

# Effect of chlorine and bromine on the nonlinear optical, electronic, optoelectronic and thermodynamic properties on the BEDT-TTF molecule : Ab initio and DFT calculations

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## Research Article

**Keywords:** DFT, BEDT-TTF, hyperpolarizability, nonlinear optical properties, electronic properties, doping

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# Effect of chlorine and bromine on the nonlinear optical, electronic, optoelectronic and thermodynamic properties on the BEDT-TTF molecule : *Ab initio* and DFT calculations.

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## Abstract

In this study, the RHF and B3LYP methods with cc-pVDZ basis set have been used to investigate the non-linear optical (NLO), electronic, optoelectronic and thermodynamic properties of bis (ethylenedithio) tetrathiafulvalene and its chlorine and bromine derivatives. The results show that the undoped molecule denoted BEDT-TTF or ET ( $E_g=3.88$  eV) and its derivatives are semi-conductors materials. However, one of them, Br4ET molecule doped with bromine, considerably improves its energy band gap  $E_g=2.88$  eV is less than 3 eV, which makes more interesting electronic properties. Some parameters such as dipole moment, average polarizability and first order hyperpolarizability have been calculated. In order to compare the results of molecules and with those of Urea, we have computed first molecular hyperpolarizability  $\beta$ , doped structures (ET chlorinated and brominated) find applications in telecommunication, in modern communication technology and data storage as NLO active materials. Moreover, the chemical potential, ionization potential, electron affinity, electronegativity, global hardness, softness, refractive index, dielectric constant, electric field and electric susceptibility have also been determined. The results show that there is a good electronic transfer within the doped molecules and could have potential applications as semiconductor components, photovoltaic and photonic devices. Finally thermodynamic properties have been also computed.

**Keywords :** DFT ; BEDT-TTF, hyperpolarizability ; nonlinear optical properties ; electronic properties, doping

## Introduction

In the last few decades the design and synthesis of nonlinear optical (NLO), electronic and optoelectronic materials have been attracting great interest due to their wide applications in optical communication, optical computing, dynamic image processing, telecommunication, information storage, optical switching, photovoltaic, light emitting diode (LED), field effect transistor (FET) and other laser devices [1]. Research on designing new high-performance NLO materials is being an intriguing issue for scientist [1].

The discovery of bis (ethylenedithio) tetrathiafulvalene abbreviated as BEDT-TTF or simply ET in 1980 [2] (Fig 1), many other organic conductors have been synthesized and studied [3]. About 30 organic superconductors based on BEDT-TTF have been synthesized with  $T_c$  up to 12,8k [4]. In the previous study, detailed Infrared and Raman studies of BEDT-TTF have been reported by Kozlov et al [5], Eldridge et al [6] and Ruifeng et al [7]. These studies have contributed much to our knowledge of the vibrational spectra of these molecules. But the nonlinear optical, electronic, optoelectronic and thermodynamics properties are still not fully understood. In recent years, *ab initio* and the density functional theory (DFT) have become a powerful tool in the investigation of electronic structure, prediction of properties [8]. The goal of this research is to look for new materials which can have applications in electronic, non-linear optical and optoelectronic materials. In the present work, we have decided to investigate the semi-conductor nature of the molecule bis (ethylenedithio)tetrathiafulvalene and some of its derivatives by doping it with some atoms which may having application in quantum dots and other material. Our objectives are: to use *ab initio* and DFT quantum mechanical calculations to decipher the electronic structure, dipole moments, average polarizability, hyperpolarizabilities, first molecular hyperpolarizabilities, HOMO-LUMO molecular orbital diagram, HOMO-LUMO energy gap, susceptibility, refractive index, dielectric constant, electrical conductivity, Electron affinity, Ionization potential and Molar refractivity of bis(ethylenedithio)tetrathiafulvalene and its derivatives. So in this study, we report here *ab initio* and DFT calculations in the ground state using Hartree-Fock (HF) and B3LYP (Becke-3-Lee-Yang-Parr) methods with cc-pVDZ basis set.

This paper is organized as follow. In section 2, we present the calculation method. In section 3, the results and discussion are presented. The conclusion is given in section 4.

