



A COMPUTATIONAL STUDY ON MOLECULAR GEOMETRIES, CHEMISTRY REACTIVITY DESCRIPTORS OF TTP DERIVATIVES

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ABSTRACT

The optimized molecular structures of TTP derivatives **1-4** have been investigated theoretically using Gaussian 09 software package. The HOMO and LUMO analysis is used to determine the charge transfer within the molecules. The stability of the molecule arising from hyper-conjugative interaction and charge delocalization has been analyzed using NBO analysis. Molecular Electrostatic Potential reveals the sites for electrophilic attack and nucleophilic reactions in the molecules. All calculations were performed by the DFT method with B3LYP/6-31G(d,p) basis sets.

KEYWORDS: tetrathiafulvalenes; density functional theory; computational chemistry; electronic structure; quantum chemical calculations.

1. INTRODUCTION

Organic chemistry is dominated by heterocyclic compounds having a share of more than half as compared to the rest of known organic compounds. The key reason for such a vast array of heterocyclic compounds is due to their practical applications in pharmaceuticals, agriculture and technology.

Heterocyclic compounds are worthy of attention for many reasons, chief among which are their biological activities, which many important drugs being heterocyclic. Therefore, organic

chemists have been making extensive efforts to produce heterocyclic compounds by developing new and efficient synthetic transformations.^[1]

In 1993, bis-fused TTF, namely 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP or TTP in short), as another promising TTF derivative was reported,^[2] and series of TTP-based conducting radical-cation salts followed.^[3]

Recently, we reported that TTP and TTPY can be utilized as positive electrode materials for rechargeable batteries.^[4]

The synthesis, structure and properties of tetrathiapentalene-based (TTP) organic conductors are reviewed. Among various TTP-type donors, bis-fused tetrathiafulvalene, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) and its derivatives afford many metallic radical cation salts stable down to low temperatures, regardless of the size and shape of the counter anions. Most BDT-TTP conductors have a β -type donor arrangement with almost uniform stacks. Introduction of appropriate substituents results in molecular packing that differs from the β -type.^[5]

In present paper, we have presented a complete description of polarizability, hyperpolarizability and dipole moments of TTP derivatives **1-4** described in literature.^[6] The (NBO) analysis and MEP have been calculated using the DFT/B3LYP method with 6-31G(d,p) basis set. The HOMO–LUMO analysis has been carried out to explain the charge transfer within the molecule. The global hardness (η), global softness (s), electronegativity (χ) and chemical potential (μ) have been calculated using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) performing same method.

2. MATERIALS AND METHODS

The structural characteristics, stability and energy of the compounds under investigation have been determined by DFT^[7,8] with the three parameter hybrid functional (B3) for the exchange part and the Lee-Yang- Parr (LYP)^[9-12] correlation functional, using 6-31G (d,p) basis set^[13,14] with Gaussian 09 program Package.^[15]

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry

The geometrical parameters (bond length, bond angles and dihedral angles) of TTP derivatives compounds are listed in Tables 1-4 using DFT/B3LYP method with 6-31G(d,p)

basis set. The optimized molecular structure of title compound is obtained from Gaussian 09W and Gauss View 5.0 programs are shown in Fig 1.

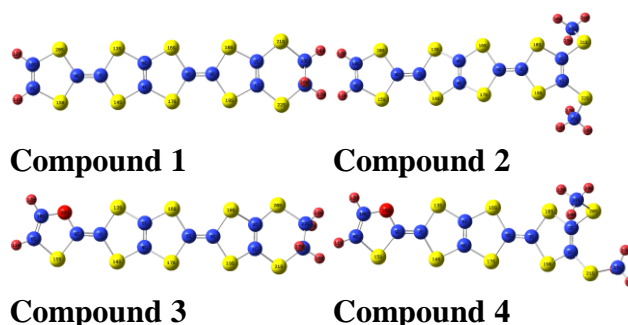


Figure 1: Optimized molecular structure of TTP derivatives 1-4.

Table 1: Optimized geometric parameters of compound 1.

