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Research Article

The Quantum Chemical Calculations of Some Tetrathiapentalene (TTP) Derivatives

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Abstract

This Letter reports a quantitative study of TTP derivatives (TMES-TTP, C_2TET-TTP, C_4TET-TTP and BEDT-TTP) **1-4**by DFT/B3LYP method and 6-31G (d, p) basis set within Gaussian 09Wprogram package. The optimized geometrical parameters and structures of the title molecules are obtained by DFT method. The global and local reactivity of the studied compounds are also investigated. The energies of important MO’s, the total electron density and electrostatic potential of the studied compounds are determined. Natural bond orbital analysis of the compounds has been performed to indicate the presence of intramolecular charge transfer. The computed dipole moment, polarizability and HOMO-LUMO energy gap were used to predict the nonlinear optical (NLO) properties.

Keywords: Tetrathiapentalene; density functional theory; computational chemistry; quantum chemical calculations.

1. Introduction

Recently, compounds that act as π-electron donors have received considerable attention in the context of the preparation of organic conductors [1,2]. Tetrathiafulvalene (TTF) derivatives [3] are very versatile electro-active molecules widely used as building blocks to prepare organic metals, for supramolecular functions [4] and in molecular electronics [5]. Tetrathiafulvalene (TTF) derivatives, which incorporate two sulfur atoms into the 1,3-dithiole rings in order to enhance the intermolecular interaction, are another family of promising materials that have realized high performance [6]. Although TTP compounds having more sulfur atoms in the outer rings have been extensively studied as components of organic superconductors [7]. We have investigated on bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP or simply TTP), which is designed by fusion of two TTF units, in other words, insertion of a tetrathiapentalene unit between two 1,3-dithiole rings of TTF [8,9].

Density functional theory (DFT) based on the Becke's three parameter hybrid exchange functional combined with the Lee -Yang-Parr non-local correlation function level of theory displays good achievement on the characterization of the organic molecules [10,11] as a consequence of the recovering of the electron correlation in the self-consistent Kohn e Sham procedure throughout the electron density functions [12,13,14].DFT/B3LYP method has been chosen for the present study because it provides an excellent compromise between computational cost and accuracy for medium to large sized molecules.

The objective of this study is to understand the electronic behaviors of TTP derivatives (TMES-TTP, C_2TET-TTP, C_4TET-TTP and BEDT-TTP) **1-4**reported in literature [15] at DFT/B3LYP method and 6-31G(d,p)basis set. The optimized parameters are obtained with same method cited above. The study of HOMO, LUMO analysis has been used to elucidate information regarding charge transfer within the molecules. In addition, electronegativity, electrophilicity index, chemical potential, electron affinity, the ionization potential, hardness and softness are determined. These are confirming the charge transfer within the molecules and also molecular electrostatic potential (MESP) contour map shows the various electrophilic and nucleophilic regions of the title molecules. NBO analysis has been applied to study the stability of the molecules arising from charge delocalization. The sites selectivity of titled compounds has been determined on the basis of local reactivity descriptors. The first hyperpolarizability (β_0) is calculated to predict the NLO applications of the compounds.

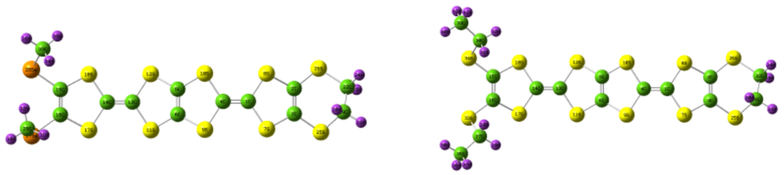
2. Materials and Methods

The gradient corrected density functional theory (DFT) with the three-parameter hybrid functional Becke3 (B3) [16,17] for the exchange part and the Lee-Yang-Parr (LYP) correlation functional[18] level of calculations have been carried out in the present investigation, using 6-31G (d,p) basic set with Gaussian-09W [19] program.

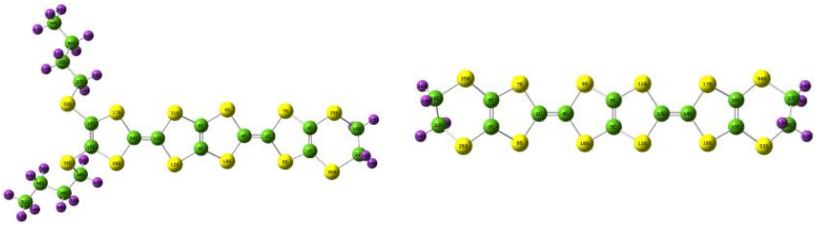
3. Results and Discussion

3.1 Molecular Geometry

The optimized structural parameters of(TMES, C_2TET, C_4TET and BEDT)-TTP **1-4** are determined at the B3LYP/6-31G(d,p) level. The optimized parameters are presented in Tables1-4 in accordance with the atom numbering scheme of the molecule as shown in Figure 1.