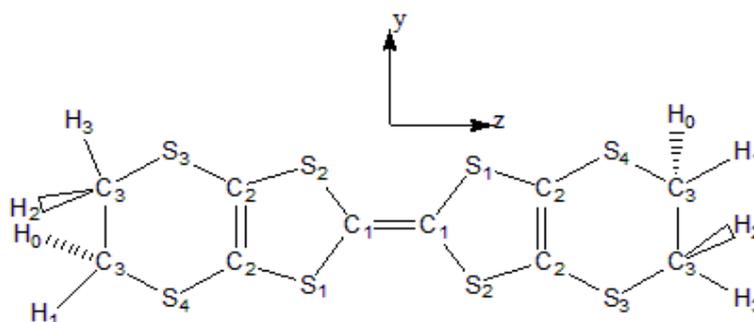


Fig 1. Molecular structure of BEDT-TTF molecule

## 1. Computational details and theoretical framework

### 1.1. Computational details

Our calculations were performed using Gaussian 09W calculation code [9]. Before investigating the electronic structure, the molecules have been constructed using Gauss View 6.0.16 modeling software [10]. So, our properties were computed with Hartree-Fock (HF) and the hybrid method B3LYP program package, adopting the standard cc-pVDZ basis set. Previous work has shown that Beck's three parameter hybrids function combined with the Lee-Yang-Parr correlation function (B3LYP) Beck's three parameter exact exchange-function (B3) combined with gradient-corrected correlational functional of Lee, Yang, and Parr (LYP) predict the best results for molecules geometry, vibrational frequencies and density of states. [8,11-12]

### 1.2. Theoretical framework

In order to investigate the relationships among molecular structures and non linear optical and optoelectronic properties, the dipole moment, the polarizabilities and first order hyperpolarizabilities of BEDT-TTF and its derivatives were calculated using RHF and B3LYP methods by employing cc-pVDZ basis set. The polarizability and hyperpolarizability tensors ( $\alpha_{xx}, \alpha_{xy}, \alpha_{yy}, \alpha_{xz}, \alpha_{yz}, \alpha_{zz}$  and  $\beta_{xxx}, \beta_{xy}, \beta_{xyy}, \beta_{yyy}, \beta_{xxz}, \beta_{xyz}, \beta_{yyz}, \beta_{xzz}, \beta_{yzz}, \beta_{zzz}$ ) can be obtained by a frequency job output file of Gaussian. However,  $\alpha$  and  $\beta$  values of Gaussian output are in atomic units (a.u). So they have been converted into electronic units (esu) and SI unit using ( $\alpha: 1.a.u = 0.1482 \times 10^{-24}$  esu =  $1.648778 \times 10^{-41} C^2 \cdot m^2 \cdot J^{-2}$ , and  $\beta: 1.a.u = 8.6393 \times 10^{-33}$  esu =  $3.206361 \times 10^{-53} C^3 \cdot m^3 \cdot J^2$ ). Therefore, the total molecular dipole moment ( $\mu$ ), the average value of the polarizability  $\langle \alpha \rangle$ , anisotropy of polarizability  $\Delta \alpha$ , and the average value of the first hyperpolarizability  $\langle \beta \rangle$  can be calculated using the equations below [13-16]:

The dipole moment is given by the relation :

$$\mu = \alpha E + \beta E^2 + \gamma E^3 \dots \quad (1)$$

Where :

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\langle \beta \rangle = \left[ (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{\frac{1}{2}} \quad (3)$$

The anisotropy of polarizability ( $\Delta \alpha$ ), is given by the equation :

$$\Delta \alpha = \frac{1}{\sqrt{2}} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 \right]^{\frac{1}{2}} \quad (4)$$

Refractive index ( $n$ ) in semiconductors [17] is given by :

$$n = \sqrt{1 + \chi_e} \quad (5)$$

The total dipole moment  $\mu_{tot}$  is calculated using the following equation [18]:

$$\mu_{tot} = \left( \mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{\frac{1}{2}} \quad (6)$$