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.347	A(2,1,19)	117.481	D(19,1,2,21)	178.851
R(1,19)	1.781	A(2,1,22)	128.857	D(22,1,2,18)	178.851
R(1,22)	1.776	A(19,1,22)	113.658	D(2,1,22,26)	14.862
R(2,18)	1.781	A(1,2,18)	117.482	D(1,2,21,23)	14.860
R(3,5)	1.350	A(18,2,21)	113.658	D(18,3,5,17)	179.982
R(3,18)	1.781	A(5,3,18)	122.914	D(19,3,5,16)	179.981
R(3,19)	1.781	A(5,3,19)	122.914	D(5,3,18,2)	179.908
R(8,10)	1.337	A(18,3,19)	114.173	D(3,5,17,4)	179.993
R(8,11)	1.083	A(3,5,16)	122.433	D(11,8,10,20)	179.992
R(8,15)	1.762	A(3,5,17)	122.433	D(15,8,10,12)	179.991
R(9,15)	1.787	A(4,6,16)	118.525	D(2,21,23,25)	75.449
R(9,20)	1.787	A(10,8,11)	124.912	D(1,22,26,28)	75.447
R(10,20)	1.762	A(10,8,15)	118.091	D(21,23,26,22)	72.537
R(21,23)	1.833	A(11,8,15)	116.997	D(24,23,26,28)	64.101

Table 2: Optimized geometric parameters of compound 2.

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.356	A(2,1,19)	116.476	D(19,1,2,21)	172.875
R(1,19)	1.790	A(2,1,22)	125.679	D(2,1,19,3)	14.012
R(1,22)	1.766	A(19,1,22)	117.482	D(19,1,22,26)	63.042
R(2,18)	1.790	A(1,2,18)	116.476	D(21,2,18,3)	172.509
R(2,21)	1.766	A(1,2,21)	125.679	D(19,3,5,16)	177.471
R(3,5)	1.350	A(18,2,21)	117.482	D(19,3,18,2)	22.869
R(3,19)	1.778	A(5,3,18)	123.882	D(5,3,19,1)	159.077
R(7,9)	1.350	A(5,3,19)	123.882	D(17,4,6,13)	179.659
R(8,10)	1.337	A(18,3,19)	112.205	D(17,4,14,7)	167.105
R(8,11)	1.083	A(14,4,17)	124.160	D(14,4,17,5)	167.201
R(8,15)	1.764	A(3,5,16)	123.032	D(3,5,16,6)	162.242
R(9,15)	1.784	A(10,8,11)	124.986	D(13,7,9,15)	178.765
R(10,20)	1.764	A(10,8,15)	117.917	D(9,7,13,6)	159.962
R(21,23)	1.837	A(11,8,15)	117.081	D(15,8,10,12)	178.474

Table 3: Optimized geometric parameters of compound 3.

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.350	A(2,1,19)	117.141	D(19,1,2,20)	177.654
R(1,19)	1.783	A(2,1,21)	123.767	D(21,1,2,20)	36.117
R(1,21)	1.763	A(19,1,21)	118.564	D(2,1,19,3)	14.384
R(2,18)	1.785	A(1,2,18)	116.780	D(2,1,21,25)	39.090
R(2,20)	1.764	A(1,2,20)	127.710	D(20,2,18,3)	167.781
R(3,5)	1.350	A(18,2,20)	115.476	D(18,2,20,22)	150.008
R(3,18)	1.782	A(5,3,18)	123.404	D(19,3,5,16)	177.565
R(3,19)	1.780	A(5,3,19)	123.727	D(19,3,18,2)	23.354
R(7,9)	1.345	A(18,3,19)	112.835	D(5,3,19,1)	158.627
R(8,10)	1.333	A(3,5,16)	123.093	D(17,4,6,13)	179.819
R(8,11)	1.079	A(9,7,14)	123.028	D(17,4,14,7)	166.470
R(8,15)	1.774	A(10,8,11)	127.495	D(14,4,17,5)	166.981
R(9,15)	1.786	A(10,8,15)	111.424	D(3,5,16,6)	163.203
R(9,28)	1.381	A(11,8,15)	121.074	D(16,5,17,4)	19.716

Table 4: Optimized geometric parameters of compound 4.

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.354	A(2,1,19)	116.865	D(21,1,2,18)	178.730
R(1,19)	1.781	A(2,1,21)	127.928	D(21,1,2,20)	24.121
R(1,21)	1.774	A(19,1,21)	115.206	D(21,1,19,3)	168.762
R(2,18)	1.787	A(1,2,18)	116.612	D(19,1,21,25)	111.159
R(2,20)	1.768	A(1,2,20)	125.977	D(1,2,18,3)	13.289
R(3,5)	1.350	A(18,2,20)	117.205	D(18,2,20,22)	73.876
R(3,18)	1.780	A(5,3,18)	123.747	D(18,3,5,17)	178.908
R(3,19)	1.782	A(5,3,19)	123.812	D(5,3,18,2)	161.135
R(8,10)	1.333	A(18,3,19)	112.431	D(18,3,19,1)	19.379
R(8,11)	1.079	A(9,7,13)	121.986	D(17,4,6,13)	173.741
R(8,15)	1.774	A(9,7,14)	122.730	D(17,4,14,7)	176.046
R(9,15)	1.786	A(10,8,11)	127.493	D(17,5,16,6)	13.636
R(9,28)	1.382	A(10,8,15)	111.448	D(3,5,17,4)	166.563
R(10,28)	1.374	A(11,8,15)	121.054	D(13,6,16,5)	178.198