Compound **1** Compound **2**



Compound **3** Compound **4**

Figure 1: Optimized molecular structure of TTPs**1-4**

Table 1: Optimized geometric parameters of compound **1**

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,4)	1.350	A(4,1,7)	123.720	D(7,1,4,10)	177.541
R(1,7)	1.779	A(3,2,8)	116.780	D(4,1,7,3)	158.781
R(2,3)	1.349	A(3,2,26)	127.701	D(26,2,8,1)	167.911
R(2,26)	1.763	A(8,2,26)	115.483	D(8,2,26,22)	149.862
R(3,7)	1.783	A(1,4,9)	122.914	D(1,4,10,5)	163.180
R(4,9)	1.789	A(9,4,10)	113.977	D(12,5,6,9)	179.884
R(5,6)	1.343	A(6,5,12)	117.921	D(11,6,9,4)	167.871
R(5,10)	1.768	A(9,6,11)	124.120	D(13,14,17,16)	168.505
R(6,11)	1.769	A(1,8,2)	93.742	D(28,15,16,17)	175.713
R(13,14)	1.348	A(5,12,13)	92.649	D(28,15,18,14)	176.728
R(14,18)	1.784	A(11,13,14)	123.032	D(17,16,27,29)	111.931
R(15,28)	1.900	A(15,16,27)	125.823	D(20,19,22,23)	171.368
R(19,20)	1.092	A(21,19,22)	109.155	D(21,19,22,23)	51.167
R(19,22)	1.521	A(16,27,29)	97.175	D(21,19,22,26)	171.478
R(33,34)	1.089	A(35,33,36)	109.618	D(15,28,33,35)	69.703

Table 2. Optimized geometric parameters of compound **2**

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,4)	1.350	A(4,1,7)	123.724	D(7,1,4,10)	177.577
R(1,7)	1.779	A(7,1,8)	112.847	D(4,1,7,3)	158.676
R(2,3)	1.349	A(3,2,8)	116.769	D(26,2,3,7)	177.622
R(2,26)	1.763	A(3,2,26)	127.805	D(26,2,8,1)	167.840
R(4,9)	1.789	A(2,3,7)	117.129	D(2,3,25,19)	38.790
R(5,6)	1.342	A(7,3,25)	118.485	D(10,5,6,11)	179.906
R(5,12)	1.769	A(1,4,10)	123.038	D(11,6,9,4)	168.113
R(13,14)	1.349	A(9,4,10)	114.001	D(5,12,13,14)	161.770
R(14,18)	1.777	A(10,5,12)	124.067	D(13,14,17,16)	159.348
R(15,16)	1.356	A(5,12,13)	92.7873	D(34,15,18,14)	172.784
R(15,34)	1.764	A(17,14,18)	112.225	D(17,16,33,27)	64.1706
R(19,20)	1.092	A(16,15,34)	125.772	D(20,19,22,24)	51.799
R(19,22)	1.521	A(29,27,33)	108.077	D(25,19,22,24)	173.927
R(27,33)	1.853	A(16,33,27)	101.886	D(21,19,25,3)	171.692
R(27,35)	1.526	A(36,35,37)	107.971	D(29,27,35,38)	58.852

Table 3. Optimized geometric parameters of compound **3**

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,4)	1.350	A(4,1,7)	123.749	D(7,1,4,10)	177.634
R(1,8)	1.781	A(7,1,8)	112.830	D(26,2,8,1)	167.632
R(2,3)	1.349	A(3,2,8)	116.759	D(2,3,25,19)	38.283
R(2,26)	1.763	A(3,2,26)	127.951	D(12,5,6,9)	179.765
R(3,7)	1.783	A(8,2,26)	115.255	D(12,13,14,17)	177.440
R(5,6)	1.342	A(1,4,9)	122.938	D(16,15,34,30)	121.437
R(13,14)	1.349	A(9,4,10)	113.963	D(20,19,22,24)	52.380
R(15,16)	1.356	A(10,5,12)	124.057	D(25,19,22,26)	55.065
R(15,34)	1.764	A(5,12,13)	92.838	D(23,22,26,2)	115.597
R(22,23)	1.091	A(15,16,33)	125.878	D(29,27,35,36)	178.347
R(30,34)	1.857	A(3,25,19)	96.414	D(31,30,38,39)	66.879
R(35,41)	1.535	A(30,38,48)	114.959	D(27,35,41,43)	58.077
R(38,48)	1.534	A(41,44,45)	111.198	D(39,38,48,49)	178.744
R(41,44)	1.531	A(49,48,50)	106.039	D(42,41,44,46)	58.078
R(51,54)	1.096	A(53,51,54)	107.703	D(50,48,51,54)	61.834