The electronegativity, based on the average of the electron affinity and ionization potential of molecules, energy gap, Softness and the Global hardness are given by [18-21]:

$$\text{Electronegativity } (\chi) = -\frac{1}{2}(E_{LUMO} + E_{HOMO}) = -M \quad (7)$$

$$\text{Chemical potential } (M) = \frac{1}{2}(E_{LUMO} + E_{HOMO}) \quad (8)$$

$$\text{Global hardness } (\eta) = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \quad (9)$$

$$\text{Softness } (S) = \frac{1}{\eta} \quad (10)$$

$$\text{Energy gap } (E_{gap}) = E_{LUMO} - E_{HOMO} \quad (11)$$

$$\text{Electrophilicity } (\omega) = \frac{\mu^2}{2\eta} \quad (12)$$

The ionization potential (IP) and electron affinity (EA) can be expressed by HOMO and LUMO orbital energies as [17]:

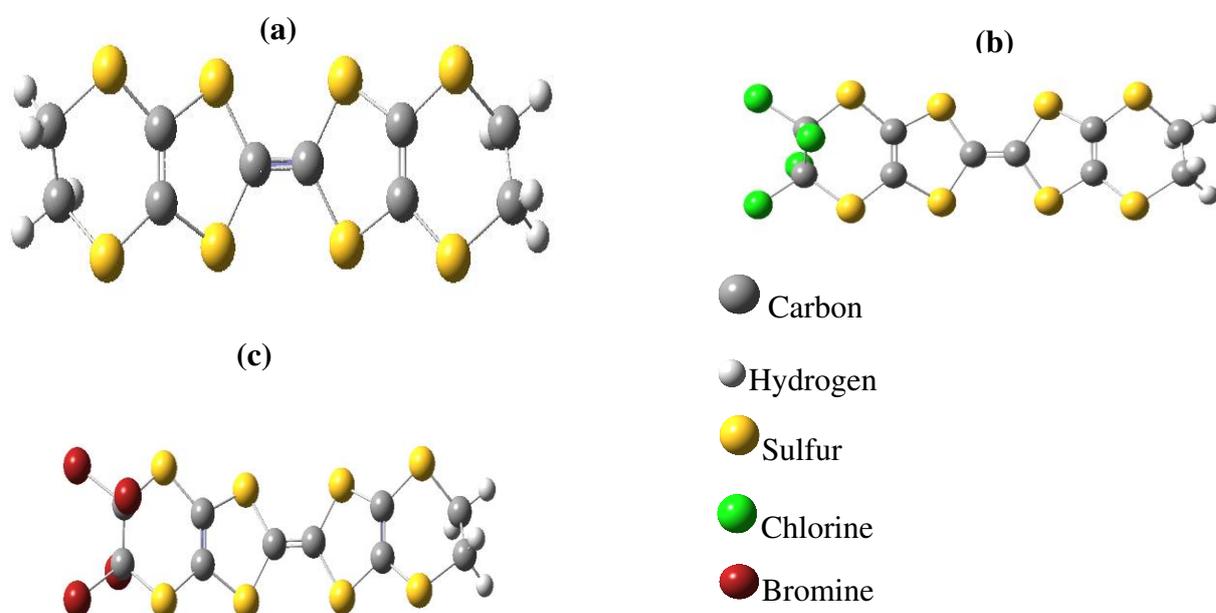
$$IP = -E_{HOMO} \text{ and } EA = -E_{LUMO} \quad (13)$$

## 2. Results and discussion.

### 2.1. Geometrical analysis of studied molecules

#### 2.1.1. Optimized structure

We obtained fully optimized structures of  $C_{10}H_8S_8$ ,  $C_{10}H_4S_8Cl_4$  and  $C_{10}H_4S_8Br_4$  using B3LYP method by employing the cc-pVDZ basis set. Figure 2, shows the optimized geometric structure undoped (**a**) ( $C_{10}H_8S_8$ ) and doped (**b**) and (**c**) respectively  $C_{10}H_4S_8Cl_4$  and  $C_{10}H_4S_8Br_4$ . Because their total energy are the lowest respectively (-3571.49 a.u), (-5409.91 a.u) and (-13865.66 a.u).



**Fig 2** : Optimized molecules of (a) bis (ethylenedithio) tetrathiafulvalene (ET), (b) doped to chlorine (Cl4ET) and (c) doped to bromine (Br4ET) with B3LYP/cc-pVDZ basis set.