3.2. Molecular Electrostatic Potential

The molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor for determining sites for electrophilic and nucleophilic reactions as well as hydrogen-bonding interactions.^[16-18] The electrostatic potential $V(r)$ is also well suited for analysing processes based on the 'recognition' of one molecule by another, as in drug-receptor and enzyme-substrate interactions, because it is through their potentials that the two species first 'see' each other.^[19,20] MEP values can be expressed as the following equation:^[21]

$$V(r) = \sum Z_A / |R_A - r| - \int \rho(r') / |r' - r| d^3r'$$

Where Z_A is the charge of nucleus A located at R_A , $\rho(r')$ is the electronic density function of the molecule, and r' is the dummy integration variable. Potential decreases in the order blue > green > yellow > orange > red. Electrophilic regions are represented by red, nucleophilic by blue and green indicates neutral electrostatic potential. To predict reactive sites for electrophilic or nucleophilic attack for the investigated molecule, the MEP at the B3LYP/6-31G(d,p) optimized geometry was calculated. The negative (red and yellow) regions of the MEP are related to electrophilic reactivity and positive (blue) regions to nucleophilic reactivity, as shown in Fig 2.

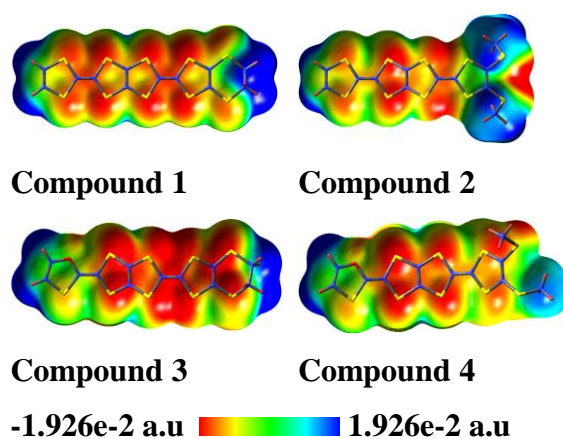


Figure 2: Molecular electrostatic potential surface of TTP derivatives 1-4.

As seen from the figure 2 that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the TTF core and groupings that contains the sulfur atoms while the regions presenting the positive potential are localized vicinity of the hydrogen atoms of alkyl and cycled groups.

3.3. Frontier Molecular Orbitals (FMOs)

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are called as FMOs, which is used to determine the way in which a molecule interacts with other species. The HOMO energy characterizes the ability of electron giving and LUMO energy characterizes the ability of electron accepting. The energy gap between HOMO and LUMO characterizes the molecular chemical stability and electron conductivity, which is the result of a significant degree of ICT from the end-capping electron donor groups to the efficient electron acceptor groups through π -conjugated path.^[22] The HOMO and LUMO orbitals of compound 1 were computed by the DFT/B3LYP method with 6-31G(d,p) basis set and visualized in Fig 3. The FMOs analysis of TTP derivatives 1-4 shows the

delocalization of charges occur within the molecule, which increases the molecular reactivity of the molecules.

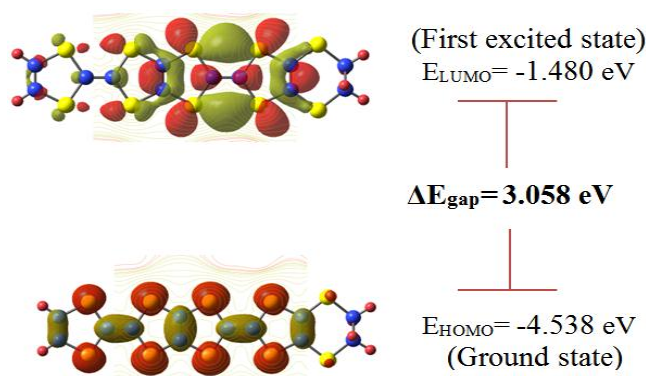


Figure 3: HOMO-LUMO Structure with the energy level diagram of compound 1.

