theoretical framework of Density Functional Theory (DFT) and Restricted Hartree Fock (RHF).

2. THEORETICAL BACKGROUND

2.1 Global Reactivity Descriptors

The chemical reactivity of the molecule has been determined on the basis of Koopmans's theorem [22]. Energies of frontier molecular orbitals (E_{HOMO}, E_{LUMO}), have been used to calculate global reactivity descriptors such as, electronegativity *(χ)*, chemical potential *(μ)*, Global hardness *(η)*, global softness *(S)*, and electrophilicity index *(ω)*. These important descriptors are calculated as follows:

The approximated form of electronegativity and chemical potential are expressed as [23];

$$\text{Electronegativity} \quad \chi = \frac{1}{2}(E_{HOMO} + E_{LUMO})$$
$$= \frac{1}{2}(IP + EA) \qquad (1)$$

$$\text{Chemical potential } \mu = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \approx -\frac{1}{2}(IP + EA) \qquad (2)$$

The global hardness and softness are given as [20];

$$\text{Global hardness } \eta = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \approx \frac{1}{2}(IP - EA) \qquad (3)$$

$$\text{Global softness } S = \frac{1}{\eta} \qquad (4)$$

and Electrophilicity index is expressed as [24];

$$\omega = \frac{\mu^2}{2\eta} \qquad (5)$$

2.2 Non-linear Optical Properties

The calculated Non-Linear Optical Properties are of paramount importance in determining the NLO properties of a material which remain like a litmus test and qualifies the material for many electronic and photonic applications. A material

should have large value of these calculated properties for it to be a good NLO. In order to calculate the non-linear optical properties (NLO) of TTF molecule, the dipole moment *(μ)*, polarizability$< \alpha >$, anisotropic polarizability *(Δα)*, and hyperpolarizability *(β and γ)* were computed at DFT/B3LYP with two basis sets.

The mean polarizability is calculated using [25];

$$< \alpha > = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (6)$$

where α_{xx}, α_{yy} and α_{zz} quantities are known as principal values of polarizability tensor.

The anisotropic polarizability is given by [26];

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} \square \alpha_{xx})2 + 6\alpha_{xx}2]1/2 \qquad (7)$$

The first hyperpolarizability is defined as [27];

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})2]1/2 \qquad (8)$$

The second order hyperpolarizability is given by [28];

$$\gamma = \frac{1}{5}[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}] \qquad (9)$$

For molecular systems, dipole moment can be obtained from [26];

$$\mu_{tot} = [\mu_x^2 + \mu_y^2 + \mu_z^2]^{1/2} \qquad (10)$$

where μ_x, μ_y and μ_z are the components of dipole moment in x, y and z coordinates.

Electric dipole polarizability is given by [29];

$$\alpha = -\frac{\partial^2 E}{\partial F_a \partial F_b} \qquad (11)$$

3. THEORETICAL METHODOLGY

The molecular structures and geometries of TTF have been completely optimized using *ab-initio* quantum mechanical calculations at the RHF and DFT levels of theory without using any symmetry constraints using different basis sets (6-31++G (d, p), 6-311+G (d), and 6-31++G (d, p)). 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. Stability check was performed on the molecule to confirm its stability status prior to geometry optimization. Geometry optimization is a name given to the procedure that attempts to

find the configuration of minimum energy of the molecule. More generally, geometry optimization was done by locating both the minima and transition states on the potential surface of the molecular orbitals. The procedure calculated the wave function and the energy at the starting geometry and then proceeded to search a new geometry of a lower energy. This was repeated until the lowest energy geometry was obtained. The optimized geometries were then used to compute the HOMO-LUMO energy gap values and global chemical index parameters. At the same levels of the theory, dipole moment, electric dipole polarizability, mean polarizability, anisotropic polarizability, hyperpolarizability, entropy and the specific heat capacity of the molecule under investigation were also computed using the same optimized geometries. The nonlinear optical properties of the molecule such as dipole moment, isotropic polarizability, anisotropic polarizability and total first and second order hyperpolarizability were also computed by using similar procedure. The IR frequencies were calculated by obtaining the Hessian matrix and the force constants for all the normal modes of the molecule. The optimized molecule obtained from geometry optimization was then used at the starting point of geometry for IR spectra calculations, and then the frequency job proceeded by computing the energy of the input structure and then finally went on to compute the frequencies of the molecules. No imaginary frequencies were seen thus confirming the stability of the molecule. Gaussian predicted the frequencies and intensities of each spectral line. All calculations were done by using Density Functional Theory (DFT) a Gaussian 03 software [30]. Analysis of the spectra was done using IRPal 2.0 version software.

4. RESULTS AND DISCUSSION

4.1 Optimized Parameters

4.1.1 Optimized bond lengths (Å) of TTF Molecule

The optimized bond lengths of TTF at two different levels of theory (RHF and B3LYP) are listed in Tables 1 and 2. The bond length is the quantifiable distance between two atoms covalently bonded together. It is worth noting that, if the bond length is shorter, then the bond energy is higher [31]. The results obtained show that the bond lengths using RHF method has the lowest average value of 1.0727Å and at DFT level, has the lowest average value of 1.0812Å.