### 2.1.2. Geometric properties

The geometric parameters optimized of bis (ethylenedithio) tetrathiafulvalene undoped molecule (a) such as the bond lengths and bond angles by RHF and B3LYP methods with cc-pVDZ as basis set are listed in **Table 1** and compared with the experimental results [22]. Based on our calculations, the result of B3LYP method has shown a better fit to experimental data than HF. Some of the calculated bond lengths (in Å) for BEDT-TTF such as C1-C1 1.354, C2-C2 1.353 and C3-C3 1.519 were approximately equal to experimental values given by Guionneau et al [22]. Moreover, the largest difference between experimental and computed bond length is about 0.056 Å for B3LYP and 0.042 Å for RHF. On the other hand, the smallest difference is about 0.001 Å for B3LYP and -0.039 Å for RHF. Those bond lengths varies slightly as we move from the uncorrelated level of theory (RHF) to the correlated level (B3LYP). It is well known that the Hartree-Fock calculation under-estimates bond lengths and the inclusion of the electron correlation makes them longer [23]. This elongation usually makes a better agreement between theory and experiment. This pattern is also observed here. Most of the bond lengths and angles obtained with B3LYP are very similar to the values reported by Guionneau et al (experimental data), by Imamura et al [3] and by Demiralp et al [4], except for the C3-S3 bond length, which is slightly greater.

The bond angles ( $^{\circ}$ ) of the undoped molecule follow the same pattern. The calculated bond angles were slightly equal to the values listed by Guionneau et al. It is noted that the experimental results and the theoretical calculations have better agreement.

**Table 1 :** Geometrical parameters optimized in bis (ethylenedithio) tetrathiafulvalene (BEDT-TTF), bond lengths (Å), angles (°)

| Parameters              | Exp. [22] | Calculated (cc-pVDZ) |        | Previous studies |       |
|-------------------------|-----------|----------------------|--------|------------------|-------|
|                         |           | B3LYP                | HF     | [4]              | [3]   |
| <b>Bond lengths (Å)</b> |           |                      |        |                  |       |
| C1-C1                   | 1.352     | 1.354                | 1.33   | 1.325            | 1.358 |
| C1-S1                   | 1.762     | 1.784                | 1.775  | 1.769            | 1.747 |
| C1-S2                   | 1.770     | 1.786                | 1.776  | 1.769            | 1.747 |
| C2-S1                   | 1.771     | 1.787                | 1.779  | 1.773            | 1.761 |
| C2-S2                   | 1.778     | 1.788                | 1.781  | 1.773            | 1.761 |
| C2-S3                   | 1.755     | 1.767                | 1.772  | 1.769            | 1.767 |
| C2-S4                   | 1.757     | 1.767                | 1.770  | 1.769            | 1.767 |
| C2-C2                   | 1.347     | 1.353                | 1.326  | 1.325            | 1.329 |
| C3-S3                   | 1.811     | 1.867                | 1.772  | 1.812            | 1.814 |
| C3-S4                   | 1.835     | 1.847                | 1.877  | 1.812            | 1.811 |
| C3-C3                   | 1.518     | 1.519                | 1.521  | 1.523            | 1.524 |
| C3-H0                   | -         | 1.099                | 1.088  | 1.083            | -     |
| C3-H1                   | -         | 1.101                | 1.090  | 1.083            | -     |
| C3-H2                   | -         | 1.099                | 1.087  | 1.083            | -     |
| C3-H3                   | -         | 1.102                | 1.090  | 1.093            | -     |
| <b>Bond angles (°)</b>  |           |                      |        |                  |       |
| C1-C1-S1                | 122.88    | 123.74               | 123.96 | 123.63           | 123.0 |
| C1-C1-S2                | 123.01    | 123.27               | 123.55 | 123.63           | 123.0 |
| S1-C2-S4                | 115.22    | 115.71               | 113.67 | 113.80           | -     |
| S2 -C2-S3               | 119.64    | 118.70               | 113.76 | 113.80           | -     |
| S1-C1-S2                | 113.99    | 112.93               | 112.44 | 112.74           | -     |
| C1-S1-C2                | 93.92     | 93.50                | 94.22  | 94.41            | 96.0  |
| C1-S2-C2                | 93.47     | 93.62                | 94.28  | 94.41            | 96.0  |
| S1-C2-C2                | 117.06    | 117.14               | 117.40 | 117.22           | 117.0 |
| S2-C2-C2                | 113.01    | 116.83               | 116.95 | 117.22           | 117.0 |