Table 4. Optimized geometric parameters of compound **4**

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,4)	1.350	A(4,1,7)	123.373	D(8,1,4,9)	177.698
R(1,8)	1.779	A(7,1,8)	112.876	D(4,1,8,2)	158.795
R(2,3)	1.349	A(3,2,26)	123.762	D(25,3,7,1)	167.930
R(2,8)	1.783	A(8,2,26)	118.566	D(10,5,6,11)	179.933
R(3,25)	1.763	A(1,4,10)	122.902	D(10,5,12,13)	167.858
R(5,6)	1.342	A(6,5,12)	117.965	D(13,14,18,15)	158.805
R(6,9)	1.768	A(9,6,11)	124.065	D(17,16,34,27)	149.875
R(13,14)	1.350	A(4,9,6)	92.881	D(21,19,22,23)	51.393
R(15,16)	1.349	A(18,15,33)	118.568	D(21,19,22,26)	173.460
R(16,17)	1.784	A(17,16,34)	115.482	D(20,19,25,3)	117.571
R(19,22)	1.521	A(14,18,15)	93.643	D(24,22,26,2)	171.497
R(19,25)	1.863	A(19,22,26)	113.092	D(28,27,30,32)	171.328
R(27,28)	1.091	A(28,27,29)	108.867	D(29,27,30,33)	173.452
R(27,30)	1.521	A(29,27,34)	105.963	D(34,27,30,33)	53.708
R(30,33)	1.843	A(16,34,27)	103.780	D(32,30,33,15)	55.334

3.2 Molecular Electrostatic Potential (MEP)

The molecular electrostatic potential (MEP) is used for grasping the molecular interactions. Recently, the MEPs have been used for interpreting and predicting relative reactive sites for electrophilic and nucleophilic attack, investigation of biological recognition, hydrogen bonding interactions, studies of zeolite, molecular cluster and crystal behavior and the correlation and prediction of a wide range of macroscopic properties [20,21]. Since MEP is related to total charge distribution of the molecule, it provides the correlations among the molecular properties such as partial charges, dipole moments, electronegativity and chemical reactivity. Therefore, MEP provides a visual method to understand the relative polarity of a molecule. The molecular electrostatic potential is the potential energy of a proton at a particular location near a molecule. The MEP, $V(r)$, at a given point r(x,y,z) in the around of molecule, is defined as the interaction energy between the charge distribution of a molecule and a unit positive test charge [21].

$$V(r)=\sum\frac{Z_A}{|R_A-r|}-\int\frac{\rho(r')}{|r'-r|}dr$$

Where Z_A donates the charge of nucleus A, located at R_A distance, $\rho(r')$ denotes the charge density at point r' and r' is the dummy integration variable. The red color parts represent the regions of negative electrostatic potential while blue ones represent the regions of positive electrostatic potential. Additionally, green color parts represent the regions of zero potential. The negative regions of $V(r)$ potential are related to electrophilic reactivity, while the positive ones are related to nucleophilic reactivity. The MEP surface of (TMES, C_2TET, C_4TET and BEDT)-TTP **1-4**were calculated by using the optimized molecular structures at the B3LYP/6-31G(d,p) level and its 3D plot is given in Figure 2.

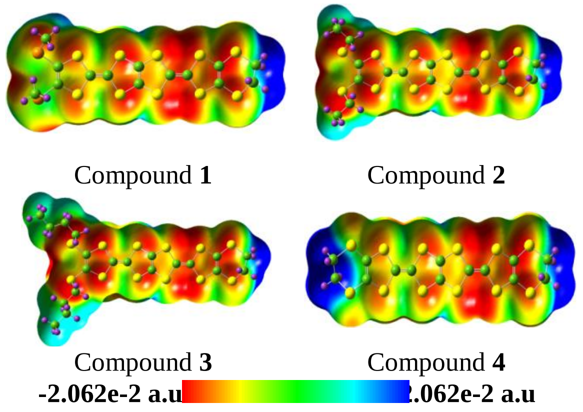

Compound **1**
Compound **2**
Compound **3**
Compound **4**

Figure 2: Molecular electrostatic potential surface of TTPs **1-4**

As observed from the figure **2** that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the TTP core and sulfur atoms while the regions presenting the positive potential are localized vicinity of the hydrogen atoms of alkyl and heterocycles groups.

3.3 Frontier Molecular Orbitals (FMOs)

The HOMO is outermost higher energy orbital containing electrons so it acts as an electron donor. The LUMO is the lowest energy orbital that has the room to accept electrons so it acts as an electron acceptor. The frontier molecular orbitals can offer a reasonable qualitative prediction of the excitation properties and the ability of electron transport [22,23]. The HOMO and LUMO are also very popular quantum chemical parameters which determine the molecular reactivity. The energies of the HOMO-1, HOMO, LUMO and LUMO+1 orbitals of compound **1** were investigated atB3LYP/6-31G (d,p) level. Figure3 shows the distributions and difference between energy levels of these orbitals.