This indicates that the values are a bit higher in DFT than in RHF which implies that the bonds will be slightly stronger in RHF than in DFT. Table 1 also shows that the basis set 6-311+G (d) gives the lowest values of the bond lengths and 6-31++G (d, p) basis set gives the highest values of the bond angles at RHF level of theory. Similarly for B3LYP, the basis set 6-311++G (d, p) gives the lowest values of the bond lengths and 6-31++G (d, p) gives the highest values. The lowest values of the bond lengths at both levels ranges between 1.0727Å to 1.0812Å. These are the strongest bonds and have the largest values of bond energy in the TTF molecule which cannot be easily broken. A large amount of energy is needed to break them. On the other hand, at both levels of theory, highest values of bond lengths range from 1.7785Å to 1.7889Å. These are the weakest bonds and less amount of energy are required to break them.

4.1.2 Optimized bond angle (Å) of TTF molecule

The bond angle is the angle between the directions of two bonds in the molecule [32]. The bond angle shades more light on the distribution of orbitals around the central atom in that molecule. The bond angles also contribute to the shape of a molecule. When electron pairs are distributed away from the central atom, repulsions are decreased allowing smaller bond angles. However, as more electron repulsion between the bonded pairs increases; bond angles increases. The optimized bond angles of TTF molecule at both levels of theory (RHF and B3LYP) are listed in Table 2. It can be observed from the table that, the average values for the lowest bond angles using RHF is 95.10º and that of DFT is 95.0º, while the average value for the highest bond angles using RHF is 124.5º and that of DFT is 124.8º. This shows that, the result obtained using DFT are a bit higher than the one obtained using RHF by about 0.3°. This indicates that, the TTF has higher stability when optimized with DFT than RHF.

4.2 Frontier Molecular Orbital (FMOs) Energies

Molecular orbitals (MO's), both the Highest Occupied Molecular Orbital *(HOMO)* and the Lowest Unoccupied Molecular Orbital *(LUMO)* and their energy gap (E_{gap}) are very useful parameters for quantum Physics. HOMO tends to act as electron donor while LUMO can be thought as an electron acceptor. A molecule having a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [33]. The energy is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity.

Tables 3, shows the calculated values of the HOMO, LUMO and HOMO-LUMO Energy gap in atomic unit (a.u) and in electron volt (eV) using RHF and DFT methods. It is clear from Table 3 that the HOMO-LUMO energy gap for the TTF molecule is higher using 6-311+G (d) basis set with value of about 8.5523(eV) followed by 6-31++G(d,p) and then 6-311++G(d,p) with values of 7.9606eV and 7.9294eV respectively at RHF level of the theory. But it is observed that at B3LYP level of theory, the highest energy gap for all basis sets used is 3.5951eV at 6-311++G (d, p) followed by 6-311+G (d) and then 6-31++G (d, p) with values of 3.5924eV and 3.5418eV respectively. The value 3.5924e V, is more in agreement to a reported value of 3.64 [21]. Thus, B3LYP calculations are more in agreement with the experimental value due to the inclusion of electron correlation compare to RHF.

4.3 Ground State Energy

Table 4 presents the total energy of the TTF molecule using RHF and DFT methods. It is clearly seen that the RHF method has nearly the same total energy across the basis sets. The same behavior was observed in DFT method. From the results obtained, it was observed that the basis set specification plays less significant role in determining the total energy of the molecule. The 6-31++G (d, p) basis set gives slightly higher values (-1823.75502576a.u and -1819.52431090a.u) than the other basis sets for both DFT and RHF. The lowest energy value is -1823.90136203a.u at 6-311++G, thus making TTF less stable with 6-311++G (d, p) basis set compare to other basis sets.

4.4 Density of State (DOS)

The important application of Density of State (DOS) plot is to demonstrate the molecular orbital and their contributions of chemical bonding through the Overlap Population Density of States (OPDOS) plot [34]. The DOS plot results show the overlapping population in the molecular orbital. 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.

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Table 1. Optimized Bond Lengths of Tetrathiafulvalene using RHF and DFT methods

Bond Lengths (Å)	RHF			B3LYP			Previous Works [21]
	6-31++G(d,p)	6-311+G(d)	6-311++G(d,p)	6-31++G(d,p)	6-311+G(d)	6-311++G(d,p)	
R(1,2)	1.7785	1.7786	1.7785	1.7889	1.7877	1.7876	1.7889
R(1,3)	1.7558	1.7572	1.7570	1.7611	1.7601	1.7600	
R(2,4)	1.7785	1.7786	1.7785	1.7889	1.7877	1.7876	
R(2,5)	1.3279	1.3253	1.3253	1.3516	1.3469	1.3468	
R(3,6)	1.3183	1.3156	1.3157	1.3396	1.3341	1.3342	1.3396
R(3,7)	1.0730	1.0727	1.0729	1.0834	1.0822	1.0812	
R(4,6)	1.7558	1.7572	1.7570	1.7611	1.7601	1.7600	
R(5,8)	1.7785	1.7786	1.7785	1.7889	1.7877	1.7876	
R(5,9)	1.7785	1.7786	1.7785	1.7889	1.7877	1.7876	
R(6,10)	1.0730	1.0727	1.0729	1.0834	1.0822	1.0812	1.0834
R(8,11)	1.7558	1.7572	1.7570	1.7611	1.7601	1.7600	1.7611
R(9,12)	1.7558	1.7572	1.7570	1.7611	1.7601	1.7600	
R(11,12)	1.3183	1.3156	1.3157	1.3396	1.3341	1.3342	1.3516
R(11,13)	1.0730	1.0727	1.0729	1.0834	1.0822	1.0812	
R(12,14)	1.0730	1.0727	1.0729	1.0834	1.0822	1.0812	