**Table 1 (continued)**

| Parameters | Exp [22] | Calculated (cc-pVDZ) |        | Previous studies |       |
|------------|----------|----------------------|--------|------------------|-------|
|            |          | B3LYP                | HF     | [4]              | [3]   |
| C2-S4-C3   | 99.75    | 97.79                | 99.09  | 100.74           | 100.7 |
| C2-S3-C3   | 100.70   | 103.78               | 102.58 | 100.74           | 100.7 |
| S3-C2-C2   | 129.7    | 129.36               | 129.31 | 128.68           | 128.8 |
| S4-C2-C2   | 127.73   | 125.88               | 127.84 | 128.68           | 128.8 |
| S4-C3-C3   | 112.34   | 112.59               | 112.50 | 112.87           | 112.8 |
| S3-C3-C3   | 115.01   | 115.036              | 113.72 | 112.87           | 112.8 |
| H2-C3-H3   | -        | 108.71               | 108.52 | 108.58           | -     |
| H0-C3-H1   | -        | 108.70               | 108.58 | 108.58           | -     |
| H0-C3-S4   | -        | 104.32               | 104.73 | 107.18           | -     |
| H1-C3-S4   | -        | 107.89               | 108.52 | 107.18           | -     |
| H2-C3-S3   | -        | 105.11               | 104.14 | 107.18           | -     |
| H3-C3-S3   | -        | 108.71               | 109.67 | 110.36           | -     |
| H0-C3-C3   | -        | 111.94               | 110.21 | 110.36           | -     |
| H1-C3-C3   | -        | 109.49               | 110.51 | 110.36           | -     |
| H2-C3-C3   | -        | 110.28               | 111.31 | 110.36           | -     |
| H3-C3-C3   | -        | 110.29               | 110.51 | 110.36           | -     |

## 2.2. Non Linear Optical properties (NLO)

Nonlinear optics play an important role in current global research, as NLO active materials find applications in telecommunications, potential applications in modern communication technologies, optical signal processing and data storage [24].

In order to understand the relationships between molecular structure and nonlinear optical properties, the first order polarizabilities and hyperpolarizabilities of BEDT-TTF and their doped derivatives were calculated using the HF and DFT / B3LYP methods with cc-pVDZ basis set. It is well known that higher values of first order dipole moment, polarizability and hyperpolarizability are important for more active NLO properties.

The results presented in Table 2 shows the parameters which characterize the NLO properties calculated by equations (2), (3), (4) and (5) given above. In this table 2, we observed that all the values of the dipole moment are different from zero, which leads to believe that these molecules are polar. On the other hand, those dipole moment values decrease from the uncorrelated method to the correlated method for doped systems. However, we observed an increase in the anisotropy of those undoped and doped systems in going from RHF to B3LYP. This anisotropy is greater with the molecule functionalized by the bromine atom in the two methods used. The result once again demonstrates the better behavior of bromine in that system because it has electrons on its outer shell which makes the system more interesting. Regarding the first order molecular hyperpolarizability, it is observed that those values also increase from RHF to B3LYP. This suggests that the B3LYP takes into account the correlation of electronic exchanges. Likewise, the undoped ET base molecule does not exhibit non-linear behavior, but when it is doped with chlorine and bromine, we realize that its  $\beta_{\text{mol}}$  values become large compared to the values of the urea molecule. Which is a prototype molecule useful for the NLO application. The values of dipole moment, polarizability and first hyperpolarizability of Urea used in the study of the properties of NLO materials ( $\mu$ ,  $\langle\alpha\rangle$  and  $\beta$  of Urea are 3.8851 Debye,  $5.047709 \times 10^{-24}$  esu and  $780.324 \times 10^{-33}$  esu respectively) [24-26]. We observed the lowest value of dipole moment of BEDT-TTF this value is equal to 1.4128D and the lowest value of first order hyperpolarizability, so BEDT-TTF neutral is not good candidate for NLO properties which justifies what we said above. But, doped molecule with chlorine and bromine have dipole moment, polarizability and first order polarizability values are greater than those of prototypical Urea, the very high values of  $\beta_{\text{mol}} = 10494.1467 \times 10^{-33}$  esu for Br-doped and  $\beta_{\text{mol}} = 4156.79 \times 10^{-33}$  esu for Cl-doped indicates that doping BEDT-TTF with the halogen (Chlorine and bromine) makes them a good NLO material. In addition, we make the conclusion that, the doping of ET gives it another field of application in the linear and nonlinear optics.