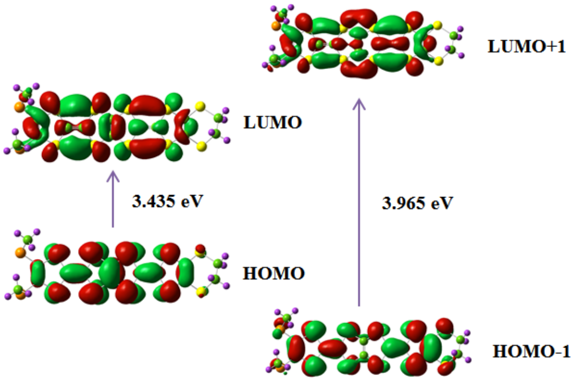


Figure 3: HOMO-LUMO Structure with the energy level diagram of compound **1**

3.4 Global Reactivity Descriptors

The global reactivity descriptors like chemical potential, electronegativity, hardness, softness and global electrophilicity index can be calculated using DFT methods. Following Parr and Pearson [24], the electronic chemical potential describing the escaping tendency of the electron from a stable system can be calculated as:

$$\mu=-\frac{(I+A)}{2}$$

Where I = ionization potential and A = electron affinity. Electronegativity (χ) is described as the negative of the electronicchemical potential. Chemical hardness (η) demonstrates the resistance to alteration in electron distribution and is well correlated with the stability and reactivity of the chemical system. Hardness is expressed by the following equation:

$$\eta=\frac{I-A}{2}$$

The inverse of hardness is expressed as global softness:

$$S=\frac{1}{2\eta}$$

The global electrophilicity index (ω), introduced by Parr et al [24] is calculated in terms of chemical potential and hardness:

$$\omega = \frac{\mu^2}{2\eta}$$

This value assesses energy decreasing due to maximal electron flow between donor and acceptor. The calculated values of the global reactivity descriptors for the title molecules are computed by B3LYP/6-31G (d,p) level and collected in Table 5.

Table 5: Quantum chemical descriptors of TTPs **1-4**

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-4.753	-4.799	-4.780	-4.778
E_{LUMO} (eV)	-1.319	-1.317	-1.302	-1.320
ΔE_{gap} (eV)	3.435	3.482	3.478	3.457
IE (eV)	4.753	4.799	4.780	4.778
A (eV)	1.319	1.317	1.302	1.320
μ (eV)	-3.036	-3.058	-3.041	-3.049
χ (eV)	3.036	3.058	3.041	3.049
η (eV)	1.717	1.741	1.739	1.729
***S*(eV)**	0.291	0.287	0.288	0.289
ω (eV)	2.684	2.686	2.659	2.689

As shown the table 5, the compound which have the lowest energetic gap is the compound **1** (ΔE_{gap} = 3.435 eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **2** (ΔE_{gap} = 3.482 eV). The compound that has the highest HOMO energy is the compound **1** (E_{HOMO} = -4.753 eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **4** (E_{LUMO} = -1.320 eV) which signifies that it can be the best electron acceptor. The two properties like *I* (potential ionization) and *A* (affinity) are so important, the determination of these two properties allow us to calculate the absolute electronegativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound **1** has lowest value of the potential ionization (*I* = 4.753 eV), so that will be the better electron donor. Compound **4** has the largest value of the affinity (*A* = 1.320 eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **1** (η = 1.717 eV, ***S***= 0.291 eV) is lesser (greater) among all the molecules. Thus, compound **1** is found to be more reactive than all the compounds. Compound **2** possesses higher electronegativity value (χ = 3.058 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **4** (ω = 2.689 eV) indicates that it is the stronger electrophiles than all compounds. Compound **1** has the smaller frontier orbital gap so, it is more polarizable and is associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule.

3.4 Local Reactivity Descriptors

The local reactivity descriptor like Fukui function indicates preferred regions where a chemical specie (molecule) will amend its density when numbers of electrons are modified or it indicates tendency of electronic density to deform at a given position upon accepting or donating electrons [25,26]. The condensed or atomic Fukui functions on the kth atom site, for electrophilic (f^-_k), nucleophilic (f^+_k) and free radical (f^0_k) attacks are defined as

$$f_j^- = q_j(N) - q_j(N-1) \text{ for nucleophilic attack}$$

$$f_j^+ = q_j(N+1) - q_j(N) \text{ for electrophilic attack}$$

$$f_j^0 = \frac{1}{2}\left[q_j(N+1) - q_j(N-1)\right] \text{ for radical attack}$$

Where q_k is atomic charge at the kth atomic site in the anionic (N+1), cationic (N-1) or neutral molecule (N). Parr and Yang [25,26]showed that sites in chemical species with the largest values of Fukui function (f_k) shows high reactivity for corresponding attacks. Fukui functions for selected atomic sites of (TMES, C_2TET, C_4TET and BEDT)-TTP **1-4**are calculated by the DFT/B3LYP method with 6-31G (d,p) basis set and shown in Tables 6-7.