Table 2. Optimized Bond Angles of Tetrathiafulvalene using RHF and DFT methods

Bond Angles (°)	RHF			B3LYP		
	6-31++G(d,p)	6-311+G(d)	6-311++G(d,p)	6-31++G(d,p)	6-311+G(d)	6-311++G(d,p)
A(2,1,3)	95.0364	95.0491	95.0797	94.9157	94.9432	94.9765
A(1,2,4)	113.5873	113.5374	113.4995	113.9351	113.7999	113.7625
A(1,2,5)	123.2061	123.2311	123.2500	123.0321	123.0998	123.1184
A(4,2,5)	123.2066	123.2316	123.2505	123.0328	123.1004	123.1191
A(1,3,6)	118.1699	118.1823	118.1707	118.1169	118.1570	118.1424
A(1,3,7)	117.4381	117.2534	117.2641	117.2287	117.0276	117.0196
A(6,3,7)	124.3920	124.5643	124.5652	124.6544	124.8154	124.8380
A(2,4,6)	95.0363	95.0490	95.0795	94.9155	94.9430	94.9763
A(2,5,8)	123.2061	123.2311	123.2500	123.0321	123.0998	123.1184
A(2,5,9)	123.2066	123.2316	123.2505	123.0328	123.1004	123.1191
A(8,5,9)	113.5873	113.5374	113.4995	113.9351	113.7999	113.7625

Bond Angles (˚)	RHF			B3LYP		
	6-31++G(d,p)	6-311+G(d)	6-311++G(d,p)	6-31++G(d,p)	6-311+G(d)	6-311++G(d,p)
A(3,6,4)	118.1700	118.1823	118.1707	118.1168	118.1569	118.1423
A(3,6,10)	124.3921	124.5644	124.5653	124.6545	124.8153	124.8380
A(4,6,10)	117.4379	117.2533	117.2640	117.2287	117.0278	117.0197
A(5,8,11)	95.0364	95.0491	95.0797	94.9157	94.9432	94.9765
A(5,9,12)	95.0363	95.0490	95.0795	94.9155	94.9430	94.9763
A(8,11,12)	118.1699	118.1823	118.1707	118.1169	118.1570	118.1424
A(8,11,13)	117.4381	117.2534	117.2641	117.2287	117.0276	117.0196
A(12,11,13)	124.3920	124.5643	124.5652	124.6544	124.8000	124.8380
A(9,12,11)	118.1700	118.1823	118.1707	118.1168	118.1569	118.1423
A(9,12,14)	117.4379	117.2533	117.2640	117.2287	117.0278	117.0197
A(11,12,14)	124.3921	124.5644	124.5653	124.6545	124.8153	124.8380

Table 3. HOMO, LUMO and HOMO-LUMO Energy gap of Tetrathiafulvalene (TTF) using RHF and DFT methods

Method	Basis sets	HOMO (a.u)	LUMO (a.u)	HOMO-LUMO Energy gap (a.u)	HOMO-LUMO Energy gap (eV)	Previous works [21] HOMO-LUMO Energy gap (eV)
RHF	6-31++G(d,p)	-0.25391	0.03864	0.2925	7.9606	
	6-311+G(d)	-0.25458	0.05971	0.3143	8.5523	
	6-311++G(d,p)	-0.25468	0.03669	0.2914	7.9294	
B3LYP	6-31++G(d,p)	-0.17399	-0.04383	0.1302	3.5418	
	6-311+G(d)	-0.17503	-0.04301	0.1320	3.5924	
	6-311++G(d,p)	-0.17535	0.04323	0.1321	3.5951	3.6400

Table 4. Total ground state energy (a.u) of TTF Molecule using RHF and DFT methods

Method	RHF	B3LYP
6-31++G(d,p)	-1819.52431090	-1823.75502576
6-311+G(d)	-1819.64352409	-1823.89362171
6-311++G(d,p)	-1819.65149384	-1823.90136203

From the density of states (DOS) of the optimized structure of TTF using DFT and RHF, the population of charges is becoming denser in the order DFT<RHF (as seen from Fig. 2). This suggests that optimizing TTF using RHF free charges, and the weak intermolecular forces affected the charges population of the molecule compared to DFT method. As observed in the entire DOSs, the population of the charges is highly concentrated in the valence region, which indicates that TTF molecule possess high tendency to behave as n-type semiconductor material. It is also observed that 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. Since the population of the charges is dense 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 using both RHF and DFT. The results of DOS using DFT are more in agreement to a reported one in the literature [21].

4.5 Global Chemical Indices

Chemical reactivity indices of TTF using RHF and DFT methods are presented in Table 5. The HOMO and LUMO of TTF are used to determine the chemical reactivity parameters of the molecule. Such parameters measure the relative stability and reactivity of the molecule. These parameters include chemical hardness *(η)*, electronic chemical potentials *(μ)* and electrophilicity *(ω)*. Chemical hardness is linked to the stability and reactivity of a chemical system. According to the frontier molecular orbital approach, chemical hardness is proportional to the energy gap. The larger the HOMO-LUMO energy gap, the harder and more stable (less reactive) the molecule [35]. From Table 5, optimizing TTF at the level of RHF using 6-311+G (d) is the most stable with the highest chemical hardness of 4.2762eV, follow by 6-31++G (d, p) (3.9803eV), and then 6-311++G (d, p) (3.9647eV). While at the level of DFT using 6-311++G (d, p) is the most stable with the highest chemical hardness of 1.7976eV, follow by 6-311+G (d) (1.7962eV), and then 6-31++G (d, p) (1.7709eV). The negative of electro-negativity is termed as electrochemical potential. The lower value of this global quantity indicates the stability of a molecule. Electrophilicity (ω) measures the capacity of a specie to accept electrons and

therefore measures the stabilization in energy after a system accepts additional electronic charge [36]. At RHF level of the theory, 6-311+G (d) basis set has strongest nucleophiles due to its lower ω while at DFT, 6-311++G (d, p) has the strongest electrophiles due to its higher ω. The results obtained for global chemical reactivity descriptors using DFT is more in agreement to a reported value in the literature [21].