3.4. Global Reactivity Descriptors

Depended on density functional descriptors, global chemical reactivity descriptors of TTP derivatives **1-4** such as hardness (η), softness (S), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) as well as local reactivity descriptors as the Fukui function and the philicity have been defined.^[23-27] Using Koopman's theorem for closed-shell compounds, η , μ , χ can be defined as:

$$\eta = (I - A) / 2$$

$$\mu = -(I + A) / 2$$

$$\chi = (I + A) / 2$$

$$S = 1 / \eta$$

$$I = -E_{HOMO} \quad \text{and} \quad A = -E_{LUMO}$$

Where I and A are the ionization potential and electron affinity of the compounds, respectively. The greater the ionization potential data, the more difficult to lose electron of the ligand. Electron affinity is the capability of a ligand to accept electron, the smaller the electron affinity data the easier to get the electron. Hardness is half of the gap between the HOMO and LUMO, we all know that the bigger the gap, the more stable the molecule, it is conceivable that "there seems to be a rule of nature that molecules arrange them-selves to be as hard as possible" as first postulated by Pearson in 1978.^[28] Softness can measure the extent of chemical reactivity of compound and it is the reciprocal of hardness. χ is defined by Iczkowski and Margrave^[29] as a generalization of the definition by Mulliken,^[30] because the fundamental relationship to μ , χ is quite different from Pauling's original meaning of

electronegativity, which was a property of an atom in a molecule. Here χ is a property of the entire molecule.^[27] Recently Parr *et al.*^[23] have defined a new descriptor to quantify the global electrophilic power of the compound as electrophilicity index (ω), which defines a quantitative classification of the global electrophilic nature of a compound. They have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index (ω) as follows:

$$\omega = \mu^2 / 2\eta$$

The electrophilicity is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a molecule within a relative scale. The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity.^[31-36] All the calculated values of HOMO–LUMO, energy gap, ionization potential, Electron affinity, hardness, potential, softness and electrophilicity index are shown in Table 5.

Table 5: Quantum chemical descriptors of TTP derivatives 1-4.

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-4.538	-4.785	-4.044	-4.628
E_{LUMO} (eV)	-1.480	-1.297	-1.177	-1.226
ΔE_{gap} (eV)	3.058	3.488	3.467	3.402
IE (eV)	4.538	4.785	4.044	4.628
A (eV)	1.480	1.297	1.177	1.226
μ (eV)	-3.009	-3.041	-2.910	-2.927
χ (eV)	3.089	3.041	2.910	2.927
η (eV)	1.529	1.744	1.734	1.701
S (eV)	0.327	0.287	0.288	0.294
ω (eV)	2.961	2.652	2.443	2.519

As presented in table 5, the compound which have the lowest energetic gap is the compound **1** ($\Delta E_{\text{gap}} = 3.058$ eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **2** ($\Delta E_{\text{gap}} = 3.488$ eV). The compound that has the highest HOMO energy is the compound **3** ($E_{\text{HOMO}} = -4.044$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **1** ($E_{\text{LUMO}} = -1.480$ 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 **3** has lowest value of the

potential ionization ($I = 4.044$ eV), so that will be the better electron donor. Compound **1** has the largest value of the affinity ($A = 1.480$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **1** ($\eta = 1.529$ eV, $S = 0.327$ eV) is lesser (greater) among all the molecules. Thus, compound **1** is found to be more reactive than all the compounds. Compound **1** possesses higher electronegativity value ($\chi = 3.089$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **1** ($\omega = 2.961$ 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.

3.5. Local Reactivity Descriptors

The most relevant local descriptor of reactivity is the Fukui function (FF). The Fukui function indicates the propensity of the electronic density to deform at a given position upon accepting or denoting electrons.^[37-39] The Fukui function is defined as:

$$f(r) = \frac{\delta p(r)}{\delta N}$$

Where $p(r)$ is the electronic density, N is the number of electrons and r is the external potential exerted by the nucleus. The local (condensed) Fukui functions (f_k^+ , f_k^- , f_k^0) are calculated using the following equations:

$$f_k^+ = [q_k(N+1) - q_k(N)] \quad \text{for nucleophilic attack}$$

$$f_k^- = [q_k(N) - q_k(N-1)] \quad \text{for electrophilic attack}$$

$$f_k^0 = [q_k(N+1) - q_k(N-1)]/2 \quad \text{for radical attack}$$

Where q_k is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the k^{th} atomic site is the neutral (N), anionic ($N+1$) or cationic ($N-1$) chemical species. While +, -, and 0 signs show nucleophilic, electrophilic and radical attack respectively. These indexes (f_k^+ , f_k^- , f_k^0) are directly concerned with the selectivity of the molecule towards. Fukui functions for selected atomic sites TTP derivatives **1-4** are shown in Tables 6-7.

