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Theoretical investigation of series of diazafluorene-functionalized TTFs by using density functional method

Tahar Abbaz[1*], Amel Bendjeddou[1], Didier Villemin[2]

[1]Laboratory of Aquatic and Terrestrial Ecosystems. Org. and Bioorg. Chem. Group, University of Mohamed-Cherif Messaadia, Souk Ahras, 41000, Algeria
[2]Laboratory of Molecular and Thio-Organic Chemistry, UMR CNRS 6507, INC3M, FR 3038, Labex EMC3, ensicaen & University of Caen, Caen 14050, France

***Abstract*— *Quantum chemical calculations of energies, geometrical structure and electronic parameters of diazafluorene-functionalized TTFs* **1-4** *were carried out by using density functional (DFT/B3LYP) method with 6-31G(d,p) as basis set. Stability of the molecule arising from hyper conjugative interactions, charge delocalization has been analyzed using natural bond orbital (NBO) analysis. The calculated HOMO and LUMO energies show that chemical activity of the molecule. The local reactivity descriptor analysis is performed to find the reactive sites within molecule.*

Keywords*—** Computational ***chemistry, Density functional theory, Electronic structure, Quantum chemical calculations

I. INTRODUCTION

The chemistry of heterocyclic compounds has a key role in the discovery of new drugs. This study field have gathered great attention over the past years, and a number of paper constructed by experimental techniques and theoretical methods have appeared in the literature. Various compounds such as alkaloids, essential amino acids, vitamins, hemoglobin, hormones, large number of synthetic drugs and dyes contain heterocyclic ring systems. There are large numbers of synthetic heterocyclic compounds, like pyrimidine, pyridine, pyrrole, pyrrolidine, diazafluorene, furan and thiophene. Heterocyclic compounds exhibits wide range of synthetic and biological activities, especially nitrogen and sulfur containing heterocyclic moieties were found to be vital for a number of biologically active compounds [1]. Density functional theory (DFT) has become the dominant tool in chemistry and physics for calculations of electronic structure as it demands less time for inclusion of electron correlation. Detailed analysis on the applicability of different methods of DFT has been performed, particularly for equilibrium structure properties of geometry, vibrational frequency, etc [2]. The general conclusion from these studies was that DFT methods, particularly with the use of nonlocal exchange-correlation functions, can predict accurate equilibrium structure properties. NBOs provide an accurate method for studying intramolecular interactions and give an efficient basis to investigate charge transfer or conjugative interaction in various molecular systems [3]. Molecular electrostatic potential (MEP) is used to map and understand the dimeric sites within the molecules. MEP is very much required for predicting structure–activity relationship and drug–receptor interactions of biomolecules.

The present work aims to investigate the molecular structure, electronic and non-linear optical properties of series of diazafluorene-functionalized TTFs **1-4** described in literature [4] and to predict their activities, we give a global study of the molecular geometry, natural bond orbital (NBO) analysis, nonlinear optical (NLO) properties, and chemical reactivity as HOMO-LUMO energy gap, chemical hardness, chemical potential and local reactivity descriptors.

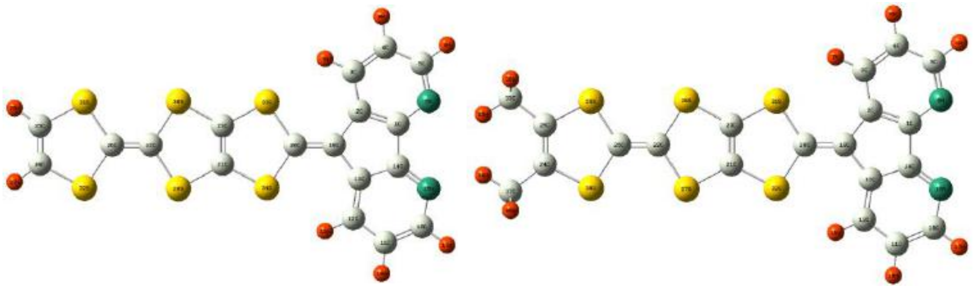
II. MATERIALS AND METHODS

All parameters and properties of diazafluorene-functionalized TTFs **1-4** were calculated using the Gaussian 09 software package on a personal computer [5]. The computations were performed at B3LYP/6-31G(d,p) level of theory to get the optimized geometries shown in Fig 1 of the title compound. DFT calculations were carried out with Becke’s three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method.

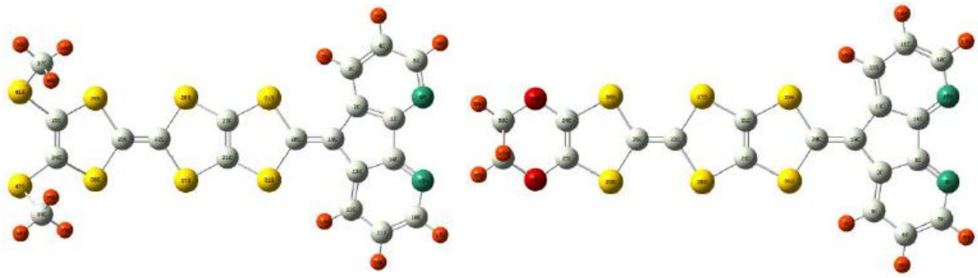
III. RESULTS AND DISCUSSION

3.1. Molecular Geometry

The molecular structure along with numbering of atoms of diazafluorene-functionalized TTFs molecules are as shown in Fig 1.The calculated global minimum energy of diazafluorene-functionalized TTFs **1-4** in C1 point group symmetries are between -3189.3021and -4064.3090 a.u. by 6-31G(d,p) basis set. The optimized bond lengths, bond angles and dihedral angles of the title compound which calculated using B3LYP method are with 6-31G(d,p) basis set are shown in Tables 1-4.



