Theoretical study of TTP derivatives (EO-TTP, TMEO-TTP, SMEO-TTP and EOET-TTP) by Density functional theory

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ABSTRACT: Quantum chemical study provides a new way to understand the relation between structure, stability and electronic properties and also offer new strategies to design new nano-materials. Therefore, in this study, we investigated the geometric, stability and electronic properties of a series of TTP derivatives **1-4** byedensity functional theory (DFT) method using 6-31G(d,p) basis set. The calculated HOMO and LUMO energies showed that charge transfer occurs within the molecules. Stability of the molecules arising from hyper conjugative interaction and charge delocalization has been analyzed using natural bond orbital (NBO) analysis. Non-linear optical (NLO) behavior of the title compounds was investigated by determining the electric dipole moment (μ), polarizability (α), and hyperpolarizability (β) using the above mentioned basis set.

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

I. INTRODUCTION

Heterocyclic compounds are worthy of attention for many reasons, chief among which are their biological activities, which many important drugs being heterocycles. Therefore, organic chemists have been making extensive efforts to produce heterocyclic compounds by developing new and efficient synthetic transformations [1].

Tetrathiapentalene (TTP) derivatives capped with alkyl groups are synthesized by a contracting-coupling reaction of two TTP molecules. These compounds have reduced donor ability in comparison with tetrathiafulvalenes (TTF) and work as organic semiconductors in high-performance organic field-effect transistors.

Quantum chemistry is really a promising area of chemistry. Presently quantum chemical calculations are being widely used in diverse areas of chemistry to forecast activity of molecules prior to experiment [2]. It helps to predict molecular behaviour in terms of energy change and electronic behaviour during the reaction.

Density Functional Theory (DFT) provides a considerable theoretical framework for deriving quantum chemistry properties [3,4]. Within DFT, the electron density contains information about the molecular properties and takes a fundamental role in calculating chemical reactivity properties.

The aim of the present Letter is a quantum chemical investigation of TTP derivatives **1-4** described in literature [5] using DFT method andB3LYP/6-31G(d,p) basis set. To predict the applications of title compounds, we give a complete study of the molecular geometry, second order perturbation analysis, First hyperpolarizability, chemical reactivity as HOMO-LUMO energy gap, chemical hardness and chemical potential and Fukui functions.

II. MATERIALS AND METHODS

The molecular structure optimization of TTP derivatives **1-4** was calculated using B3LYP exchange correlation functional [6-12] which consist of the Lee-Yang-Parr correlation functional in conjunction with a hybrid exchange functional first proposed by Becke. The three-parameter hybrid exchange-correlation functional (B3LYP) [13] employing 6-31G(d,p) basis set [14-16] as implemented in Gaussian 09 package [17]. Gaussian 09 program package was used without any constraint on the geometry with the double split valence basis set along with polarization functions; 6-31G(d,p). By combining the results of the GAUSSVIEW [18] program with symmetry considerations.

III. RESULTS AND DISCUSSION

MOLECULAR GEOMETRY: The optimized structural parameters such as bond lengths, bond angles and dihedral angles of TTP derivatives **1-4** were determined at B3LYP/ DFT level theories with 6-31G(d,p) basis set and are presented in Tables 1-4 in accordance with the atom numbering scheme of the molecule shown in Fig 1.

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

Compound **3**   Compound **4**
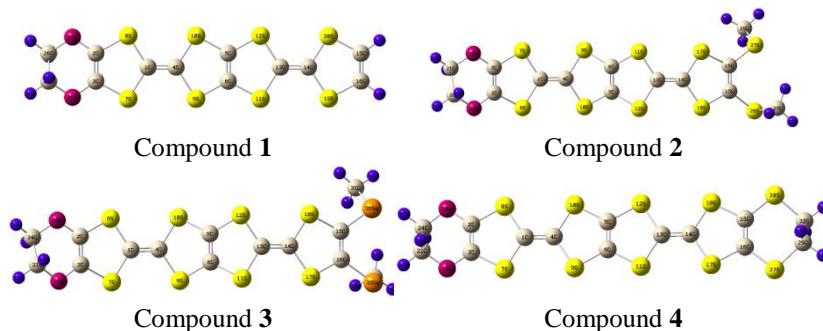
Fig. 1.Optimized molecular structure of TTP derivatives 1-4