Table 6: Order of the reactive sites on compounds **1** and **2**

Compound 1					Compound 2				
Atom	4C	16C	13C	14C	**Atom**	16C	4C	13C	14C
f^+	0.042	0.026	0.024	0.021	f^+	0.049	0.045	0.043	0.024
Atom	15C	13C	3C	4C	**Atom**	15C	27C	30C	13C
f^-	0.024	0.009	0.003	0.004	f^-	0.028	0.012	0.002	0.000
Atom	4C	13C	3C	2C	**Atom**	13C	4C	27C	30C
f^0	0.019	0.017	0.004	0.003	f^0	0.022	0.020	0.004	0.004

Table 7: Order of the reactive sites on compounds **3** and **4**

Compound 3					**Compound 4**				
Atom	16C	4C	13C	14C	**Atom**	13C	4C	16C	3C
f^+	0.053	0.045	0.043	0.024	f^+	0.045	0.045	0.022	0.022
Atom	15C	27C	48C	30C	**Atom**	15C	2C	13C	4C
f^-	0.033	0.013	0.003	0.001	f^-	0.003	0.003	0.002	0.002
Atom	13C	4C	3C	27C	**Atom**	13C	4C	2C	15C
f^0	0.022	0.020	0.004	0.004	f^0	0.020	0.020	0.004	0.004

From the tables 6-7, the parameters of local reactivity descriptors show that 16C is the more reactive site in compounds **2** and **3** and 4C, 13C are the more reactive sites in compounds **1** and **4** respectively for nucleophilic attacks. The more reactive site for electrophilic attacks is 15C for all compounds. The more reactive sites in radical attacks are 13C for compounds **2**, **3** and **4** and 4C for compounds **1**.

3.5 Natural Bond Orbital Analysis (NBO)

NBO analysis provides an efficient method of studying individual bonds and lone-pair energy that play a vital role in the chemical processes [27-29]. It is an important tool for studying hybridization, covalence, hydrogen bonding, and Van der Waals interactions. In other words Natural Bond Orbital (NBO) provides supplementary structural information.NBO method gives the information about various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem. This is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energy by second order perturbation theory. For each donor (i) and acceptor NBO (j) the stabilization energy E(2) associated with electron delocalization between donor and acceptor is estimated as [30]:

$$E(2)= \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

Where q_i is the orbital occupancy, ε_i and ε_j are diagonal elements and F_{ij} is the off-diagonal NBO Fock matrix element. Larger the E(2) (stabilization energy or energy of hyper-conjugative interaction) values points towards the greater interaction between electron donors and electron acceptors i.e. greater the donating tendency from electron donors to electron acceptors, greater the extent of conjugation in the system. NBO analysis has been performed on (TMES, C_2TET, C_4TET and BEDT)-TTP **1-4** at the DFT/B3LYP/6-31G (d,p) level. Second order perturbation theory analysis of the Fock matrix in NBO basis for (TMES, C_2TET, C_4TET and BEDT)-TTP molecules is presented in Tables 8-11.

Table 8: Second order perturbation theory analysis of Fock matrix on NBO of compound **1**

Donor(i)	**ED/e**	**Acceptor(j)**	**ED/e**	**E(2) Kcal/mol**	**E(j)-E(i) a.u**	**F(i.j) a.u**
LP (2) S17	1.76477	π*(C15-C16)	0.29755	22.45	0.24	0.067
LP (2) S18	1.77278	π*(C15-C16)	0.29755	21.40	0.24	0.065
LP (2) S9	1.79352	π*(C5-C6)	0.37195	20.42	0.24	0.065
LP (2) S10	1.79393	π*(C5-C6)	0.37195	20.38	0.24	0.065
LP (2) S11	1.80267	π*(C5-C6)	0.37195	20.16	0.24	0.064
LP (2) S12	1.80358	π*(C5-C6)	0.37195	20.10	0.24	0.064
LP (2) S7	1.79081	π*(C2-C3)	0.36711	19.61	0.24	0.063
LP (2) S8	1.79138	π*(C2-C3)	0.36711	19.58	0.24	0.063
LP (2) S26	1.85626	π*(C2-C3)	0.36711	17.11	0.24	0.060
LP (2) S17	1.76477	π*(C13-C14)	0.37274	16.68	0.26	0.061
LP (2) S18	1.77278	π*(C13-C14)	0.37274	15.98	0.26	0.060
LP (2) S9	1.79352	π*(C1-C 4)	0.37019	14.08	0.26	0.056
LP (2) S10	1.79393	π*(C1-C4)	0.37019	14.07	0.26	0.056
LP (2) S7	1.79081	π*(C1-C4)	0.37019	13.71	0.26	0.055
LP (2) S8	1.79138	π*(C1-C4)	0.37019	13.50	0.26	0.055
LP (2) S11	1.80267	π*(C13-C14)	0.37274	12.49	0.26	0.054
LP (2) S12	1.80358	π*(C13-C14)	0.37274	12.47	0.26	0.054
LP (2) S25	1.87421	π*(C2-C3)	0.36711	10.16	0.24	0.047
σ (C3-S7)	1.97043	σ*(C2-S26)	0.02967	5.55	0.84	0.061
σ (C2-S8)	1.96896	σ*(C3-S25)	0.02896	5.26	0.84	0.059