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



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

Fig.1: Optimized molecular structure of diazafluorene-functionalized TTFs 1-4

Table.1: Optimized geometric parameters of compound 1

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(25,28)	1.082	A(27,24,32)	117.002	D(6,1,2,19)	179.999
R(24,25)	1.336	A(24,25,28)	124.925	D(1,2,3,7)	179.999
R(25,31)	1.762	A(24,32,26)	94.977	D(16,12,13,14)	179.999
R(26,31)	1.786	A(22,26,32)	123.049	D(2,19,20,34)	179.998
R(22,26)	1.349	A(29,22,30)	115.248	D(13,19,20,33)	179.999
R(22,30)	1.795	A(21,34,20)	95.537	D(33,23,30,20)	179.999
R(5,9)	1.088	A(15,10,17)	116.124	D(27,24,25,31)	180.000
R(1,2)	1.421	A(2,3,7)	122.964	D(22,26,31,25)	179.999
R(5,6)	1.340	A(3,4,8)	120.291	D(6,1,2,3)	53.175
R(3,4)	1.396	A(2,1,6)	125.556	D(6,1,14,15)	64.203
R(21,34)	1.757	A(1,14,15)	126.229	D(23,21,29,22)	47.100
R(13,19)	1.476	A(12,13,19)	134.005	D(29,22,30,23)	59.001
R(14,15)	1.330	A(1,2,19)	108.848	D(24,25,31,26)	96.023
R(19,20)	1.366	A(33,20,34)	113.311	D(31,26,32,24)	83.000
R(2,3)	1.397	A(11,12,16)	119.169	D(27,24,32,26)	179.999

Table.2: Optimized geometric parameters of compound 2

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,2)	1.421	A(5,4,8)	119.949	D(6,1,2,19)	179.999
R(1,14)	1.467	A(2,1,6)	125.559	D(1,2,3,7)	179.998
R(5,6)	1.340	A(1,2,19)	108.858	D(3,2,19,13)	179.998
R(5,9)	1.088	A(3,2,19)	134.004	D(1,2,19,20)	180.000
R(4,8)	1.085	A(2,19,13)	105.870	D(9,5,6,1)	179.999
R(2,19)	1.476	A(10,15,14)	115.917	D(1,14,15,10)	179.999
R(19,20)	1.366	A(1,14,15)	126.234	D(2,19,20,32)	179.993
R(20,31)	1.784	A(31,20,32)	113.288	D(13,19,20,31)	179.993

R(21,23)	1.342	A(23,21,27)	118.675	D(19,20,31,23)	179.999
R(22,26)	1.349	A(26,22,27)	122.380	D(32,21,23,28)	179.998
R(24,37)	1.502	A(25,24,30)	117.158	D(32,21,27,22)	179.998
R(33,34)	1.095	A(28,25,33)	127.158	D(27,21,32,20)	179.999
R(33,35)	1.090	A(22,26,29)	123.302	D(28,22,27,21)	70.003
R(26,29)	1.777	A(25,33,35)	111.269	D(25,24,37,39)	120.247
R(25,29)	1.781	A(38,37,39)	107.930	D(30,24,37,40)	59.752

Table.3: Optimized geometric parameters of compound 3

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(5,9)	1.088	A(4,5,9)	120.126	D(39,37,41,25)	178.120
R(4,5)	1.397	A(5,4,8)	119.932	D(22,26,30,24)	160.466
R(5,6)	1.339	A(2,3,4)	117.870	D(24,,25,41,37)	123.928
R(1,2)	1.421	A(3,2,19)	133.998	D(41,25,29,26)	173.253
R(1,14)	1.467	A(2,19,20)	127.075	D(30,24,25,41)	172.808
R(19,20)	1.366	A(1,14,13)	108.225	D(26,22,28,23)	161.774
R(20,31)	1.785	A(19,20,31)	123.408	D(28,22,26,30)	177.695
R(23,31)	1.756	A(31,20,32)	113.157	D(27,21,32,20)	174.248
R(21,23)	1.342	A(27,22,28)	114.204	D(32,21,27,22)	170.939
R(23,28)	1.769	A(38,37,40)	110.352	D(32,21,23,28)	176.999
R(22,28)	1.791	A(27,21,32)	124.071	D(13,19,20,31)	178.998
R(22,26)	1.349	A(26,22,27)	122.881	D(12,13,14,1)	179.869
R(25,29)	1.789	A(25,24,42)	125.702	D(6,1,2,19)	179.912
R(24,25)	1.355	A(34,33,42)	105.492	D(9,5,6,1)	179.994
R(33,42)	1.837	A(29,26,30)	112.357	D(10,11,12,16)	179.972