**Table 2 :** Calculated values of dipole moment  $\mu$  (debye), average polarizability  $\langle \alpha \rangle$  (e.s.u)  $\times 10^{-24}$ , anisotropy  $\Delta\alpha$  ( $\times 10^{-24}$  esu) and first order hyperpolarizability  $\beta_{mol}$  ( $\times 10^{-33}$  esu) of **ET**, **Cl4ET** and **Br4ET** obtained using RHF and B3LYP with cc-pVDZ basis set.

| ET                       | Cl4ET         |               | Br4ET           |                |               |                  |
|--------------------------|---------------|---------------|-----------------|----------------|---------------|------------------|
| Parameter                | RHF           | B3LYP         | RHF             | B3LYP          | RHF           | B3LYP            |
| $\mu$ (D)                | <b>0.9747</b> | <b>1.4128</b> | <b>4.8996</b>   | <b>4.6169</b>  | <b>4.2882</b> | <b>4.1329</b>    |
| $\alpha_{xx}$            | 223.014       | 231.322       | 430.449         | 506.917        | 460.877       | 545.942          |
| $\alpha_{xy}$            | 1.328         | 2.799         | -0.472          | -1.238         | 3.513         | 0.921            |
| $\alpha_{yy}$            | 335.462       | 393.014       | 243.292         | 256.262        | 249.898       | 265.027          |
| $\alpha_{xz}$            | -0.113        | -1.09         | 11.449          | 7.367          | 15.346        | 9.915            |
| $\alpha_{yz}$            | -93.013       | -113.655      | -12.487         | -12.65         | -26.612       | -25.534          |
| $\alpha_{zz}$            | 156.211       | 172.172       | 165.221         | 174.92         | 202.95        | 213.044          |
| $\langle \alpha \rangle$ | <b>35.305</b> | <b>39.35</b>  | <b>41.444</b>   | <b>46.343</b>  | <b>45.138</b> | <b>50.586</b>    |
| $\Delta\alpha$           | <b>33.344</b> | <b>41.387</b> | <b>35.152</b>   | <b>44.144</b>  | <b>36.15</b>  | <b>46.505</b>    |
| $\beta_{xxx}$            | 0.116         | 0.0465        | 118.88          | -545.69        | 39.166        | -1157.53         |
| $\beta_{xxy}$            | -3.892        | -9.337        | 8.1138          | 16.63          | 21.52         | 35.895           |
| $\beta_{xyy}$            | -9.435        | -24.498       | 22.72           | 41.173         | 6.307         | 1.265            |
| $\beta_{yyy}$            | 45.937        | -61.544       | -3.77           | -7.14          | -7.976        | -11.025          |
| $\beta_{zxx}$            | -9.385        | -22.04        | 38.078          | -0.40          | 35.247        | 10.23            |
| $\beta_{xyz}$            | -8.903        | -23.83        | 12.754          | 26.85          | 20.104        | 13.78            |
| $\beta_{zyy}$            | 26.344        | -34.33        | -15.25          | -23.53         | -4.709        | -14.6            |
| $\beta_{yzz}$            | 9.041         | 24.477        | 31.405          | 23.59          | -5.004        | -57.76           |
| $\beta_{xzz}$            | -16.52        | 27.681        | 4.51            | -3.522         | 15.225        | 8.958            |
| $\beta_{zzz}$            | 42.98         | -46.254       | 23.885          | 10.42          | 29.13         | 26.098           |
| $\beta_{mol}$            | <b>716.07</b> | <b>973.45</b> | <b>1550.116</b> | <b>4156.79</b> | <b>670.68</b> | <b>10494.146</b> |

### 2.3. Electronic properties

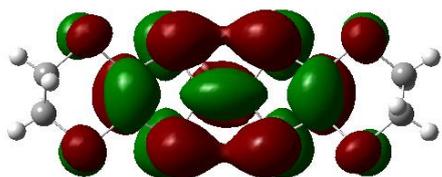
Energy gap is the difference between LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital). This parameter is very important for explain the stability and the reactivity of structure [24-27]. **Table3** gives details of HOMO and LUMO and other related parameters. The parameters that can be obtained from HOMO-LUMO values are given by equations (7), (8) (9), (10), (11) and (12) given above.