Table 9. Second order perturbation theory analysis ofFock matrix on NBO of compound **2**

Donor(i)	**ED/e**	**Acceptor(j)**	**ED/e**	**E(2) Kcal/mol**	**E(j)-E(i) a.u**	**F(i.j) a.u**
LP (2) S9	1.79396	π*(C5-C6)	0.37264	20.43	0.24	0.065
LP (2) S10	1.79406	π*(C5-C6)	0.37264	20.40	0.24	0.065
LP (2) S11	1.79735	π*(C5-C6)	0.37264	20.30	0.24	0.065
LP (2) S12	1.79746	π*(C5-C6)	0.37264	20.30	0.24	0.065
LP (2) S7	1.79102	π*(C2-C3)	0.36733	19.55	0.24	0.063
LP (2) S8	1.79153	π*(C2-C3)	0.36733	19.53	0.24	0.063
LP (2) S18	1.78223	π*(C15-C16)	0.31370	19.21	0.25	0.063
LP (2) S17	1.78233	π*(C15-C16)	0.31370	19.20	0.25	0.063
LP (2) S26	1.85585	π*(C2-C3)	0.36733	17.34	0.24	0.061
LP (2) S17	1.78233	π*(C13-C14)	0.36920	14.38	0.26	0.056
LP (2) S18	1.78223	π*(C13-C14)	0.36920	14.38	0.26	0.056
LP (2) S10	1.79406	π*(C1-C4)	0.37017	14.07	0.26	0.056
LP (2) S9	1.79396	π*(C1-C4)	0.37017	14.06	0.26	0.056
LP (2) S7	1.79102	π*(C1-C4)	0.37017	13.73	0.26	0.055
LP (2) S11	1.79735	π*(C13-C14)	0.36920	13.53	0.26	0.055
LP (2) S12	1.79746	π*(C13-C14)	0.36920	13.53	0.26	0.055
LP (2) S8	1.79153	π*(C1-C4)	0.37017	13.51	0.26	0.055
LP (2) S25	1.87402	π*(C2-C3)	0.36733	10.27	0.24	0.047
σ (C3-S7)	1.97036	σ*(C2-S26)	0.02968	5.57	0.84	0.061
σ (C15-S18)	1.97153	σ*(C16-S33)	0.03047	5.37	0.84	0.060

Table 10. Second order perturbation theory analysis of Fock matrix on NBO of compound **3**

Donor(i)	**ED/e**	**Acceptor(j)**	**ED/e**	**E(2) Kcal/mol**	**E(j)-E(i) a.u**	**F(i.j) a.u**
LP (2) S12	1.79753	π*(C5-C6)	0.37271	20.39	0.24	0.065
LP (2) S11	1.79749	π*(C5-C6)	0.37271	20.38	0.24	0.065
LP (2) S9	1.79432	π*(C5-C6)	0.37271	20.34	0.24	0.065
LP (2) S10	1.79428	π*(C5-C6)	0.37271	20.33	0.24	0.065
LP (2) S7	1.79138	π*(C2-C3)	0.36761	19.49	0.24	0.063
LP (2) S8	1.79200	π*(C2-C3)	0.36761	19.47	0.24	0.063
LP (2) S17	1.78119	π*(C15-C16)	0.31084	19.39	0.25	0.063
LP (2) S18	1.78149	π*(C15-C16)	0.31084	19.25	0.25	0.063
LP (2) S26	1.85554	π*(C2-C3)	0.36761	17.63	0.24	0.061
LP (2) S17	1.78119	π*(C13-C14)	0.37007	14.53	0.26	0.057
LP (2) S18	1.78149	π*(C13-C14)	0.37007	14.53	0.26	0.057
LP (2) S10	1.79428	π*(C1-C4)	0.36951	14.04	0.26	0.056
LP (2) S9	1.79432	π*(C1-C4)	0.36951	14.03	0.26	0.056
LP (2) S7	1.79138	π*(C1-C4)	0.36951	13.73	0.26	0.055
LP (2) S11	1.79749	π*(C13-C14)	0.37007	13.50	0.26	0.055
LP (2) S8	1.79200	π*(C1-C4)	0.36951	13.49	0.26	0.055
LP (2) S12	1.79753	π*(C13-C14)	0.37007	13.49	0.26	0.055
LP (2) S25	1.87380	π*(C2-C3)	0.36761	10.44	0.24	0.047
σ (C3-S7)	1.97023	σ*(C2-S26)	0.02976	5.59	0.84	0.061
σ (C15-S18)	1.97163	σ*(C16-S33)	0.03033	5.38	0.84	0.060