Table.4: Optimized geometric parameters of compound 4

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(4,5)	1.397	A(3,4,5)	119.751	D(6,1,2,19)	179.973
R(4,8)	1.085	A(4,5,6)	123.760	D(14,1,6,5)	179.984
R(19,20)	1.366	A(6,1,14)	126.235	D(2,3,4,8)	179.996
R(2,19)	1.476	A(1,2,19)	108.855	D(9,5,6,1)	180.000
R(19,20)	1.366	A(10,15,14)	115.920	D(2,19,20,32)	179.887
R(20,31)	1.784	A(2,19,13)	105.854	D(27,21,32;20)	179.978
R(23,31)	1.757	A(2,19,20)	127.073	D(27,22,26,29)	179.745
R(21,23)	1.342	A(19,20,31)	123.349	D(30,24,34,38)	164.277
R(23,28)	1.763	A(31,20,32)	113.303	D(29,25,33,35)	164.251
R(26,29)	1.788	A(28,23,31)	123.555	D(25,33,35,36)	165.327
R(25,29)	1.771	A(22,28,23)	93.722	D(25,33,35,38)	44.664
R(33,35)	1.436	A(27,22,28)	115.268	D(24,34,38,39)	165.316
R(35,36)	1.091	A(21,23,28)	118.643	D(33,35,38,40)	58.105
R(35,38)	1.528	A(29,25,33)	116.933	D(37,35,38,40)	178.864
R(38,40)	1.097	A(33,35,36)	106.298	D(36,35,38,39)	61.869

3.2. Molecular Electrostatic Potential (MEP)

The MEP is related to the electronic density and is a very useful descriptor for determining the sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [6]. 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 [7,8]. For the system studied the V(r) values were calculated as described previously using the equation [9].

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

The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the ordered (most negative) < orange < yellow < green < blue (most positive). To predict reactive sites of 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 the positive (blue) regions to nucleophilic reactivity, as shown in Fig 2. As can be seen from the figure, this molecule has several possible sites for electrophilic and nucleophilic attacks.

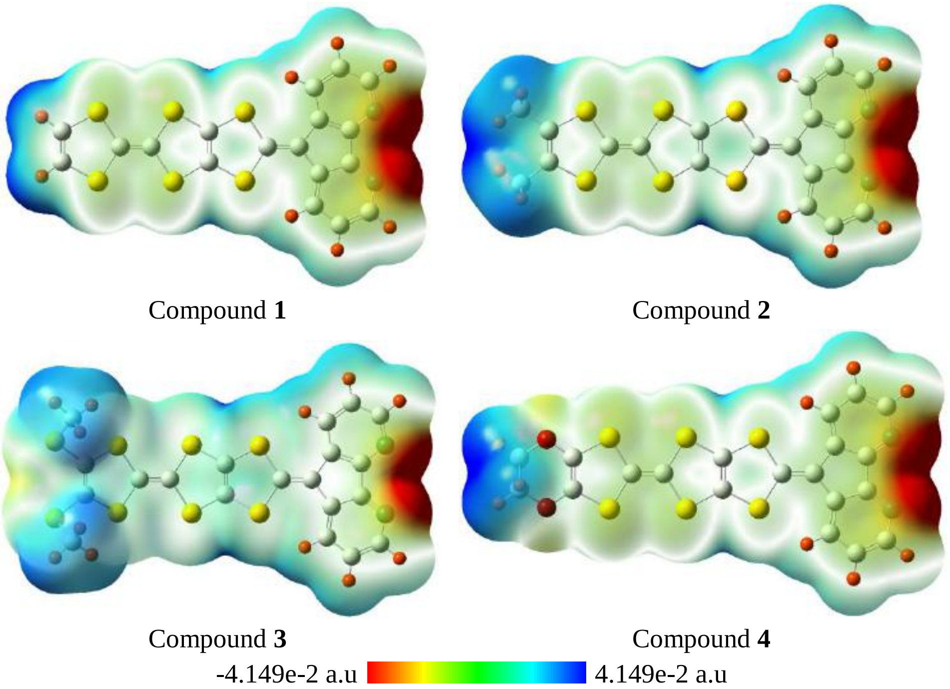


Fig.2: Molecular electrostatic potential surface of diazafluorene-functionalized TTFs 1-4

According to these calculated results, the MEP map shows that in all molecules, the regions exhibiting the negative electrostatic potential are localized near the nitrogen atoms while the regions presenting the positive potential are localized vicinity of the hydrogen atoms of alkyl and cycled groups. These sites give information about the region from where the compound can have intermolecular interactions.