4.6 Non-Linear Optical Properties

The Non-linear Optical (NLO) Properties such as dipole moment, polarizability (isotropic and anisotropy) and first order hyperpolarizability for the studied molecule are shown in Table 6. These properties of a material are important in determining its potentials in electronic and photonic applications. Organic materials that exhibit large NLO properties have emerged as an important class of electronic materials with interesting characteristics. From the table, it can be seen from the RHF and DFT methods that the dipole moment and the first order hyperpolarizability of TTF have almost diminished (equals to zero) for both 6-311+G(d) and 6-311+G(d) basis sets. It can also be observed that basis set specification has shown little impact on the NLO properties. For both isotropic and anisotropic polarizability, the RHF and DFT methods have the largest values of 189.9772a.u and 197.6116a.u respectively using 6-311+G (d) basis set. The 6-31++G (d, p) basis set lifted and yielded good values of NLO properties than the other basis set.

4.7 Thermodynamic Properties

The computed thermodynamic parameters of TTF are presented in Tables 7a and 7b. The analysis of thermodynamic parameters is important to estimate the outcome of a chemical reaction [37]. Our findings show that the specific heat capacity and entropy of TTF are found to increase due to the influence of the basis sets. On the other hand, the zero-point vibrational energy (ZPVE) of TTF decreases for both methods used. By analyzing the results obtained, the thermodynamic properties changes slightly due to the effect of the theory and basis sets used. Therefore, we conclude that DFT method has greater influence on the thermodynamic properties of TTF than RHF. The results affirm that optimizing TTF using DFT method has higher chemical reactivity and thermal resistivity than RHF due to the increase in their kinetic energy. By comparing the results of the three basis sets, we can conclude that the basis set 6-

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311++G (d, p) gives higher values of specific heat capacity and entropy than 6-31++G (d, p) and 6-311+G (d, p) basis sets for RHF and DFT methods. While 6-31++G (d, p) gives the highest value ZPVE at the same level of theory.

4.7 Vibrational Frequencies and IR Intensities

The main idea of frequency analysis is to get the vibrational modes connected with precise molecular structure of the compound [38]. Tables 8a and 8b show the calculated values of the vibrational frequencies and intensities of TTF. No imaginary frequency is found, which shows that the molecule is indeed stable. From the results,

the most intense frequency of TTF using RHF ranges between $739.0429 cm^{-1}$ - $752.6293 cm^{-1}$ with corresponding intensities between 137.5138 km/mol - 145.0963 km/mol. At these frequencies, s #C-Cl stretch, m C-H out of plane, s S-R esters and s (broad) N-H wag amines were observed. While for DFT [39] methods, the frequencies range between $643.2925 cm^{-1}$ - $647.0979 cm^{-1}$ with corresponding intensities between 131.6045 km/mol - 134.7277 km/mol. At these frequencies, s #C-H bend and s C-Br stretch were observed. IRPAL 2.0 was used to interpret these frequencies. Comparing the results presented, RHF method has slightly higher peak values of frequencies with corresponding intensities [40].
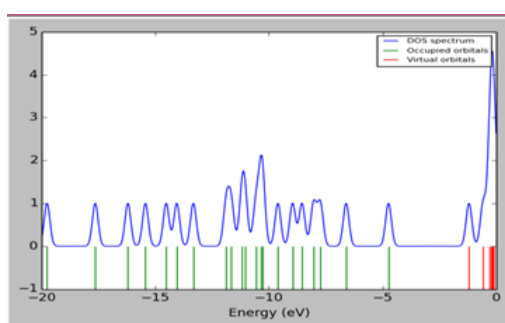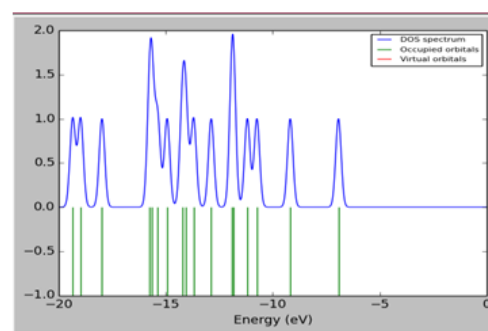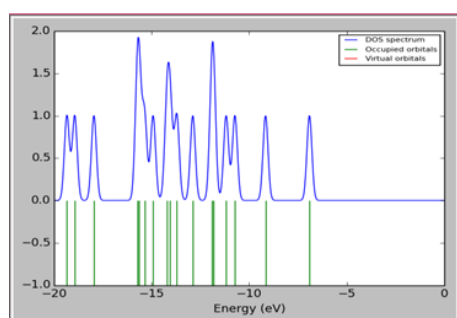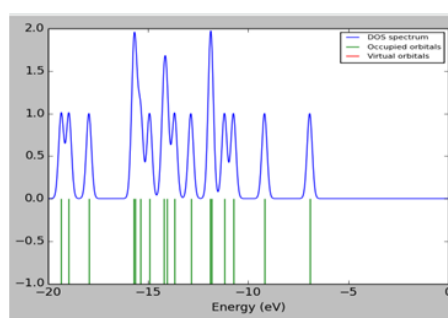