Table 1.Optimized geometric parameters of compound 1

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,4)	1.350	A(4,1,7)	122.172	D(7,1,4,10)	179.767
R(1,7)	1.789	A(4,1,8)	122.172	D(8,1,4,9)	179.770
R(1,8)	1.789	A(7,1,8)	115.655	D(8,2,3,21)	179.197
R(2,3)	1.341	A(3,2,8)	118.468	D(22,2,3,7)	179.192
R(2,8)	1.771	A(3,2,22)	124.605	D(8,2,22,26)	164.248
R(2,22)	1.367	A(8,2,22)	116.919	D(7,3,21,23)	164.255
R(3,7)	1.771	A(2,3,7)	118.468	D(1,4,10,5)	179.991
R(3,21)	1.367	A(2,3,21)	124.606	D(10,5,12,13)	180.001
R(11,13)	1.794	A(7,3,21)	116.918	D(11,6,9,4)	179.992
R(15,20)	1.762	A(1,4,9)	122.426	D(3,21,23,24)	165.393
R(16,18)	1.083	A(1,7,3)	93.704	D(21,23,26,28)	58.013
R(16,19)	1.762	A(1,8,2)	93.704	D(24,23,26,22)	179.471
R(21,23)	1.436	A(16,15,17)	124.902	D(24,23,26,27)	61.715
R(22,26)	1.436	A(16,15,20)	118.094	D(25,23,26,22)	58.012
R(23,24)	1.092	A(22,26,23)	110.476	D(25,23,26,28)	178.799

Table 2.Optimized geometric parameters of compound 2

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,4)	1.351	A(4,1,7)	122.501	D(8,1,4,9)	177.833
R(1,7)	1.786	A(4,1,8)	122.314	D(8,1,7,3)	14.492
R(1,8)	1.787	A(7,1,8)	115.164	D(4,1,8,2)	167.203
R(2,3)	1.341	A(3,2,8)	118.161	D(8,2,3,19)	176.390
R(2,8)	1.774	A(3,2,20)	124.714	D(19,3,7,1)	174.622
R(2,20)	1.367	A(8,2,20)	117.107	D(7,3,19,21)	160.376
R(3,7)	1.773	A(2,3,7)	118.189	D(1,4,9,6)	160.406
R(3,19)	1.367	A(2,3,19)	124.535	D(9,4,10,5)	21.544
R(4,9)	1.790	A(7,3,19)	117.177	D(12,5,6,9)	179.845
R(4,10)	1.790	A(10,5,12)	124.153	D(12,5,10,4)	167.052
R(5,6)	1.343	A(9,6,11)	124.177	D(10,5,12,13)	167.009
R(16,27)	1.768	A(1,7,3)	93.138	D(5,6,9,4)	13.108
R(19,21)	1.436	A(3,19,21)	110.360	D(5,6,11,13)	12.715
R(20,24)	1.436	A(2,20,24)	110.823	D(6,11,13,14)	161.393
R(21,22)	1.092	A(19,21,22)	106.353	D(5,12,13,11)	20.957

Table 3.Optimized geometric parameters of compound 3

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,4)	1.351	A(4,1,7)	122.329	D(7,1,4,10)	177.728
R(1,7)	1.787	A(4,1,8)	122.479	D(4,1,7,3)	167.308
R(1,8)	1.786	A(7,1,8)	115.169	D(7,1,8,2)	14.433
R(2,3)	1.341	A(3,2,8)	118.195	D(20,2,3,7)	176.353
R(2,8)	1.773	A(3,2,20)	124.524	D(20,2,8,1)	174.695
R(2,20)	1.367	A(8,2,20)	117.180	D(8,2,20,24)	160.209
R(3,7)	1.774	A(2,3,7)	118.158	D(2,3,7,1)	88.627
R(3,19)	1.367	A(2,3,19)	124.723	D(7,3,19,21)	168.569
R(13,14)	1.349	A(7,3,19)	117.098	D(10,4,9,6)	21.370
R(15,16)	1.347	A(1,4,9)	123.100	D(1,4,10,5)	160.682
R(15,18)	1.774	A(1,4,10)	123.088	D(10,5,6,11)	179.893
R(15,36)	1.901	A(16,15,18)	117.258	D(6,5,10,4)	13.010
R(16,17)	1.771	A(16,15,36)	124.151	D(11,6,9,4)	167.101
R(16,35)	1.910	A(18,15,36)	118.326	D(9,6,11,13)	166.680
R(31,34)	1.089	A(28,27,29)	110.497	D(6,11,13,12)	21.591