Table 11. Second order perturbation theory analysis of Fock matrix on NBO of compound **4**

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i.j) a.u
LP (2) S10	1.79399	π*(C5-C6)	0.37301	20.42	0.24	0.065
LP (2) S12	1.79400	π*(C5-C6)	0.37301	20.42	0.24	0.065
LP (2) S9	1.79418	π*(C5-C6)	0.37301	20.40	0.24	0.065
LP (2) S11	1.79419	π*(C5-C6)	0.37301	20.40	0.24	0.065
LP (2) S8	1.79037	π*(C2-C3)	0.36718	19.61	0.24	0.063
LP (2) S18	1.79036	π*(C15-C16)	0.36719	19.61	0.24	0.063
LP (2) S7	1.79074	π*(C2-C3)	0.36718	19.60	0.24	0.063
LP (2) S17	1.79073	π*(C15-C16)	0.36719	19.60	0.24	0.063
LP (2) S25	1.85618	π*(C2-C3)	0.36718	17.12	0.24	0.060
LP (2) S34	1.85619	π*(C15-C16)	0.36719	17.12	0.24	0.060
LP (2) S9	1.79418	π*(C1-C4)	0.37002	13.98	0.26	0.056
LP (2) S10	1.79399	π*(C1-C4)	0.37002	13.98	0.26	0.056
LP (2) S11	1.79419	π*(C13-C14)	0.37001	13.98	0.26	0.056
LP (2) S12	1.79400	π*(C13-C14)	0.37001	13.97	0.26	0.056
LP (2) S8	1.79037	π*(C1-C4)	0.37002	13.79	0.26	0.055
LP (2) S18	1.79036	π*(C13-C14)	0.37001	13.79	0.26	0.055
LP (2) S7	1.79074	π*(C1-C4)	0.37002	13.58	0.26	0.055
LP (2) S17	1.79073	π*(C13-C14)	0.37001	13.58	0.26	0.055
LP (2) S26	1.87421	π*(C2-C3)	0.36718	10.16	0.23	0.047
σ (C15-S18)	1.87421	σ*(C16-S33)	0.36719	5.16	0.23	0.047

The intra molecular interaction for the title compounds is formed by the orbital overlap between: σ(C3-S7)and σ*(C2-S26) for compound **1**,σ(C3-S7) and σ*(C2-S26) for compound **2**, σ(C3-S7) and σ*(C2-S26) for compound **3** and σ(C15-S18) and σ*(C16-S33) for compound **4**respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of σ(C3-S7)to σ*(C2-S26) for compound **1**, σ(C3-S7) to σ*(C2-S26) for compound **2**, σ(C3-S7) to σ*(C2-S26) for compound **3** and σ(C15-S18) to σ*(C16-S33) for compound **4** lead to highest stabilization of 5.55, 5.57, 5.59 and 5.16 kJ mol^{-1} respectively. In case of LP (2) S17 orbital to the π*(C15-C16) for compound **1**, LP (2) S9 orbital to π*(C5-C6) for compound **2**, LP (2) S12 orbital to π*(C5-C6) for compound **3**,LP (2) S10 orbital to π*(C5-C6) for compound **4** respectively, show the stabilization energy of 22.45, 20.43, 20.39 and 20.42 kJ mol^{-1} respectively.

3.6 Nonlinear Optical Properties (NLO)

Quantum chemical calculations have been shown to be useful in the explanation of the relationship between the electronic structure of the systems and its nonlinear optical properties[31].Studies of nonlinear optical properties are tedious, however employing relatively inexpensive DFT calculations NLO properties can be initially assessed. In discussing NLO properties, the polarization of the molecule by an external radiation field is often approximated as the creation of an induced dipole moment by an external electric field. The first hyperpolarizability (β_0) of thismolecular system is calculated using B3LYP/6-31G (d,p)method, based on the finite field approach. The mean first order hyperpolarizability β_0,total static dipole moment μ_{tot}, the mean polarizability $\alpha_0$and the anisotropy of the polarizability Δα using the x, y and z components from Gaussian 09 W output are defined as follows.

$$\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

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

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

and

$$\beta_x = \left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)$$

$$\beta_y = \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)$$

$$\beta_z = \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)$$

The calculated hyperpolarizability and other parameters values of (TMES, C_2TET, C_4TET and BEDT)-TTP**1-4** are given in Table 12.