3.3. Frontier Molecular Orbitals (FMOs)

Frontier molecular orbitals i.e. the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very popular quantum chemical parameters. They determine the molecular reactivity and light absorption ability. The vicinal orbitals of HOMO and LUMO play the role of electron donor and electron acceptor, respectively. The HOMO-LUMO energy gap (ΔE_{gap}) is an important stability index. The conjugated molecules are characterized by HOMO-LUMO separation, which is the result of a significant degree of intramolecular charge transfer (ICT) from the end-capping electron donor groups to the efficient electron-acceptor groups through π-conjugated path. Therefore, an electron density (ED) transfer occurs from the aromatic part of the π-conjugated system in the electron donor side to its electron-withdrawing part [10]. The HOMO-LUMO energy gap that reflects the chemical reactivity of the molecule, calculated at B3LYP/6-31G(d,p) level. The HOMO- LUMO plots of compound **4** are given in Figure 3. According to Figure 3, the positive phase is shown as green color region whereas the negative one is provided as red color region. Table 5 illustrates the change of $\Delta E_{LUMO\ -\ HOMO}$ (E_{gap}) energy gap value of title compound.

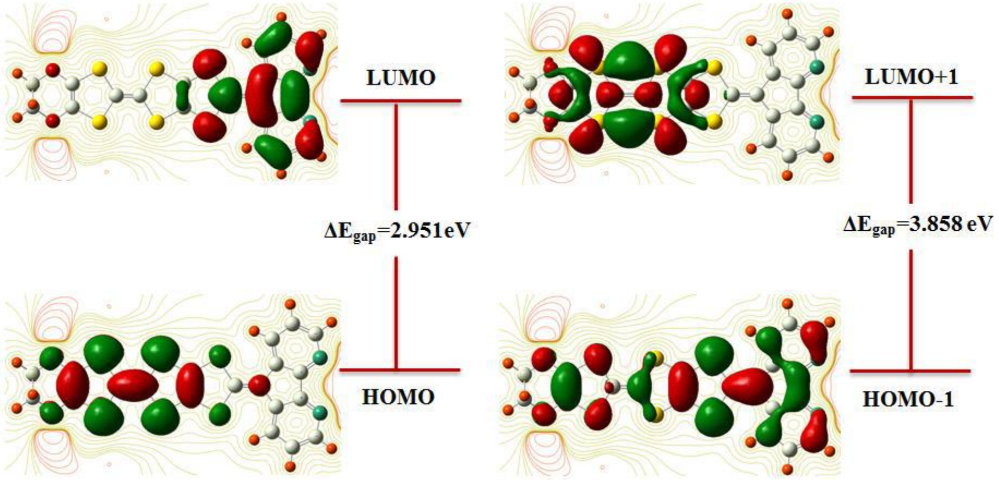


Fig.3: HOMO-LUMO Structure with the energy level diagram of compound 4

3.4. Global Reactivity Descriptors

By using HOMO and LUMO energy values of a molecule, the global chemical reactivity descriptor of molecules such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined [11-15]. The HOMO and LUMO energies, the energy gap (ΔE), ionization potential (I), electron affinity (A), absolute electronegativity (χ) absolute hardness (η) and softness (*S*) of the diazafluorene-functionalized TTFs **1-4** molecules have been computed by DFT/B3LYP/6-31G(d,p) method are listed in Table 5. The chemical potential [13] provide a global reactivity index and related to charge transfer from a system of higher chemical potential to lower chemical potential. The reactivity index is the measure of stabilization in energy when the system acquires an additional electronic charge (ΔN). A molecule or atom that has a positive electron affinity is often called an electron acceptor and may undergo charge transfer reactions. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital. The overall energy balance (ΔE), i.e., energy gained or lost, in an electron donor-acceptor transfer is determined by the difference between the acceptor's electron affinity (EA) and the ionization potential (IP) as ΔE=EA-IP. Electronegativity is a chemical property that describes the ability of an atom or a functional group to attract electrons or electron density towards itself. Parr et al. [13, 14] have defined a new descriptor to quantity the global electrophilic power of the compound as electrophilicity index (ω) which defines a quantitative classification of global electrophilic nature of a compound. Parr et al. [13, 14] have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. The usefulness of this new reactivity quantity has been recently demonstrated understanding the toxicity of various pollutants in terms of their reactivity and site selectivity. The electrophilicity index is positive, definite quantity and direction of the charge transfer is fully determined by the chemical potential (μ) of the molecule. Because an electrophile is a chemical species, it has an electron accepting capability from the environment and its energy must decrease upon accepting electronic charge, therefore, its electronic chemical potential must be negative. The chemical hardness [14-17] is the second derivative of the electronic energy with respect to the number of electrons for a constant external potential. Pauling introduced the concept of electronegativity as the power of an atom in a compound to attract electrons to it. Using Koopman's theorem for closed shell compounds the electronegativity and chemical hardness can be calculated as follow:

$$\chi = (E_{HOMO} - E_{LUMO})/2$$

$$\mu = -(IE + EA)/2 = (E_{N+1} - E_{N-1})/2 = -\chi$$

$$\eta = (IE - EA)/2 = (E_{N-1} - E_{N+1} - 2E_N)/2$$

$$S = 1/2\eta$$

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

Where I and A are ionization potential and electron affinity, I = E_{HOMO} and A = E_{LUMO} respectively as shown in Table 5. The large HOMO-LUMO gap means a hard molecule and small HOMO-LUMO gap means a soft molecule. One can also relate the stability of the molecule to hardness, which means that the molecule with least HOMO-LUMO gap means it is more reactive.