Table 4.Optimized geometric parameters of compound 4

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,4)	1.350	A(4,1,7)	122.174	D(4,1,7,3)	180.050
R(1,7)	1.789	A(4,1,8)	122.174	D(8,2,3,19)	179.185
R(1,8)	1.789	A(7,1,8)	115.653	D(20,2,3,7)	179.188
R(2,3)	1.341	A(3,2,8)	118.470	D(8,2,20,24)	164.259
R(2,8)	1.771	A(3,2,20)	124.596	D(7,3,19,21)	164.253
R(2,20)	1.367	A(8,2,20)	116.926	D(1,4,10,5)	179.999
R(3,7)	1.771	A(2,3,7)	118.470	D(10,5,6,11)	179.960
R(3,19)	1.367	A(2,3,19)	124.595	D(11,6,9,4)	180.037
R(4,9)	1.793	A(7,3,19)	116.927	D(5,12,13,14)	179.985
R(4,10)	1.793	A(1,4,9)	122.424	D(11,13,14,18)	179.951
R(19,21)	1.436	A(18,15,28)	113.657	D(12,13,14,17)	179.949
R(20,24)	1.436	A(15,16,27)	128.856	D(13,14,17,16)	179.900
R(21,22)	1.092	A(17,16,27)	113.657	D(18,15,16,27)	178.858
R(21,24)	1.528	A(2,20,24)	110.612	D(28,15,16,17)	178.855
R(29,32)	1.528	A(27,29,30)	109.850	D(16,15,28,32)	14.848

MOLECULAR ELECTROSTATIC POTENTIAL (MEP): Molecular electrostatic potential is related to the ED and is a very useful descriptor in understanding sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [19,20]. The electrostatic potential V(r) is also well suited for analyzing 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 [21,22]. In the present study, the MEP map figure for TTP derivatives molecule is shown in Fig 2. The MEP which is a plot of electrostatic potential increases in the order red < orange < yellow < green < blue. The negative (red and yellow) regions of MEP were related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity. To predict reactive sites of electrophilic and nucleophilic attacks for the investigated molecules, MEP at the B3LYP/6-31G(d,p) optimized geometries were calculated.
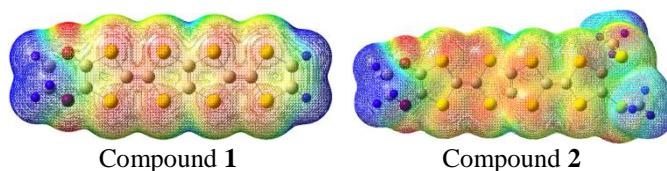

Compound **1**   Compound **2**

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

-2.050e-2 a.u   2.050e-2 a.u
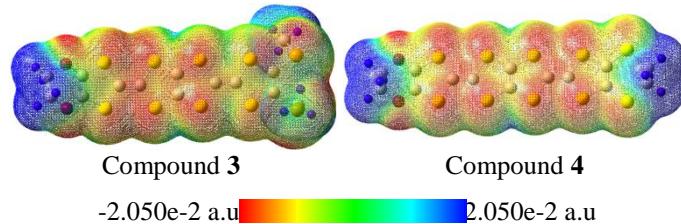
Fig. 2. Molecular electrostatic potential surface of TTP derivatives 1-4

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

FRONTIER MOLECULAR ORBITALS (FMOS): Molecular interactions with other species can be determined from the studies of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of a molecule, which are known as Frontier Molecular Orbitals (FMO). The band gap energy, the energy difference between HOMO and LUMO orbitals, plays an important role in determining the chemical stability [23] and reactivity of a molecule. The HOMO and LUMO represents the ability to donate an electron and the ability to obtain an electron, respectively. The HOMO and LUMO orbitals are shown in Fig 3 and the values of HOMO and LUMO energy calculated by B3LYP/6-31G(d,p) method are given in Table 5.