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

Compound 1					Compound 2				
Atom	7 C	5 C	3 C	2 C	Atom	5 C	7 C	3 C	1 C
f^+	0.031	0.030	0.014	0.003	f^+	0.031	0.031	0.011	0.007
Atom	7 C	5 C	2 C	1 C	Atom	5 C	7 C	1 C	2 C
f^-	0.021	0.017	0.004	0.004	f^-	0.031	0.022	0.009	0.009
Atom	7 C	5 C	3 C	2 C	Atom	5 C	7 C	1 C	2 C
f^0	0.026	0.024	0.004	0.003	f^0	0.031	0.026	0.008	0.008

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

Compound 3					Compound 4				
Atom	3 C	7 C	5 C	6 C	Atom	3 C	7 C	4 C	6 C
f^+	0.035	0.026	0.018	-0.003	f^+	0.071	0.020	0.006	0.004
Atom	5 C	2 C	7 C	1 C	Atom	5 C	7 C	2 C	1 C
f^-	0.035	0.025	0.021	0.013	f^-	0.034	0.021	0.009	0.005
Atom	5 C	7 C	3 C	2 C	Atom	3 C	7 C	4 C	6 C
f^0	0.026	0.024	0.016	0.005	f^0	0.032	0.021	0.004	0.003

From the tables 6-7, the parameters of local reactivity descriptors show that 3C is the more reactive site in compounds 3 and 4 and 7C, 5C are the more reactive sites in compounds 1 and 2 respectively for nucleophilic attacks. The more reactive sites in radical attacks are 7C, 3C, for compounds 1, 4 respectively and 5C for the both compounds 2 and 3. The more reactive sites for electrophilic attacks are 7C for compound 1 and 5C for compounds 2, 3 and 4 respectively.

3.6. Natural Bond Orbital Analysis (NBO)

NBO analysis describes the Lewis-like molecular bonding pattern of electron pairs (or of individual electrons in the open-shell case) in optimally compact form. NBOs determine the localized Natural Lewis Structure (NLS) representation of the wave function, while the remaining “non-Lewis”-type NBOs complete the span of the basis and describe the residual “delocalization effects” by the second-order perturbation energies $E(2)$ [donor (i) \rightarrow acceptor (j)] that involve the most important delocalization and are given by:^[40-43]

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

With q_i is the donor orbital occupancy; ϵ_i, ϵ_j the diagonal elements; F_{ij} is the off diagonal NBO Fock matrix element. In NBO analysis large $E(2)$ value shows the intensive interaction between electron-donors and electron-acceptors, and greater the extent of conjugation of the whole system, the possible intensive interaction are given as supporting material (Tables 8-11).

Thus, NBOs provide a valence bond-type description of the wave function, closely linked to classical Lewis structure concepts and is a helpful tool for understanding the delocalization of electron density.^[42,44]

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) S15	1.78008	$\pi^*(C8-C10)$	0.21624	22.32	0.26	0.067
LP(2) S20	1.78008	$\pi^*(C8-C10)$	0.21624	22.32	0.26	0.067
LP(2) S13	1.80227	$\pi^*(C4-C6)$	0.38052	21.19	0.24	0.066
LP(2) S14	1.80227	$\pi^*(C4-C6)$	0.38052	21.19	0.24	0.066
LP(2) S16	1.80146	$\pi^*(C4-C6)$	0.38052	21.18	0.24	0.066
LP(2) S17	1.80146	$\pi^*(C4-C6)$	0.38052	21.18	0.24	0.066
LP(2) S18	1.79861	$\pi^*(C3-C5)$	0.41755	20.52	0.24	0.066
LP(2) S19	1.79861	$\pi^*(C3-C5)$	0.41755	20.52	0.24	0.066
LP(2) S15	1.78008	$\pi^*(C7-C9)$	0.41782	20.39	0.24	0.065
LP(2) S20	1.78008	$\pi^*(C7-C9)$	0.41782	20.39	0.24	0.065
LP(2) S21	1.86814	$\pi^*(C1-C2)$	0.37342	20.26	0.24	0.066
LP(2) S22	1.86814	$\pi^*(C1-C2)$	0.37343	20.25	0.24	0.066
LP(2) S18	1.79861	$\pi^*(C1-C2)$	0.37344	19.76	0.24	0.064
LP(2) S16	1.80146	$\pi^*(C3-C5)$	0.41755	18.86	0.24	0.064
LP(2) S17	1.80146	$\pi^*(C3-C5)$	0.41755	18.86	0.24	0.064
LP(2) S13	1.80227	$\pi^*(C7-C9)$	0.41782	18.73	0.24	0.063
LP(2) S14	1.80227	$\pi^*(C7-C9)$	0.41782	18.73	0.24	0.063
$\sigma(C1-S19)$	1.96930	$\sigma^*(C2-S21)$	0.03064	5.85	0.83	0.062
$\sigma(C8-H11)$	1.97504	$\sigma^*(C10-S20)$	0.01922	5.45	0.76	0.058
$\sigma(C5-S17)$	1.96890	$\sigma^*(C3-S18)$	0.03854	5.16	0.82	0.058