Table.5: Quantum chemical descriptors of diazafluorene-functionalized TTFs 1-4

Parameters	**Compound 1**	**Compound 2**	**Compound 3**	**Compound 4**
E_{HOMO} (eV)	-4.969	-4.846	-5.205	-4.837
E_{LUMO} (eV)	-1.900	-1.853	-1.929	-1.886
ΔE_{gap} (eV)	3.068	2.993	3.277	2.951
IE (eV)	4.969	4.846	5.205	4.837
A (eV)	1.900	1.853	1.929	1.886
μ (eV)	-3.435	-3.349	-3.567	-3.362
χ (eV)	3.435	3.349	3.569	3.362
η (eV)	1.534	1.496	1.638	1.475
S (eV)	0.326	0.334	0.305	0.339
ω (eV)	3.845	3.748	3.830	3.830

As presented in table 5, the compound which have the lowest energetic gap is the compound **4** (ΔE_{gap} = 2.951 eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **3** (ΔE_{gap} = 3.277 eV).The compound that has the highest HOMO energy is the compound **4** (E_{HOMO} - 4.837 eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **3** (E_{LUMO} = -1.929 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 = 4.837 eV), so that will be the better electron donor. Compound **3** has the largest value of the affinity (A = 1.929 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 = 1.475 eV, **S** = 0.339 eV) is lesser (greater) among all the molecules. Thus, compound **4** is found to be more reactive than all the compounds. Compound **3** possesses higher electronegativity value (χ = 3.569 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **1** (ω = 3.845 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.

3.5. Local Reactivity Descriptors

To describe the chemical reactivity of an atom in a molecule, it is necessary to obtain the values of condensed Fukui function (FF) around each atomic site. Thus, for an atom k in a molecule, three kinds of condensed FF, namely, f_k^{+}, f_k^{-} and f_k° can be used to describe the electrophilic, nucleophilic and radical reactivity, respectively, which are defined by Eqs. (5)-(7) in a finite difference approximation [18]. The higher FF values indicate more reactivity of this atom than other ones.

For nucleophilic attack $f^{+} = \left[q(N+1) - q(N)\right]$

For electrophilic attack $f^{-} = \left[q(N) - q(N-1)\right]$

For radical attack $f^{0} = \left[q(N+1) - q(N-1)\right]/2$

where, q is the gross charge of atom k in the molecule and N, N+1, N-1 are electron systems containing neutral, anion, cation form of molecule respectively. Where +, -, 0 signs show nucleophilic, electrophilic and radical attack respectively. Fukui functions for selected atomic sites in diazafluorene-functionalized TTFs **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	23 C	21 C	22 C	26 C	**Atom**	21 C	23 C	22 C	24 C
f^{+}	0.030	0.030	0.022	-0.003	**f^{+}**	0.026	0.026	0.025	0.003
Atom	14 C	1 C	19 C	2 C	**Atom**	1 C	2 C	20 C	22 C
f^{-}	0.143	0.143	0.103	0.091	**f^{-}**	0.143	0.091	0.029	0.010
Atom	14 C	1 C	19 C	2 C	**Atom**	1 C	2 C	22 C	21 C
f^{0}	0.059	0.059	0.048	0.029	**f^{0}**	0.059	0.029	0.017	0.013

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

Compound 3					**Compound 4**				
Atom	15 N	6 N	20 C	22 C	**Atom**	21 C	22 C	23 C	34 O
f^+	0.248	0.248	0.205	0.085	f^+	0.034	0.030	0.019	-0.001
Atom	14 C	1 C	19 C	2 C	**Atom**	20 C	26 C	22 C	21 C
f^-	0.146	0.146	0.114	0.091	f^-	0.027	0.008	0.001	0.000
Atom	24 C	25 C	26 C	22 C	**Atom**	21 C	22 C	23 C	26 C
f^0	-0.007	-0.007	-0.009	-0.010	f^0	0.017	0.015	0.010	-0.001

From the tables 6-7, the parameters of local reactivity descriptors show that 21C is the more reactive site in compounds **2** and **4** and 23C, 15N are the more reactive sites in compounds **1** and **3** respectively for nucleophilic attacks. The more reactive sites in radical attacks are 14C, 1C, 24C and 21C for compounds **1**, **2**, **3** and **4** respectively. The more reactive sites for electrophilic attacks are 14C for compounds **1**, **3** and 1C, 20C for compounds **2** and **4** respectively.