E_{LUMO}= -1.484 eV

ΔE_{gap}=**2.999 eV**

E_{HOMO}= -4.483 eV
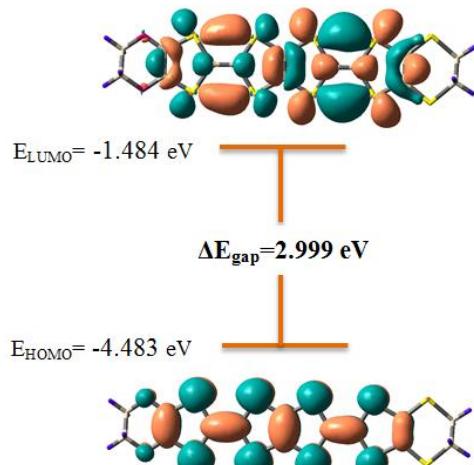
Fig. 3. HOMO-LUMO Structure with the energy level diagram of compound 4

GLOBAL REACTIVITY DESCRIPTORS: The energies of frontier molecular orbitals (ε_{HOMO} , ε_{LUMO}), band gap (ε_{LUMO}-ε_{HOMO}) , electronegativity (χ), chemical potential (μ), chemical hardness (η), global softness (S), global electrophilicity index (ω) [24-28] of TTP derivatives **1-4** have been calculated using following Eqs. (1)-(5) and listed in Table 5.

$$\chi = -1/2(\varepsilon_{LUMO} + \varepsilon_{HOMO}) \ (1)$$
$$\mu = -\chi = 1/2(\varepsilon_{LUMO} + \varepsilon_{HOMO}) \ (2)$$
$$\eta = 1/2(\varepsilon_{LUMO} - \varepsilon_{HOMO}) \ (3)$$
$$S = 1/2\eta \ (4)$$
$$\omega = \mu^2/2\eta \ (5)$$

According to Parr et al., electrophilicity index (ω) is as a global reactivity index similar to the chemical hardness and chemical potential. The electrophilicity index (ω) is positive, definite quantity and the direction of the charge transfer is completely determined by the electronic chemical potential (μ) of the molecule because an electrophile is a chemical species capable of accepting electrons from the environment and its energy must decrease upon accepting electronic charge.

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

Parameters	compound 1	compound 2	compound 3	compound 4
E_{HOMO} (eV)	-4.490	-4.686	-4.657	-4.483
E_{LUMO} (eV)	-1.436	-1.318	-1.312	-1.484
ΔE_{gap} (eV)	3.054	3.368	3.346	2.999
IE (eV)	4.490	4.686	4.657	4.483
A (eV)	1.436	1.318	1.312	1.484
μ (eV)	-2.963	-3.002	-2.985	-2.983
χ (eV)	2.963	3.002	2.985	2.983
η (eV)	1.527	1.684	1.673	1.500
S (eV)	0.327	0.297	0.299	0.333
ω (eV)	2.875	2.676	2.662	2.967

As presented in table 5, the compound which have the lowest energetic gap is the compound **4** (ΔE_{gap} = 2.999 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} = 3.368 eV).The compound that has the highest HOMO energy is the compound **4** (E_{HOMO} = -4.483 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} = -1.484 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 **4** has lowest value of the potential ionization (I = 4.483 eV), so that will be the better electron donor. Compound **4** has the largest value of the affinity (A = 1.484 eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **4** (η = 1.500 eV, **S** = 0.333 eV) is lesser (greater) among all the molecules. Thus, compound **4** is found to be more reactive than all the compounds. Compound **2** possesses higher electronegativity value (χ = 3.002 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **4** (ω = 2.967 eV) indicates that it is the stronger electrophiles than all compounds. Compound **4** 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.