DFT/6-31++G (d, p)
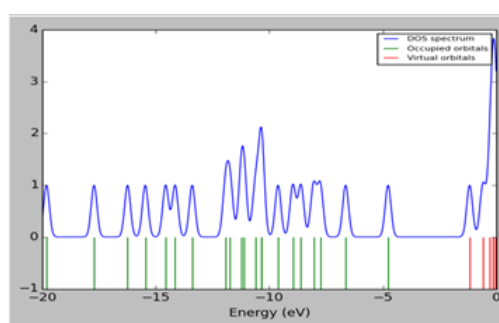
DFT/6-311+G (d)
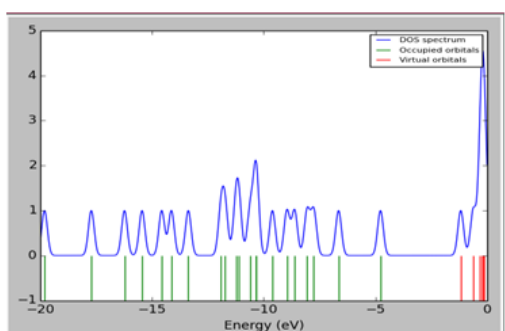
DFT/6-311++G (d, p)

RHF/6-31++G (d, p)

RHF/6-311+G (d)

RHF/6-311++G (d, p)

Fig. 2. Computed density of states (DOS) of TTF

Table 5. Global Chemical Indices for Tetrathiafulvalene using RHF and DFT methods

Methods	RHF			DFT			Previous works [21]
Basis sets	6-31++G(d, p)	6-311+G(d)	6-311++G(d, p)	6-31++G(d, p)	6-311+G(d)	6-311++G(d, p)	
$\eta(eV)$	3.9803	4.2762	3.9647	1.7709	1.7962	1.7976	1.936
$S(eV)$	0.2512	0.2339	0.2522	0.5647	0.5567	0.5563	
$\chi (eV)$	2.9289	2.6513	2. 9659	2.9636	2. 9666	1.7976	
$\mu (eV)$	-2.9289	-2.6513	-2. 9659	-2.9636	-2. 9666	-1.7976	
$\omega(eV)$	1.0031	0.8220	1.1094	2.4798	2.4498	0.8987	2.4798

Table 6. Calculate Non-linear Optical Properties of TTF Molecules using RHF and DFT methods

RHF					B3YLP			
NLO	μ_{tot}	$\langle\alpha\rangle$	$\langle\Delta\alpha\rangle$	β_{tot}	μ_{tot}	$\langle\alpha\rangle$	$\langle\Delta\alpha\rangle$	β_{tot}
6-31++G(d, p)	0.0044	-81.3248	152.1614	0.1161	0.0043	-81.4019	152.1272	0.1130
6-311+G(d)	0.0006	-104.3837	189.9772	0.0157	0.0000	-114.3740	197.6116	0.0001
6-311++G(d, p)	0.0000	-62.9025	132.4064	0.0004	0.0000	-62.9494	187.1292	0.0002

Table 7a. Thermodynamics properties of the optimized structure of TTF using RHF

Molecules	6-31++G (d, p)		6-311+G (d)		6-311++G (d, p)	
Positions	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
Translational	2.981	41.842	2.981	41.842	2.981	41.842
Rotational	2.981	29.748	2.981	29.747	2.981	29.747
Vibrational	25.368	20.981	25.636	21.175	27.612	30.272
Total	31.330	92.571	31.597	92.764	33.573	101.861
Rotational Constants (GHz)	1.62764 0.55679 0.41487		1.62875 0.55691 0.41501		1.62951 0.55671 0.41495	
ZPVE (Kcal/Mol)	55.86679		55.50077		55.39728	

Table 7b. Thermodynamics properties of the optimized structure TTF using B3LYP

Molecules	6-31++G (d, p)			6-311+G (d)			6-311++G (d, p)		
Positions	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	
Translational	2.981	41.842		2.981	41.842		2.981	41.842	
Rotational	2.981	29.793		2.981	29.786		2.981	29.786	
Vibrational	28.316	23.512		28.471	23.768		28.446	23.752	
Total	34.278	95.146		34.433	95.395		34.407	95.380	
Rotational Constants (GHz)	1.60012	0.54935	0.40895	1.60521	0.55032	0.40982	1.60594	0.55012	0.40976
ZPVE (Kcal/Mol)	51.23578			50.96271			50.95526		

Table 8a. Vibrational Frequencies and Intensities of TTF molecule using RHF

Mode	RHF					
	6-31++G (d, p)		6-311+G(d)		6-311++G(d,p)	
	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
1.	4.5947	6.4055	3.8422	6.6630	5.7499	6.6272
2.	64.9243	0.0001	66.1091	0.0001	66.1945	0.0001
3.	99.4340	0.0000	99.2818	0.0000	99.1205	0.0000
4.	126.4629	0.9629	124.3763	0.9892	124.4141	0.9795
5.	274.8416	0.0000	272.8912	0.0000	272.8391	0.0000
6.	280.7109	0.2454	278.2857	0.1434	279.4473	0.1621
7.	336.2174	0.0000	334.7301	0.0000	334.8243	0.0000
8.	453.6573	0.0000	447.6005	0.0000	447.3049	0.0000
9.	457.2765	0.0000	452.4447	0.0000	452.6466	0.0000
10.	474.1990	17.9559	469.5122	19.2484	469.4918	19.1647
11.	510.7495	0.0000	505.5620	0.0000	505.6016	0.0000
12.	612.3995	0.0000	604.5518	0.0000	603.4211	0.0000
13.	664.9411	0.0000	660.4713	0.0000	659.8978	0.0000
14.	677.0015	0.5084	672.7700	0.7910	672.2664	0.7823
15.	751.6154	0.0000	738.3153	0.0001	743.0337	0.0000
16.	752.6293	145.9063	739.0429	140.9426	745.3345	137.5138
17.	796.7957	9.5495	787.3103	10.9982	787.5053	10.8674
18.	799.6582	0.0000	790.0034	0.0000	790.1994	0.0000