3.6. Natural Bond Orbital Analysis (NBO)

Weak occupancies of the valence anti-bonds signal irreducible withdraw from an idealized localized Lewis structure which means true “delocalization effects” [19]. NBO analysis provides the most accurate possible natural Lewis structure picture of orbits because all the orbital details are mathematically selected to include the highest possible percentage of the electron density. The NBO method gives information about interactions in both completed and virtual orbital spaces that could improve the analysis of intra and inter-molecular interactions. In NBO analysis the donor-acceptor interactions are computed by carrying out the second order Fock matrix [20]. The interactions consequence is the loss of occupancy from the localized natural bond orbital of the idealized Lewis structure into a vacant non- Lewis orbital. For each donor (i) and acceptor (j) the stabilization energy $E_{(2)}$ related with the delocalization i - j is approximated as

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

Where F(i,j) is the off diagonal NBO Fock matrix element and qi is the donor orbital occupancy, 2j and 2i are diagonal elements. NBO analysis provides a suitable basis for investigating conjugative interaction or charge transfer in molecular systems. This is a powerful method for studying inter and intra molecular bonding and interaction among bonds. As a result of some electron donor orbital, acceptor orbital and the interacting stabilization energy, the second order micro disturbance theory is reported [21, 22]. If the values $E_{(2)}$ is larger, the interaction between electron donors and electron acceptors becomes more intensive i.e., the more donating propensity from electron donors to electron acceptors and larger the amount of conjugation of the whole molecular system. The stabilizing donor-acceptor interaction arises due to delocalization of electron density between occupied Lewis-type (lone pair or bond) and properly unoccupied (Rydberg or anti-bond) non Lewis NBO orbitals. NBO analysis has been performed on the diazafluorene-functionalized TTFs molecules at the B3LYP/6-31G (d,p) level for the sake of elucidate the re-hybridization, intramolecular and delocalization of electron density within the molecule.

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**
π(C5-N6)	1.70308	π*(C1-C2)	0.42259	27.22	0.32	0.085
π(C14-N15)	1.69674	π*(C10-C11)	0.31921	26.17	0.32	0.081
π(C3-C4)	1.65658	π*(C5-N6)	0.37754	26.13	0.27	0.076
π(C12-C13)	1.63552	π*(C14-N15)	0.39725	24.65	0.28	0.075
π(C1-C2)	1.55690	π*(C3-C4)	0.32855	22.56	0.27	0.072
π(C1-C2)	1.55690	π*(C19-C20)	0.35069	22.27	0.24	0.067
LP(2) S31	1.77785	π*(C24-C25)	0.21458	22.17	0.26	0.067
LP(2) S32	1.77785	π*(C24-C25)	0.21458	22.17	0.26	0.067
LP(2) S33	1.75038	π*(C21-C23)	0.38475	22.00	0.24	0.067
LP(2) S34	1.75038	π*(C21-C23)	0.38475	22.00	0.24	0.067
π(C10-C11)	1.63494	π*(C12-C13)	0.36158	21.99	0.28	0.070
LP(2) S29	1.80130	π*(C21-C23)	0.38475	21.68	0.23	0.066

LP(2) S30	1.80130	π*(C21-C23)	0.38475	21.68	0.23	0.066
LP(2) S31	1.77785	π*(C22-C26)	0.41752	20.82	0.24	0.066
LP(2) S32	1.55690	π*(C22-C26)	0.41752	20.82	0.24	0.066
π(C1-C2)	1.55690	π*(C14-N15)	0.39725	20.60	0.27	0.067
LP(2) S33	1.75038	π*(C19-C20)	0.35069	18.41	0.28	0.066
LP(2) S29	1.80130	π*(C22 -C26)	0.35069	18.31	0.24	0.063
π(C12-C13)	1.63552	π*(C10-C11)	0.31921	17.82	0.28	0.064
π(C1 – C2)	1.55690	π*(C5 –N6)	0.37754	17.75	0.26	0.062

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**
π(C10-N15)	1.70363	π*(C13-C14)	0.42287	27.16	0.32	0.085
π(C1-N6)	1.69685	π*(C4-C5)	0.31988	26.16	0.32	0.081
π(C11-C12)	1.65694	π*(C10-N15)	0.37798	26.12	0.27	0.076
π(C2-C3)	1.63513	π*(C1-N6)	0.39770	24.64	0.28	0.075
π(C13-C14)	1.55654	π*(C11-C12)	0.32870	22.55	0.27	0.072
π(C13-C14)	1.55654	π*(C19-C20)	0.35229	22.24	0.24	0.067
π(C4-C5)	1.63537	π*(C2-C3)	0.36172	21.96	0.28	0.070
LP(2) S31	1.74975	π*(C21-C23)	0.38500	21.91	0.24	0.067
LP(2) S29	1.79135	π*(C22-C26)	0.41598	21.53	0.23	0.067
π(C13-C14)	1.55654	π*(C1-N6)	0.39770	20.64	0.27	0.067
LP(2) S32	1.74975	π*(C19-C20)	0.35229	18.50	0.28	0.066
π(C2-C3)	1.63513	π*(C4-C5)	0.31988	17.86	0.28	0.064
π(C11-C12)	1.65694	π*(C13-C14)	0.42287	17.51	0.29	0.064
π(C4-C5)	1.63537	π*(C1-N6)	0.39770	16.08	0.28	0.060
π(C1-N6)	1.69685	π*(C2-C3)	0.36172	12.57	0.32	0.057
LP(1) N6	1.91890	σ*(C1-C2)	0.03865	11.92	0.87	0.092
LP(1) N15	1.91890	σ*(C13-C14)	0.03865	11.92	0.87	0.092
π(C19-C20)	1.84851	π*(C2-C3)	0.36172	11.00	0.33	0.057
π(C1-N6)	1.69685	π*(C13-C14)	0.42287	10.12	0.32	0.052
LP(1) N6	1.91890	σ*(C4-C5)	0.02577	9.66	0.90	0.084