LOCAL REACTIVITY DESCRIPTORS: The fukui function [29,30] was one of the most fundamental and widespread reactivity descriptors in Density-Functional Theory (DFT) [31-34]. This function is defined as the derivative of electron density, ρ(r), with respect to total number of electrons of the system, *N*, under a constant external potential, υ(r),

$$\rho(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{\upsilon(r)}$$

The Fukui function indicates the propensity of the electronic density to deform at a given position upon accepting or donating electrons [35,36]. Three types of Fukui function for a system, namely f^+_k for nucleophilic attack, f_k for electrophilic attack and f^0_k for radical attack that were defined as follows:

$$f^+ = [q(N+1) - q(N)]\text{, for nucleophilic attack,}$$

$$f^- = [q(N) - q(N-1)]\text{, for electrophilic attack,}$$

$$f^0 = [q(N+1) - q(N-1)]/2\text{, for radical attack.}$$

Where q_k is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the kth 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. 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	7S	8S	10S	9S	**Atom**	9S	7S	8S	10S
f^+	0.122	0.122	0.117	0.117	f^+	0.111	0.111	0.110	0.109
Atom	13C	4C	1C	6C	**Atom**	13C	4C	1C	6C
f^-	0.046	0.033	0.010	0.000	f^-	0.031	0.028	0.013	0.000

Atom	13C	4C	1C	6C	Atom	13C	15C	4C	16C
f^0	0.007	0.001	0.000	-0.001	f^0	0.002	0.002	-0.001	-0.002

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

Compound 3				Compound 4			
Atom	9S	10S	36Se	8S	**Atom**	12S	11S	18S	17S
f^+	0.106	0.105	0.105	0.104	f^+	0.109	0.109	0.106	0.106
Atom	13C	4C	1C	14C	**Atom**	13C	4C	16C	15 C
f^-	0.033	0.030	0.010	0.001	f^-	0.039	0.032	0.004	0.004
Atom	15C	13C	4C	1C	**Atom**	13C	16C	15C	4C
f^0	0.012	0.005	0.000	-0.005	f^0	0.004	0.002	0.002	0.002

From the tables 6-7, the parameters of local reactivity descriptors show that 9S is the more reactive site in compounds **2** and **3** and 7S, 12S are the more reactive sites in compounds **1** and **4** respectively for nucleophilic attacks. The more reactive sites in radical attacks are 13C forcompounds **1**, **2** and **4** and 15C for compound **3**. The more reactive sites for electrophilic attacks are 13C for all compounds.

NATURAL BOND ORBITAL ANALYSIS (NBO): Natural bond orbital analysis transforms molecular orbital wave functions into one-center (lone pair) and two-center (bond) representations [37]. The advantage of NBO analyses is that they provide insight into the interactions between various parts of the molecules [38]. The bond-antibond and lone-pair-antibond interactions can be calculated by two difference procedures following the NBO method [39]. The first one is an indirect procedure as suggested by Weinhold, which involves comparison of barrier energies calculated with and without the Fock matrix element (F ij) [40]. The second procedure involves the estimations of all possible interactions between ''filled'' (donor) Lewis type NBOs and ''empty'' (acceptor) non-Lewis NBOs, by considering their energetic importance using second order perturbation theory. Since these interactions lead to the donation of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals, they are referred to as ''delocalization'' corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor (j), the stabilization energy E(2) associated with delocalization i - j is represented as:

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

Where q_i is the donor orbital occupancy, F ij is the off-diagonal and ε_i, ε_j are diagonal elements specifying the respective orbital energies of the NBO Fock matrix. NBO analysis has been performed on TTP derivatives **1-4** at the B3LYP/6-31G(d,p) level in order to elucidate the delocalization of electron density within the molecules. The second order perturbation theory of Fock-matrix in the NBO analysis shows intramolecular hyper conjugative interactions, which are presented in Tables 8-11.

Table 8.Second order perturbation theory analysis ofFock 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) O21	1.86762	π*(C2-C3)	0.35060	27.42	0.33	0.090
LP (2) O22	1.86762	π*(C2-C3)	0.35060	27.42	0.33	0.090
LP (2) S19	1.78018	π*(C15-C16)	0.21629	22.32	0.26	0.067
LP (2) S20	1.78018	π*(C15-C16)	0.21629	22.32	0.26	0.067
LP (2) S9	1.80123	π*(C5-C6)	0.38045	21.20	0.24	0.066
LP (2) S10	1.80123	π*(C5-C6)	0.38045	21.20	0.24	0.066
LP (2) S11	1.80236	π*(C5-C6)	0.38045	21.16	0.24	0.066
LP (2) S12	1.80236	π*(C5-C6)	0.38045	21.16	0.24	0.066
LP (2) S19	1.78018	π*(C13-C14)	0.41772	20.37	0.24	0.065
LP (2) S20	1.78018	π*(C13-C14)	0.41772	20.37	0.24	0.065
LP (2) S 7	1.81054	π*(C1-C4)	0.41767	19.86	0.24	0.065
LP (2) S8	1.81054	π*(C1-C4)	0.41767	19.86	0.24	0.065
LP (2) S7	1.81054	π*(C2-C3)	0.35060	19.45	0.26	0.066