Table 12: The dipole moments μ_{tot} (D), polarizability α_0(esu), the anisotropy of the polarizability Δα (esu) and the first hyperpolarizability β_0 (esu) of TTPs**1-4**

Parameters	compound 1	compound 2	compound 3	compound 4
β_{xxx}	254.8959	708.4655	-790.5580	-0.0070
β_{yyy}	16.0575	0.2294	13.5672	0.4569
β_{zzz}	13.5557	19.5200	19.4071	0.0018
β_{xyy}	-190.9076	-104.4664	107.2995	0.0025
β_{xxy}	40.0501	5.3075	10.5407	15.6657
β_{xxz}	196.8760	212.5839	227.8182	0.0477
β_{xzz}	-177.9428	-31.0233	12.2249	0.0011
β_{yzz}	-4.1715	-0.1714	0.0996	-0.5547
β_{yyz}	15.7289	28.5026	22.5231	0.0002
β_{xyz}	-12.5294	-3.1873	-7.2442	-5.2053
β_0(esu)x10^{-33}	281.0304	629.4806	723.6272	15.5680
μ_x	1.4975	2.7050	-2.1011	0.0002
μ_y	1.1295	0.0161	0.4620	0.0867
μ_z	3.4639	3.8962	4.0517	0.0005
μ_{tot}(D)	3.9391	4.7432	4.5875	0.0867
α_{xx}	-167.6106	-187.6739	-203.0774	-123.8181
α_{yy}	-246.3095	-241.2818	-266.9210	-241.2391
α_{zz}	-248.0693	-251.6387	-280.7504	-241.9793
α_{xy}	-5.0281	0.5450	1.7695	0.0005
α_{xz}	-9.9705	-11.2602	7.0490	11.4671
α_{yz}	1.6506	-0.0514	-0.7339	0.0001
α_0(esu)x10^{-24}	81.9595	62.5904	72.8715	119.4556
$\Delta\alpha$(esu)x10^{-24}	12.1464	9.2759	10.7996	17.7033

Since the values of the polarizabilities (Δα) and the hyperpolarizabilities (β_0) of the GAUSSIAN 09 output are obtained in atomic units (a.u.), the calculated values have been converted into electrostatic units (e.s.u.) (for α; 1 a.u = 0.1482 x 10^{-24} e.s.u., for β; 1 a.u = 8.6393 x 10^{-33} e.s.u.). The calculated values of dipole moment (μ_{tot}) for the title compounds were found to be 3.9391, 4.7432, 4.5875 and 0.0867 D respectively, which are approximately four times than to the value for urea (μ = 1.3732 D). Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore, it has been used frequently as a threshold value for comparative purposes. The calculated values of polarizability are 81.9595 x 10^{-24}, 62.5904 x 10^{-24}, 72.8715 x 10^{-24} and 119.4556 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 12.1464, 9.2759, 10.7996 and 17.7033 esu, respectively. The magnitude of the molecular hyperpolarizability (β_0) is one of important key factors in a NLO system. The DFT/6-31G(d,p) calculated first hyperpolarizability value (β_0) of (TMES, C_2TET, C_4TET and BEDT)-TTP molecules are equal to 281.0304 x 10^{-33}, 629.4806 x 10^{-33}, 723.6272 x 10^{-33} and 15.5680 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.82, 1.83, 2.11 and 0.04 times than those of urea (β of urea is 343.272 x10^{-33} esu obtained by B3LYP/6-311G (d,p) method). The above results show that only compounds **2** (C_2TET-TTP) and **3** (C_4TET-TTP) might have the NLO applications.

4. Conclusion

A complete quantum chemical analysis of(TMES, C_2TET, C_4TET and BEDT)-TTP **1-4** is by performed DFT/B3LYP method and 6-31G(d,p) basis set level. The difference in HOMO and LUMO energy supports the charge transfer interaction within the molecules. Energy gap and other molecular properties like ionization potential, electron affinity, global hardness, chemical potential and electrophilicity were calculated.NBO analysis was made and it is indicating the intramolecular charge transfer between the bonding and anti-bonding orbitals.DFT calculations of quantum-molecular descriptors describing the local reactivity and indicate reactive centers in the molecules. The geometrical parameters such as bond length, bond angles and dihedral angles of the title compounds are also reported. The predicted MEP figure revealed the negative regions of the molecules, were subjected to the electrophilic attack of this compounds.

Furthermore, the polarizability, the first hyperpolarizability and total dipole moment properties of (TMES, C2TET, C4TET and BEDT)-TTP molecules have been calculated and the results are discussed.

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