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**
π(C10-N15)	1.70320	π*(C13-C14)	0.42225	27.21	0.32	0.085
π(C1-N6)	1.69642	π*(C4-C5)	0.31928	26.19	0.32	0.081
π(C11-C12)	1.65666	π*(C10-N15)	0.37712	26.13	0.27	0.076
π(C2-C3)	1.63540	π*(C1-N6)	0.39750	24.67	0.28	0.075
π(C13-C14)	1.55725	π*(C11-C12)	0.32827	22.55	0.27	0.072
π(C13-C14)	1.55725	π*(C19-C20)	0.34935	22.21	0.24	0.067
π(C4-C5)	1.63460	π*(C2-C3)	0.36154	22.01	0.28	0.070
LP(2) S31	1.74885	π*(C21-C23)	0.38033	21.79	0.24	0.067
LP(2) S32	1.74885	π*(C21-C23)	0.38033	21.79	0.24	0.067
LP(2) S27	1.79859	π*(C21-C23)	0.38033	20.84	0.23	0.065
LP(2) S28	1.79859	π*(C21-C23)	0.38033	20.84	0.23	0.065
π(C13-C14)	1.55725	π*(C1-N6)	0.39750	20.61	0.27	0.067
LP(2) S29	1.77996	π*(C24-C25)	0.31190	19.26	0.25	0.063
LP(2) S30	1.77996	π*(C24-C25)	0.31190	19.26	0.25	0.063
LP(2) S31	1.74885	π*(C19-C20)	0.34935	18.34	0.28	0.065
LP(2) S32	1.74885	π*(C19-C20)	0.34935	18.34	0.28	0.065

π(C13-C14)	1.55654	π*(C4-C5)	0.31928	17.81	0.28	0.064
π(C13-C14)	1.55654	π*(C10-N15)	0.37712	17.72	0.26	0.061
π(C11-C12)	1.65666	π*(C13-C14)	0.42225	17.52	0.29	0.064
π(C2-C3)	1.63540	π*(C19-C20)	0.34935	16.94	0.26	0.059

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) O33	1.86696	π*(C24-C25)	0.35091	27.62	0.33	0.090
LP(2) O34	1.86696	π*(C24-C25)	0.35091	27.62	0.33	0.090
π(C1-N6)	1.69649	π*(C4-C5)	0.31948	26.19	0.32	0.081
π(C14-N15)	1.69649	π*(C10-C11)	0.31948	26.19	0.32	0.081
π(C2-C3)	1.63530	π*(C1-N6)	0.39766	24.67	0.28	0.075
π(C12-C13)	1.63530	π*(C14-N15)	0.39766	24.67	0.28	0.075
LP(2) S31	1.75021	π*(C21-C23)	0.38546	22.01	0.24	0.067
LP(2) S32	1.75021	π*(C21-C23)	0.38546	22.01	0.24	0.067
π(C4-C5)	1.63473	π*(C2-C3)	0.36171	22.00	0.28	0.070
π(C10-C11)	1.63473	π*(C12-C13)	0.36171	22.00	0.28	0.070
LP(2) S27	1.80007	π*(C21-C23)	0.38546	21.75	0.23	0.067
LP(2) S28	1.80007	π*(C21-C23)	0.38546	21.75	0.23	0.067
LP(2) S29	1.80795	π*(C22-C26)	0.41778	20.33	0.23	0.065
LP(2) S30	1.80795	π*(C22-C26)	0.41778	20.33	0.23	0.065
LP(2) S29	1.80795	π*(C24-C25)	0.35091	19.39	0.26	0.066
LP(2) S30	1.80795	π*(C24-C25)	0.35091	19.39	0.26	0.066
LP(2) S27	1.80007	π*(C22-C26)	0.41778	18.44	0.24	0.063
LP(2) S28	1.80007	π*(C22-C26)	0.41778	18.44	0.24	0.063
LP(2) S31	1.75021	π*(C19-C20)	0.35079	18.42	0.28	0.066
LP(2) O33	1.86696	π*(C24-C25)	0.35091	27.62	0.33	0.090

The intra molecular interaction for the title compounds is formed by the orbital overl ap between: π(C5-N6) and π*(C1-C2) for compound **1**, π(C10-N15) and π*(C13-C14) for compound **2**, π(C10-N15) and π*(C13-C14) for compound **3** and π(C1-N6) and π*(C4-C5) for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π(C5-N6) to π*(C1-C2) for compound **1**, π(C10-N15) to π*(C13-C14) for compound **2**, π(C10-N15) to π*(C13-C14) for compound **3** and π(C1-N6) to π*(C4-C5) for compound **4** lead to highest stabilization of 27.22, 27.16, 27.21 and 26.19 kJ mol^{-1} respectively. In case of LP(2) S31orbital to the π*(C24-C25) for compound **1**, LP(2) S31 orbital to π*(C21-C23) for compound **2**, LP(2) S31orbital to π*(C21-C23) for compound **3,** LP(2) O33 orbital to π*(C24-C25) for compound **4** respectively, show the stabilization energy of 22.17, 21.91, 21.79 and 27.62 kJ mol^{-1} respectively.