Table 9: Second order perturbation theory analysis of Fock 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) S15	1.77258	$\pi^*(C8-C10)$	0.21262	21.50	0.26	0.067
LP(2) S20	1.77258	$\pi^*(C8-C10)$	0.21262	21.50	0.26	0.067
LP(2) S16	1.79619	$\pi^*(C4-C6)$	0.37140	20.28	0.24	0.065
LP(2) S17	1.79619	$\pi^*(C4-C6)$	0.37140	20.28	0.24	0.065
LP(2) S13	1.80445	$\pi^*(C4-C6)$	0.37140	20.10	0.24	0.064
LP(2) S14	1.80445	$\pi^*(C4-C6)$	0.37140	20.10	0.24	0.064
LP(2) S18	1.78388	$\pi^*(C1-C2)$	0.31271	19.22	0.25	0.063
LP(2) S19	1.78388	$\pi^*(C1-C2)$	0.31271	19.22	0.25	0.063
LP(2) S15	1.77258	$\pi^*(C7-C9)$	0.38022	17.03	0.26	0.062
LP(2) S20	1.77258	$\pi^*(C7-C9)$	0.38022	17.03	0.26	0.062
LP(2) S18	1.78388	$\pi^*(C3-C5)$	0.36867	14.13	0.26	0.056
LP(2) S19	1.78388	$\pi^*(C3-C5)$	0.36867	14.13	0.26	0.056

LP(2) S16	1.79619	$\pi^*(C3-C5)$	0.36867	13.73	0.26	0.056
LP(2) S13	1.80445	$\pi^*(C7-C9)$	0.38022	12.56	0.26	0.054
LP(2) S14	1.80445	$\pi^*(C7-C9)$	0.38022	12.56	0.26	0.054
$\sigma(C8-H11)$	1.97522	$\sigma^*(C10-S20)$	0.02220	5.43	0.76	0.057
$\sigma(C10-H12)$	1.97522	$\sigma^*(C8-S15)$	0.02220	5.43	0.76	0.057
$\sigma(C1-S19)$	1.97162	$\sigma^*(C2-S21)$	0.03333	5.36	0.84	0.060
$\sigma(C2-S18)$	1.97162	$\sigma^*(C1-S22)$	0.03333	5.36	0.84	0.060
$\sigma(C5-S16)$	1.96890	$\sigma^*(C3-S19)$	0.04646	5.13	0.83	0.058

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) O28	1.78378	$\pi^*(C8-C10)$	0.18884	28.59	0.35	0.090
LP(2) O28	1.78378	$\pi^*(C7-C9)$	0.35572	25.07	0.36	0.088
LP(2) S16	1.79297	$\pi^*(C4-C6)$	0.36905	20.40	0.24	0.065
LP(2) S17	1.79367	$\pi^*(C4-C6)$	0.36905	20.27	0.24	0.065
LP(2) S13	1.81780	$\pi^*(C4-C6)$	0.36905	20.12	0.23	0.064
LP(2) S19	1.79178	$\pi^*(C1-C2)$	0.36710	19.61	0.24	0.063
LP(2) S18	1.79216	$\pi^*(C1-C2)$	0.36710	19.59	0.24	0.063
LP(2) S14	1.82137	$\pi^*(C4-C6)$	0.36905	19.09	0.24	0.063
LP(2) S15	1.79061	$\pi^*(C7-C9)$	0.35572	19.03	0.28	0.067
LP(2) S15	1.79061	$\pi^*(C8-C10)$	0.18884	17.35	0.27	0.061
LP(2) S20	1.85661	$\pi^*(C1-C2)$	0.36710	17.11	0.24	0.060
LP(2) S16	1.79297	$\pi^*(C3-C5)$	0.36993	14.21	0.26	0.057
LP(2) S17	1.79367	$\pi^*(C3-C5)$	0.36993	14.19	0.26	0.057
LP(2) S19	1.79178	$\pi^*(C3-C5)$	0.36993	13.59	0.26	0.055
LP(2) S18	1.79216	$\pi^*(C3-C5)$	0.36993	13.39	0.26	0.055
LP(2) S13	1.81780	$\pi^*(C7-C9)$	0.35572	11.00	0.27	0.050
LP(2) S14	1.82137	$\pi^*(C7-C9)$	0.35572	10.83	0.27	0.050
$\sigma(C7-S14)$	1.96966	$\sigma^*(C9-O28)$	0.04209	5.89	0.95	0.067
$\sigma(C7-S13)$	1.96652	$\sigma^*(C9-S15)$	0.04822	5.74	0.80	0.061
$\sigma(C1-S19)$	1.97042	$\sigma^*(C2-S20)$	0.02975	5.56	0.84	0.061