Mode	RHF					
	6-31++G (d, p)		6-311+G(d)		6-311++G(d,p)	
	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
19.	840.1464	36.3159	832.8485	39.1834	832.9716	39.4482
20.	870.7038	53.6938	862.1269	55.7047	861.6307	57.1448
21.	880.3781	0.0000	870.9656	0.0000	870.5255	0.0000
22.	949.3929	7.5179	939.7386	6.4988	939.6254	6.5729
23.	1028.6896	0.0000	1014.5929	0.0000	1019.1419	0.0000
24.	1029.2986	0.0000	1014.6858	0.0000	1019.8024	0.0000
25.	1116.4837	0.0000	1104.4275	0.0000	1104.5152	0.0000
26	1226.1314	0.9529	1224.4625	0.6216	1217.6978	0.4502
27	1226.4411	0.0000	1224.8066	0.0000	1218.0565	0.0000
28	1418.5930	0.2430	1417.2680	0.2463	1407.4805	0.1457
29	1421.0538	0.0000	1419.9507	0.0000	1410.0748	0.0000
30	1756.7197	0.0000	1747.1304	0.0000	1745.3970	0.0000
31	1777.7129	38.4701	1767.6930	39.3365	1764.1306	40.3678
32	1807.0858	0.0000	1797.4260	0.0000	1795.8218	0.0000
33	3387.9065	0.0000	3373.8423	0.0000	3359.4520	0.0000
34	3388.1580	6.7911	3374.0927	2.7835	3359.7381	6.7143
35	3410.4407	1.7373	3396.9557	7.4861	3382.7485	2.1748
36	3410.5356	0.0000	3397.0793	0.0000	3382.8609	0.0000

Table 8b. Vibrational Frequencies and Intensities of TTF molecule using B3LYP

Mode	B3LYP					
	6-31++G(d,p)		6-311+G(d)		6-311++G(d,p)	
	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
1	24.4007	3.8318	28.9767	3.8990	28.2373	3.7866
2	79.3824	0.0001	76.5265	0.0002	76.5584	0.0002
3	83.3416	0.0000	81.5440	0.0000	81.0886	0.0000
4	109.2491	0.5881	107.6472	0.5928	107.6761	0.5729
5	236.0493	0.9265	236.6532	0.8593	237.5959	0.8796
6	251.3433	0.0001	250.3095	0.0001	250.2600	0.0001
7	306.3438	0.0000	304.9430	0.0000	305.0130	0.0000
8	413.2807	0.0000	408.7902	0.0000	407.6907	0.0000

Mode	B3LYP					
	6-31++G(d,p)		6-311+G(d)		6-311++G(d,p)	
	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
9	417.5773	0.0000	414.5768	0.0000	414.8000	0.0000
10	438.2210	19.1177	435.0479	20.4719	435.0598	20.3545
11	471.3317	0.0000	468.3228	0.0000	468.3674	0.0000
12	503.7803	0.0002	513.3126	0.0002	512.4114	0.0002
13	616.5712	0.0000	615.5252	0.0000	614.8623	0.0000
14	626.4571	1.6788	625.3876	2.0973	624.7912	2.0915
15	646.3426	0.0001	634.8459	0.0001	641.0365	0.0001
16	647.0979	134.7277	635.0243	138.5738	643.2925	131.6045
17	735.8517	12.0613	729.7503	12.3846	729.7315	12.1780
18	738.6558	0.0000	732.4783	0.0000	732.4050	0.0000
19	772.0953	24.8138	768.9901	25.7783	768.9768	26.1163
20	798.2178	54.2874	792.1273	54.3712	791.5905	55.4767
21	807.1190	0.0000	801.1665	0.0000	800.5423	0.0000
22	839.3278	5.2404	830.8170	6.4659	830.4742	6.1810
23	862.4252	0.0000	855.0132	0.0000	862.2408	0.0000
24	862.6842	0.0000	855.2116	0.0000	863.2276	0.0000
25	979.5186	0.0000	972.5556	0.0000	972.6813	0.0000
26	1125.0057	3.1089	1127.3606	2.9832	1121.6268	2.5574
27	1125.3409	0.0000	1127.7274	0.0000	1122.0201	0.0000
28	1287.2131	0.0308	1292.6654	0.0013	1284.1174	0.0019
29	1289.6470	0.0000	1295.0773	0.0000	1286.4421	0.0000
30	1584.5121	0.0000	1576.1299	0.0000	1574.7862	0.0000
31	1604.7630	41.4233	1598.4684	40.4271	1594.7101	42.3440
32	1629.6972	0.0000	1622.0244	0.0000	1619.9591	0.0000
33	3228.0590	0.0000	3205.6332	0.0000	3206.8385	0.0000
34	3228.2624	5.6876	3205.8436	2.6979	3207.0669	5.8909
35	3247.5597	0.1103	3225.6804	1.9872	3226.8519	0.0222
36	3247.6238	0.0000	3225.7578	0.0000	3226.9335	0.0000