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) S8	1.81054	π*(C2-C3)	0.35060	19.45	0.26	0.066
LP (2) S9	1.80123	π*(C1-C4)	0.41767	18.87	0.24	0.064
LP (2) S10	1.80123	π*(C1-C4)	0.41767	18.87	0.24	0.064
LP (2) S11	1.80236	π*(C13-C14)	0.41772	18.73	0.24	0.063
LP (1) O21	1.96108	σ*(C2-C3)	0.03451	6.04	1.19	0.076
LP (2) O21	1.86762	σ*(C23-H25)	0.02320	6.04	0.75	0.062
LP (1) O22	1.96108	σ*(C2-C3)	0.03451	6.04	1.19	0.076

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) O20	1.86637	π*(C2-C3)	0.34804	28.56	0.33	0.092
LP (2) O19	1.86712	π*(C2-C3)	0.34804	25.65	0.33	0.087
LP (2) S18	1.76736	π*(C15-C16)	0.30744	21.76	0.23	0.065
LP (2) S17	1.77665	π*(C15-C16)	0.30744	20.41	0.24	0.063
LP (2) S12	1.79816	π*(C5-C6)	0.37159	20.25	0.24	0.065
LP (2) S10	1.80050	π*(C5-C6)	0.37159	20.20	0.24	0.065
LP (2) S9	1.80084	π*(C5-C6)	0.37159	20.17	0.24	0.065
LP (2) S11	1.79904	π*(C5-C6)	0.37159	20.16	0.24	0.065
LP (2) S7	1.80361	π*(C2-C3)	0.34804	19.13	0.26	0.065
LP (2) S8	1.80385	π*(C2-C3)	0.34804	19.12	0.26	0.065
LP (2) S8	1.80385	π*(C1-C4)	0.37798	15.90	0.26	0.060
LP (2) S7	1.80361	π*(C1-C4)	0.37798	15.83	0.26	0.060
LP (2) S18	1.76736	π*(C13-C14)	0.37075	15.16	0.26	0.058
LP (2) S17	1.77665	π*(C13-C14)	0.37075	14.93	0.26	0.058
LP (2) S12	1.79816	π*(C13-C14)	0.37075	13.28	0.26	0.055
LP (2) S11	1.79904	π*(C13-C14)	0.37075	13.27	0.26	0.055
LP (2) S10	1.80050	π*(C1-C 4)	0.37798	13.05	0.26	0.054
LP (2) S9	1.80084	π*(C1-C4)	0.37798	13.03	0.26	0.054
LP (2) S28	1.89688	σ*(C15-S18)	0.05114	6.44	0.42	0.047
LP (1) O20	1.96081	σ*(C2-C3)	0.03537	6.25	1.18	0.077

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) O19	1.86635	π*(C2-C3)	0.34802	28.59	0.33	0.092
LP (2) O20	1.86724	π*(C2-C3)	0.34802	25.59	0.33	0.087
LP (2) S17	1.76513	π*(C15-C16)	0.29752	22.46	0.24	0.067
LP (2) S18	1.77315	π*(C15-C16)	0.29752	21.41	0.24	0.065
LP (2) S9	1.80040	π*(C5-C6)	0.37115	20.19	0.24	0.065
LP (2) S10	1.80066	π*(C5-C6)	0.37115	20.17	0.24	0.065
LP (2) S11	1.80236	π*(C5-C6)	0.37115	20.11	0.24	0.064
LP (2) S12	1.80321	π*(C5-C6)	0.37115	20.05	0.24	0.064
LP (2) S7	1.80414	π*(C2-C3)	0.34802	19.13	0.26	0.065
LP (2) S8	1.80389	π*(C2-C3)	0.34802	19.13	0.26	0.065
LP (2) S17	1.76513	π*(C13-C14)	0.37248	16.59	0.26	0.061
LP (2) S18	1.77315	π*(C13-C14)	0.37248	15.90	0.26	0.060
LP (2) S7	1.80414	π*(C1-C4)	0.37815	15.86	0.26	0.060
LP (2) S8	1.80389	π*(C1-C4)	0.37815	15.79	0.26	0.060
LP (2) S9	1.80040	π*(C1-C4)	0.37815	13.10	0.26	0.054
LP (2) S10	1.80066	π*(C1-C4)	0.37815	13.07	0.26	0.054
LP (2) S11	1.80236	π*(C13-C14)	0.37248	12.54	0.26	0.054
LP (2) S12	1.80321	π*(C13-C14)	0.37248	12.52	0.26	0.054
LP (1) O19	1.96081	σ*(C2-C3)	0.03537	6.25	1.18	0.077