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) O28	1.78585	$\pi^*(C8-C10)$	0.18929	28.77	0.35	0.090
LP(2) O28	1.78585	$\pi^*(C7-C9)$	0.36089	24.35	0.36	0.087
LP(2) S19	1.77175	$\pi^*(C1-C2)$	0.30795	21.68	0.23	0.065
LP(2) S18	1.78157	$\pi^*(C1-C2)$	0.30795	20.28	0.24	0.063
LP(2) S13	1.81674	$\pi^*(C4-C6)$	0.36796	19.68	0.25	0.066
LP(2) S16	1.79558	$\pi^*(C4-C6)$	0.36796	19.64	0.25	0.066
LP(2) S17	1.79574	$\pi^*(C4-C6)$	0.36796	19.59	0.25	0.066
LP(2) S14	1.82046	$\pi^*(C4-C6)$	0.36796	18.90	0.25	0.065
LP(2) S15	1.79343	$\pi^*(C7-C9)$	0.36089	18.58	0.28	0.067

LP(2) S15	1.79343	$\pi^*(\text{C8-C10})$	0.18929	17.36	0.27	0.061
LP(2) S17	1.79574	$\pi^*(\text{C3-C5})$	0.37851	14.74	0.26	0.058
LP(2) S16	1.79558	$\pi^*(\text{C3-C5})$	0.37851	14.72	0.26	0.058
LP(2) S19	1.77175	$\pi^*(\text{C3-C5})$	0.37851	14.40	0.26	0.057
LP(2) S18	1.78157	$\pi^*(\text{C3-C5})$	0.37851	14.16	0.26	0.057
LP(2) S13	1.81674	$\pi^*(\text{C7-C9})$	0.36089	11.79	0.27	0.053
$\sigma(\text{C7-S14})$	1.96988	$\sigma^*(\text{C9-O28})$	0.04178	5.85	0.95	0.067
$\sigma(\text{C7-S13})$	1.96660	$\sigma^*(\text{C9-S15})$	0.04736	5.79	0.80	0.061
LP(2) S20	1.89872	$\sigma^*(\text{C2-S18})$	0.05767	5.76	0.41	0.044
$\sigma(\text{C2-S18})$	1.97162	$\sigma^*(\text{C1-S21})$	0.03299	5.53	0.83	0.061
$\sigma(\text{C1-S19})$	1.97155	$\sigma^*(\text{C2-S20})$	0.03319	5.44	0.84	0.060

The intra molecular interaction for the TTP derivatives **1-4** is formed by the orbital overlap between: $\sigma(\text{C1-S19})$ and $\sigma^*(\text{C2-S21})$ for compound **1**, $\sigma(\text{C8-H11})$ and $\sigma^*(\text{C10-S20})$ for compound **2**, $\sigma(\text{C7-S14})$ and $\sigma^*(\text{C9-O28})$ for compound **3** and $\sigma(\text{C7-S14})$ and $\sigma^*(\text{C9-O28})$ for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of $\sigma(\text{C1-S19})$ to $\sigma^*(\text{C2-S21})$ for compound **1**, $\sigma(\text{C8-H11})$ to $\sigma^*(\text{C10-S20})$ for compound **2**, $\sigma(\text{C7-S14})$ to $\sigma^*(\text{C9-O28})$ for compound **3** and $\sigma(\text{C7-S14})$ to $\sigma^*(\text{C9-O28})$ for compound **4** lead to highest stabilization of 5.85, 5.43, 5.89 and 5.85 kJ mol^{-1} respectively. In case of LP(2) S15 orbital to the $\pi^*(\text{C8-C10})$ for compound **1**, LP(2) S15 orbital to $\pi^*(\text{C8-C10})$ for compound **2**, LP(2) O28 orbital to $\pi^*(\text{C8-C10})$ for compound **3**, LP(2) O28 orbital to $\pi^*(\text{C8-C10})$ for compound **4** respectively, show the stabilization energy of 22.32, 21.50, 28.59 and 28.77 kJ mol^{-1} respectively.

3.7. Nonlinear Optical Properties (NLO)

In discussing nonlinear optical 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. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first order hyperpolarizability (β_0) of the title compound is calculated based on the finite-field approach. The first-order hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components from the 3D matrix can be reduced to 10 components due to the Kleinman symmetry.^[45] The components of β are the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E^0 - \mu_i F_i - 1/2 \alpha_{ij} F_i F_j - 1/6 \beta_{ijk} F_i F_j F_k + \dots$$

Where E_0 is the energy of the unperturbed molecule, F_i is the field at the origin, μ_i , α_{ij} and β_{ijk} are the components of dipole moment, polarizability, the first hyperpolarizabilities, and second hyperpolarizabilities, respectively.