5. CONCLUSION

In this work, the optimized parameters, electronic properties, density of state, thermodynamic parameters, non-linear optical properties, [41] and vibrational frequencies of TTF have been investigated using different basis sets. It was revealed that the RHF method increases the bond energy of the titled molecule than DFT method. The average bond angles of the molecule increases with DFT method. Our main aim was to study the effect of different mechanical methods for the better understanding of the electronic structure of this compound. The global chemical descriptors have been used to investigate the reactivity of TTF. The HOMO-LUMO energy gap shows that the title compound is more stable using RHF than DFT. Our finding further reveals that the band gaps increase with 6-311+G (d) basis set for the investigated molecule. On the other hand, the thermodynamic properties show that the DFT method improves the chemical reactivity and thermal resistivity of the molecule than RHF. In the frequencies and intensities computations, it was found that the most intense frequency was $752.6293 cm^{-1}$ with corresponding intensities of 145.0963 km/mol using RHF method. While for DFT method, [42] the most intense frequency was $647.0979 cm^{-1}$ with corresponding intensities of 134.7277km/mol. Finally, we hope to investigate the ionic and mono-halogen effects on the TTF for better understanding of its applications as optoelectronic material in our next paper.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1.   Lior N. Energy resources and use: The present situation and possible paths to the future. Energy. 2008;33(6):842-857. ISSN 0360-5442
2.   Hottel H. Fifty years of solar energy research supported by the Cabot Fund. Solar Energy. 1989;43(2):107-128. ISSN 0038-092X
3.   Acheson RM. An introduction to the chemistry of heterocyclic compounds. John Willey, BSP Books New Delhi, India;2009.
4.   Torrance JB. The difference between metallic and insulating salts of tetracyanoquinodimethone (TCNQ): How to design an organic metal. Acc. Chem. Res. 1979;12(3):79-86.
5.   Bryce MR, Murphy LC. Organic metals. Nature. 1984;309:119-126.
6.   Herranz MA, Sanchez L, Martin N. Tetrathiafulvalene: A Paradigmatic Electron Donor Molecule.Phosphorus, Sulfur Silicon" Relat. Elem. 2005;180:1133–1148.
DOI: 10.1002/chin.200534152
7.   Uemura T, Naka K, Chujo Y. Functional Macromolecules with Electron-Donating Dithiafulvene Unit". Adv. Polym. Sci. 2004;167:81–106.
DOI: 10.1007/b12305
8.   Maruccio G, Cingolani R, Rinaldi R. Projecting the Nanoworld: Concepts, Results and Perspectives of Molecular Electronics". J. Mater. Chem. 2004;14:542–554.
DOI: 10.1039/B311929G
9.   Yamada J, Sugimoto T. Fundamentals and Applications of Tetrathiafulvalene" TTF Chemistry: Eds.; Kodansha-Springer: Tokyo;2004.
10. Martín N, Sánchez L, Illescas B, Pérez I. C60-Based Electroactive Organofullerenes". Chem. Rev. 1998;98:2527–2547.
DOI: 10.1021/cr9701039
11. Metzger RM. Electrical Rectification by a Molecule: The Advent of Unimolecular Electronic Devices". Acc. Chem. Res. 1999;32:950–957.
DOI: 10.1021/ar9900663
12. Bendikov M, Wudl F, Perepichka DF. Tetrathiafulvalenes, Oligoacenenes, and Their Buckminsterfullerene Derivatives: The Brick and Mortar of Organic Electronics. Chem. Rev. 2004;104:4891–4945
DOI: 10.1021/cr030666m
13. Gorgues A, Hudhomme P, Sallé M. Highly Functionalized Tetrathiafulvalenes: Riding along the Synthetic Trail from Electrophilic Alkynes. Chem. Rev. 2004;104:5151–5184.
DOI: 10.1021/cr0306485
14. Segura JL, Martín N. New Concepts in Tetrathiafulvalene Chemistry. Angew. Chem., Int Ed. 2001;40:1372–1409.
DOI: 10.1002/1521-3773(20010417)40:8<1372::AID-ANIE1372>3.0.CO;2-I
15. Ravikumar C, Hubert JI, Sajan D. Vibrational Contributions to the Second-Order Nonlinear Optical Properties of π-Conjugated Structure Acetoacetanilide". J.Chem. Phys. 2010;369:1-7.

DOI: 10.1016/j.chemphys.2010.01.022

16. Saleha BA. Structure and vibrational spectra of mononitrated benzo [a] pyrenes. Journal of Molecular Structure. 2009;915(47).

17. Bendjeddou A, Abbaz T, Gouasmia AK, Villemin D. Molecular Structure, HOMO-LUMO, MEP and Fukui Function Analysis of Some TTF-donor Substituted Molecules Using DFT (B3LYP) Calculations" Int. Res. J. of Pure & App. Chem. 2016;ISSN: 2231-3443

18. Abbaz T, Bendjeddou A, Hanane T, Didier V. Molecular structure, NBO analysis, first-hyperpolarizability, and HOMO-LUMO studies of bis(dithiolylidene)-tetrathiapentalene(BDT-TTP) by quantum computational calculations" V 4 (12) Int. J. of Multi. Res. and Dev. ISSN: 2017;2349-4182;66-73

19. Gnanamozhi P, Pandiyan V, Srinivasan P, David Stephen A. Exploring the Structure, Electron Density and HOMO-LUMO Studies of Tetrathiafulvalene (TTF) as Organic Superconductors: A DFT and AIM Analysis" Journal of Atomic, Molecular, Condensate & Nano Physics. 2019;10(1):33–43.