| LP (2) O19 | 1.86635 | $\sigma*$(C21-H23) | 0.02309 | 6.09 | 0.75 | 0.062 |

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) O19	1.86760	$\pi*$(C2-C3)	0.35072	27.42	0.33	0.090
LP (2) O20	1.86760	$\pi*$(C2-C3)	0.35072	27.42	0.33	0.090
LP (2) S9	1.80110	$\pi*$(C5-C6)	0.38097	21.23	0.24	0.066
LP (2) S10	1.80110	$\pi*$(C5-C6)	0.38097	21.23	0.24	0.066
LP (2) S11	1.80142	$\pi*$(C5-C6)	0.38097	21.19	0.24	0.066
LP (2) S12	1.80142	$\pi*$(C5-C6)	0.38097	21.19	0.24	0.066
LP (2) S17	1.79862	$\pi*$(C13-C14)	0.41749	20.51	0.24	0.066
LP (2) S18	1.79862	$\pi*$(C13-C14)	0.41749	20.51	0.24	0.066
LP (2) S28	1.86814	$\pi*$(C15-C16)	0.37347	20.26	0.24	0.066
LP (2) S27	1.86814	$\pi*$(C15-C16)	0.37347	20.25	0.24	0.066
LP (2) S7	1.81040	$\pi*$(C1-C4)	0.41774	19.87	0.23	0.065
LP (2) S8	1.81040	$\pi*$(C1-C4)	0.41774	19.87	0.23	0.065
LP (2) S17	1.79862	$\pi*$(C15-C16)	0.37347	19.77	0.24	0.064
LP (2) S18	1.79862	$\pi*$(C15-C16)	0.37347	19.77	0.24	0.064
LP (2) S7	1.81040	$\pi*$(C2-C3)	0.35072	19.47	0.26	0.066
LP (2) S8	1.81040	$\pi*$(C2-C3)	0.35072	19.47	0.26	0.066
LP (2) S9	1.80110	$\pi*$(C1-C4)	0.41774	18.87	0.24	0.064
LP (2) S10	1.80110	$\pi*$(C1-C4)	0.41774	18.87	0.24	0.064
LP (2) S11	1.80142	$\pi*$(C13-C14)	0.41749	18.86	0.24	0.064
LP (2) S12	1.80142	$\pi*$(C13-C14)	0.41749	18.86	0.24	0.064

The intra molecular interaction for the title compounds is formed by the orbital overlap between: LP (2) O21 orbital to the $\pi*$(C2-C3) for compound **1**, LP (2) O20 orbital to $\pi*$(C2-C3) for compound **2**, LP (2) O19 orbital to $\pi*$(C2-C3) for compound **3**,LP (2) O19 orbital to $\pi*$(C2-C3) for compound **4** respectively, show the stabilization energy of 27.42, 28.56, 28.59 and 27.42 kJ mol^{-1} respectively.

NONLINEAR OPTICAL PROPERTIES (NLO): Non-linear optical effects arise from the interactions of electromagnetic fields in various media to produce a new field altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [41]. NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in the areas such as telecommunications, signal processing, and optical interconnections [42-45]. The non-linear optical response of an isolated molecule in an electric field $E_i(x)$ can be represented by a Taylor series expansion of the total dipole moment, μ_{tot}; induced by the field:

$$\mu_{tot} = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \dots$$

Where α is the linear polarizability, $\mu_0$the permanent dipole moment and β_{ijk} are the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability is defined as [46]:

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

First hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrix. The 27 components of 3D matrix can be reduced to 10 components due to the Kleinman symmetry [47] $\beta_{xyy} = \beta_{yxy} = \beta_{yyx} = \beta_{yyx} = \beta_{yyx} = \beta_{yyx}; \dots$ likewise other permutations can also take same value). The output from the Gaussian 09 provides 10 components of this matrix as $\beta_{xxx}; \beta_{xxy}; \beta_{xyy}; \beta_{yyy}; \beta_{xxz}; \beta_{xyz}; \beta_{yyz}; \beta_{xzz}; \beta_{yzz}; \beta_{zzz}$ respectively. The components of the first hyperpolarizability can be calculated using the following equation [46]:

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{iij} + \beta_{jjj} + \beta_{jji})$$

Using the x, y and z components of b, the magnitude of the first hyperpolarizability tensor can be calculated by:

$$\beta_{tot} = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)}$$

The complete equation for calculating the magnitude of b from the Gaussian 09W output is given as follows:

$$\beta_{tot} = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2}$$

The calculations of the total molecular dipole moment (μ), linear polarizability (α) and first-order hyperpolarizability (β) from the Gaussian output were explained in detail previously [48], and DFT has been extensively used as an effective method to investigate the organic NLO materials [49].Table 12 shows the calculated values of μ_{tot}, α_{tot} and β_{tot} for the title compounds.

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}	165.6023	-371.5984	450.1582	-160.5723
B_{yyy}	-0.0010	0.0006	25.7716	-0.0005
B_{zzz}	0.0023	0.0059	-0.5802	0.0041
B_{xyy}	-14.8030	9.9891	-213.4133	-16.2825
B_{xxy}	-0.0095	0.0240	19.1999	-0.0135
B_{xxz}	0.0531	0.0487	75.0108	0.0071
B_{xzz}	40.3795	1.8141	-117.1265	-25.6732
B_{yzz}	-0.0002	-0.0061	-6.9312	-0.0010
B_{yyz}	0.0014	0.0048	9.7075	-0.0009
B_{xyz}	5.9548	-28.3802	24.5828	1.3657
B_{tot}(esu)x10^{-33}	215.7496	398.1645	369.3432	184.8798
μ_x	1.4787	-0.7858	1.9077	-0.1609
μ_y	-0.0001	0.0000	1.1526	-0.0001
μ_z	0.0006	0.0009	1.5723	-0.0001
μ_{tot}(D)	1.4787	0.7858	2.7276	0.1609
α_{xx}	-97.6771	-117.1205	-143.7035	-100.8221
α_{yy}	-184.9569	-226.6368	-225.5054	-227.6363
α_{zz}	-187.5392	-222.5482	-234.3209	-224.6472
α_{xy}	-0.0008	0.0020	-4.9816	0.0007
α_{xz}	-0.0063	0.0044	-8.9445	0.0010
α_{yz}	0.7233	-5.3333	-2.1036	-1.2740
α(esu)x10^{-24}	88.6080	107.9263	88.4201	125.3658
$\Delta\alpha$(esu)x10^{-24}	13.1317	15.9946	13.1038	18.5792

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 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) for the title compounds were found to be 1.4787, 0.7858, 2.7276 and 0.1609 D respectively, which are approximately two 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 88.6080 x 10^{-24}, 107.9263 x 10^{-24}, 88.4201 x 10^{-24} and 125.3658 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 13.1317, 15.9946, 13.1038 and 18.5792 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 215.7496 x 10^{-33}, 398.1645 x 10^{-33}, 369.3432 x 10^{-33} and 184.8798 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.63, 1.15, 1.08 and 0.54 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 TTP derivatives **1-4** might have the NLO applications for compounds **2** and **3**.

IV. CONCLUSION

In this Letter, through computational study based on density functional theory (DFT) methods, we report predictions of the electrophilic and nucleophilic centers, the optimized geometric parameters and different behaviors for TTP derivatives compounds. The HOMO and LUMO analysis are used to determine the charge transfer within the molecules

and the HOMO-LUMO energy gap shows the chemical activity of the molecules.The stability of the molecules arising from hyper-conjugative interaction and charge delocalization has been studied using NBO analysis. The chemical reactivity is understood from chemical potential, electrophilicity and global hardness. MEP predicts the most reactive part in the molecules.

V. ACKNOWLEDGMENTS

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