3.7. Nonlinear Optical Properties (NLO)

The first hyperpolarizabilities (β_{total}) of this novel molecular system, and related properties (β, α_0 and α) of diazafluorene-functionalized TTFs molecules were calculated using B3LYP/6-31G(d,p) basis set, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field [23]. They determine not only the strength of molecular interactions (long-range inter induction, dispersion force, etc.) as well as the cross sections of different scattering and collision process and also the nonlinear optical properties (NLO) of the system [23, 24]. First hyperpolarizability is a third rank tensor that can be described by 3 × 3 × 3 matrix. The 27 components of the 3D matrix can be reduced to μ_0 components due to the Kleinman symmetry [24]. The components of first hyperpolarizability (β_{total}) are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external 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 molecules, F_α the field at the origin μ_α, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moments, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moments l, the mean polarizabilities α₀, the anisotropy of the polarizabilities Δα and the mean first hyperpolarizabilities β_{total}, using the x, y and z components they are defined as: [25, 26].

The total static dipole moment is

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

The isotropic polarizability is

$$\alpha = \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)/3$$

The polarizability anisotropy invariant is

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

and the average hyperpolarizability is

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

and

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

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

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

The total molecular dipole moment (μ), mean polarizability (α₀) and anisotropy polarizability (Δα) and first hyperpolarizability (β_{total}) of diazafluorene-functionalized TTFs 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 Δα (esu), and the first hyperpolarizability β (esu) of diazafluorene-functionalized TTFs 1-4 calculated by B3LYP/6-31G(d,p) method

Parameters	**Compound 1**	**Compound 2**	**Compound 3**	**Compound 4**
β_{xxx}	677.1939	-830.9894	-432.3042	1135.9456
B_{yyy}	0.0000	0.0006	0.0563	0.0015
B_{zzz}	0.0000	0.0013	22.0873	0.0097
B_{xyy}	-63.1921	62.7291	35.8198	-99.9727
B_{xxy}	-0.0001	-0.0045	0.1253	-0.0073
B_{xxz}	0.0026	0.0070	67.5898	0.0369
B_{xzz}	-4.4989	-8.8737	-61.1122	41.3088
B_{yzz}	0.0000	0.0000	-0.0078	0.0011
B_{yyz}	0.0004	0.0017	34.0753	0.0013
B_{xyz}	-0.0010	-0.0110	-0.0041	6.3277
B_{tot}**(esu)x10^{-33}**	672.694	839.8741	138.0195	1138.5821
μ_x	7.2251	-8.5208	-5.0318	8.5982
μ_y	0.0000	0.0000	0.0033	0.0000
μ_z	0.0000	0.0001	2.0817	0.0002
μ_{tot}**(D)**	7.2251	8.5208	5.4454	8.5982
α_{xx}	-186.9905	-195.8329	-274.7100	-198.0445
α_{yy}	-168.9288	-181.5590	-200.1455	-196.1587
α_{zz}	-196.7445	-209.0996	-228.7712	-217.0407
α_{xy}	0.0000	-0.0006	-0.0205	0.0019
α_{xz}	0.0006	-0.0028	-21.2170	0.0068
α_{yz}	0.0000	-0.0017	-0.0011	0.5477
α**(esu)x10^{-24}**	25.2388	23.8561	74.8018	20.0058
$\Delta\alpha$**(esu)x10^{-24}**	3.7403	3.5354	11.0856	2.9648

Since the values of the polarizabilities (Δα) 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 7.2251, 8.5208, 5.4454 and 8.5982 D respectively, which are approximately eight 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 25.2388 x 10^{-24}, 23.8561 x 10^{-24}, 74.8018 x 10^{-24} and 20.0058 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 3.7403, 3.5354, 11.0856 and 2.9648 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 diazafluorene-functionalized TTFs molecules are equal to 672.694 x 10^{-33}, 839.8741 x 10^{-33}, 138.0195 x 10^{-33} and 1138.5821 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 1.96, 2.45, 0.40 and 3.32 times than those of urea (β of urea is 343.272 x10^{-33} esu obtained by B3LYP/6-311G (d,p) method). This result indicates the non-linearity of the diazafluorene-functionalized TTFs **1-4**.

IV. CONCLUSION

The investigation of the present work is illuminate about computational study of series of diazafluorene-functionalized TTFs molecules by using (DFT/B3LYP) method with 6-31G(d,p) as basis set. The study of global reactivity descriptors confirmed that compound **4** has the smaller frontier orbital gap so; it is more polarizable and has a high chemical reactivity. The MEP map shows that the negative potential sites are on electronegative atoms (nitrogen atoms) while the positive potential sites are around the hydrogen atoms of alkyl and cycled groups. These sites give information about the region from where the compound can undergo non-covalent interactions. NBO analysis revealed that the π(C5-N6) → π*(C1-C2) interaction gives the strongest stabilization to the system. The predicted nonlinear optical (NLO) properties of the title compound are much greater than those of urea.

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