The total dipole moment (μ_0), the mean polarizability (α_0), the anisotropy of the polarizability ($\Delta\alpha$) and the total first hyperpolarizability (β_0) using x, y, z components are defined as.^[46]

$$\mu_0 = [\mu_x^2 + \mu_y^2 + \mu_z^2]^{1/2}$$

$$\alpha_0 = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

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

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

Where

$$\beta_x = \beta_{xxx} + \beta_{xyz} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xyy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The total molecular dipole moment (μ), mean polarizability (α_0) and anisotropy polarizability ($\Delta\alpha$) and first hyperpolarizability (β_{total}) of TTP derivatives **1-4** are computed and are depicted in Table 12.

Table 12: The dipole moments μ (D), polarizability α , the average polarizability α (esu), the anisotropy of the polarizability $\Delta\alpha$ (esu), and the first hyperpolarizability β (esu) of TTP derivatives 1-4 calculated by B3LYP/6-31G(d,p) method.

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	66.9563	4.7967	18.9398	171.7301
B_{yyy}	0.0001	177.8824	10.3578	10.4783
B_{zzz}	0.0003	0.0000	-0.0650	0.7153
B_{xyy}	-28.7439	146.6419	39.5548	14.9077
B_{xxy}	0.0009	-37.9920	49.6094	48.9501
B_{xxz}	0.0206	0.0000	-0.4695	5.0662
B_{xzz}	20.6452	12.5623	-10.3926	-30.8009
B_{yzz}	-0.0001	-7.0146	2.4028	2.4471
B_{yyz}	0.0001	0.0000	-0.0246	0.3968
B_{xyz}	-4.3916	0.0000	-5.1747	34.7826
$B_{tot}(\text{esu}) \times 10^{-33}$	83.2099	134.0048	62.4636	186.3904
μ_x	1.4177	2.8407	-0.7077	-0.0721
μ_y	0.0000	-0.1893	0.5204	0.5155

μ_z	0.0002	0.0000	-0.0044	0.0507
$\mu_{tot}(D)$	1.4177	2.8470	0.8784	0.5230
α_{xx}	-112.2743	-202.6259	-102.5760	-117.2174
α_{yy}	-199.2285	-133.5167	-192.3876	-191.5088
α_{zz}	-205.3716	-197.8506	-195.9547	-193.7417
α_{xy}	0.0001	-18.0921	5.0593	5.0960
α_{xz}	-0.0009	0.0000	-0.0465	0.4824
α_{yz}	-0.3414	0.0000	0.4388	-3.9742
$\alpha(esu) \times 10^{-24}$	90.1847	73.8298	92.0683	76.2631
$\Delta\alpha(esu) \times 10^{-24}$	13.3653	10.9415	13.64453	11.3022

Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_{tot}) 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. = 0.1482×10^{-24} e.s.u., for β ; 1 a.u. = 8.6393×10^{-33} e.s.u.). The calculated values of dipole moment (μ) for the title compounds were found to be 1.4177, 2.8470, 0.8784 and 0.5230 D respectively, which are approximately two times than to the value for urea ($\mu = 1.3732$ 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 90.1847×10^{-24} , 73.8298×10^{-24} , 92.0683×10^{-24} and 76.2631×10^{-24} esu respectively; the values of anisotropy of the polarizability are 13.3653, 10.9415, 13.64453 and 11.3022 esu, respectively. The magnitude of the molecular hyperpolarizability (β) is one of important key factors in a NLO system. The DFT/6-31G(d,p) calculated first hyperpolarizability value (β) of TTP derivatives molecules are equal to 83.2099×10^{-33} , 134.0048×10^{-33} , 62.4636×10^{-33} and 186.3904×10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.24, 0.39, 0.18 and 0.54 times than those of urea (β of urea is 343.272×10^{-33} esu obtained by B3LYP/6-311G (d,p) method). The above results show that TTP derivatives **1-4** might have not the NLO applications.

CONCLUSION

In this work, we performed DFT study of TTP derivatives **1-4** with B3LYP/6-31G(d,p) basis sets. The optimized geometric parameters (bond lengths, bond angles and dihedral angles) are theoretically determined. The NBO analysis indicated the intermolecular charge transfer between the bonding and anti-bonding orbital's. MEP confirmed the different negative and positive potential sites of the molecules in accordance with the total electron density surface. The calculated dipole moment and first order hyperpolarizability results indicate that the title compounds have not a reasonable good non-linear optical behavior.

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