20. Shahab H, Husain Y. Theoretical Study for Chemical Reactivity Descriptors of Theoretical Study for Chemical Reactivity Descriptors of Tetrathiafulvalene in gas phase and solvent phases based on Tetrathiafulvalene in gas phase and solvent phases based on Density Functional Theory" Passer Journal. 2021;3(2):167-173
DOI: 10.24271 28

21. Muhammad R.N, Mahraz N.M, Gidado A. S, Musa A. Theoretical Study of Solvent Effects on the Electronic and Thermodynamic Properties of Tetrathiafulvalene (TTF) Molecule Based on DFT" Asian Journal of Research and Reviews in Physics. 5(2):42-54,2021; Article no.AJR2P.77309 ISSN: 2582-5992

22. Parr RG, Yang W. Density functional theory of atoms and molecules" Oxford University Press, Oxford, New York;1989.

23. Nahida BH. Theoretical study of electronic properties of some aromatic rings: B3LYP/DFT calculations. J. of Inst. for Sci. Tech. and Edu. 2013;24(83-84).

24. Babaji G, Gidado A .S, Abdulbaki M. A. Determination of molecular structure, electronic and non-optical properties of hydralazine molecule. Transaction of the Nigerian Association of Mathematical Physics (NAMP). 2016;2:35-48.

25. Oftadeh M, Naseh S, Hamadanian M. Electronic properties and dipole polarizability of thiophene and thiophenol derivatives via density functional theory. Elsevier Journal of Computational and Theoretical Chemistry. 2011;966(20- 25).

26. Oyeneyin OE. Structural and solvent dependence of the electronic properties and corrosion inhibitive potentials of 1,3,4-thiadiazole and its substituted derivatives: A theoretical investigation. Phys. Sci. int. J. 2017;16(2):1-8.

27. Khan MF, Rashid BR, Hossain A, Rashid MA. Computational study of solvation free energy, dipole moment, polarizability, hyperpolarizability and molecular properties of botulin, a constituent of Corypha taliera (Roxb.). Dhaka Univ. J. Pharm. Sci. 2017;16(1):1-8.

28. Abbas H, Shkir M, AlFaify S. Density functional of spectroscopy, electronic structure, linear and non-linear optical properties of L-proline lithium chloride and L-proline lithium bromide monohydrate: For laser applications. Int. J. Phys. Sci. 2015;(12):2342-2344.

29. Abdulaziz H, Gidado A. S, Musa A, Lawal. Electronic structure and non-linear optical properties of neutral and ionic pyrene and its derivatives based on density functional theory. J Mater. Sci. Rev. 2019;2(3):1-13.

30. Frisch MJHM, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B., Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian PH, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL. Gaussian Software. Gaussian, INC. 2004;27.
Mason PE, Brady JW. Tetrahedrality and the Relationship between Collective Structure and Radial Distribution Functions in Liquid Water. J. Phys. Chem. 2007;111(20):5669–5679.

31. Robert CW, Melvin JA, William HB, Van Allen JA. Hand book of chemistry and physics. 65th Edition, CRC Press LLC, U.S.A;1984.

32. Robertson JM, White JG. The crystal structure of pyrene. A quantitative X-ray investigation. Journal of the Chemical Society. 1947;1(358-368).

33. Hlel A, Mabrouk A, Chemek M, Ben Khalifa I, Alimi K. A DFT study of charge-transfer and opto-electronic properties of some new materials involving carbazole units

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Computational Condensed Matter. 2015;3:30-40.

34. Suzuki S, Morita Y, Fukui K, Sato K, Shiomi DT, Nakasuji K. Aromaticity on the pancake-bonded Dimer of Neutral phenalenyl Radical as studied by MS and NMR Spectroscopies and NICS Analysis. J. Am. Chem. Soc. 2006;128(8): 2530-2531.

35. Mason PE, Brady JW. Tetrahedrality and the relationship between collective structure and radial distribution functions in liquid water. J. Phys. Chem. 2007;111(20):5669–5679.

36. Lewis DFV, Loannides C, Parke DV. Interaction of a series of nitriles with the alcohol-inducible isoform of P450: Computer analysis of structure-activity relationships. Xenobiotica. 1994;24(5): 401-408.

37. Fukui K, Yonezawa T, Shingu H. A molecular orbital theory of reactivity in aromatic hydrocarbons. J Chem. Phys. 1952;20(4): 722-725.

38. Cho LH, Kerterz M. Conformational information from vibrational spectra of styrene, trans-Stilbene, and cis-Stilbene. J Phys. Chem. A. 1997;101(20):3823-3831.

39. Vektariene A, Vektaris G, Svoboda J. A Theoretical approach to the nucleophilic behavior of benzofused thieno [3,2-b] furans Using DFT and HF based reactivity descriptors. Archive for Organic Chemistry. 2009;7:311-329.

40. AlShamaileh E. DFT study of monochlorinated pyrene compounds. Journal of Computational Chemistry. 2014;2(43-49).

41. idhya V, Austine A, Arivazhagan M. Quantum chemical determination of molecular geometries and spectral investigation of 4-ethoxy-2,3-difluorobenzamide, Heliyon. 2019;5(11): e02365.

42. Hamm P, Lim M, Hochstrasser RM. Structure of the amide 1 bond of peptides measured by Femtosecond nonlinear- infrared spectroscopy. J. Phys. Chem. B. 1998;102(31) 6123.

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