HOMO-LUMO energy gap of bis (ethylenedithio) tetrathiafulvalene (ET) undoped molecule, Cl<sub>4</sub>ET and Br<sub>4</sub>ET (doped with chlorine and bromine) are calculated as 3.81 eV, 3.62 eV and 2.88eV respectively using B3LYP/cc-pVDZ. The small energy gap means that the molecule doped is a good semiconductor material. In literature, energy gap of semi-conductor is less than 3eV ( $E_{\text{gap}} < 3 \text{ eV}$ ) [13]. Therefore, the molecule of Br<sub>4</sub>ET is a good semiconductor. On the other hand for ET, the gap energy is more than 3eV, therefore the molecule is a good dielectric as reported in literature [27-30]. From our calculated values, we can deduce that our systems are very reactive because they have low values of chemical potentials. Chemical hardness ( $\eta$ ) is a very useful parameter that is generally used to describe the chemical stability and reactivity of a compound. The greater the chemical hardness, the more stable the molecular system. Molecules of low chemical hardness are more reactive. Our different systems have low chemical hardnesses which further confirms what we said above that our molecules are stable and reactive. When we observe the HOMO-LUMO diagram given in Figure 3 and Figure 4, we observe a good charge distribution on the double bonds in the ethylene group of the undoped molecule as well as for the doped molecules. Also there is a strong contribution of chlorine and bromine in the LUMO of doped systems which increases an electronic displacement and consequently favors the transfer of charge in the molecules. These results make our systems more interesting in electronic devises.

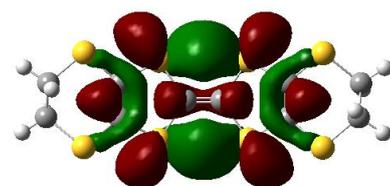
**Table 3 :** Calculated Energy values of ET, Cl4ET and Br4ET using RHF and B3LYP methods with cc-pVDZ basis set.

| ET<br>Properties       | ET          |             | Cl4ET       |             | Br4ET       |             |
|------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
|                        | RHF         | B3LYP       | RHF         | B3LYP       | RHF         | B3LYP       |
| $E_{HOMO}(eV)$         | -7.07       | -4.77       | -7.49       | -5.14       | -7.44       | -5.11       |
| $E_{LUMO}(eV)$         | 2.89        | -0.96       | 2.42        | -1.52       | 1.82        | -2.23       |
| Ionization potential   | 7.07        | 4.77        | 7.49        | 5.14        | 7.44        | 5.11        |
| Electron affinity      | -2.89       | 0.96        | -2.42       | 1.52        | -1.82       | 2.23        |
| <b>Energy gap</b>      | <b>9.96</b> | <b>3.81</b> | <b>9.91</b> | <b>3.62</b> | <b>9.26</b> | <b>2.88</b> |
| Electronegativity      | 2.09        | 2.86        | 2.53        | 3.33        | 2.81        | 3.67        |
| Chemical potential     | -2.09       | -2.86       | -2.53       | -3.33       | -2.81       | -3.67       |
| Global hardness        | 4.98        | 1.91        | 4.96        | 1.82        | 4.63        | 1.44        |
| Chemical Softness      | 0.20        | 0.52        | 0.20        | 0.55        | 0.22        | 0.69        |
| Refractive index       | 1.96        | 1.95        | 1.93        | 1.96        | 1.96        | 2.03        |
| Electrophilicity index | 0.44        | 2.14        | 0.65        | 3.05        | 0.85        | 4.68        |

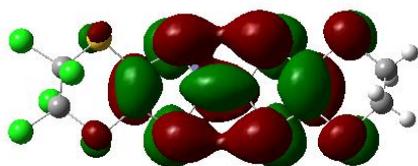
$C_{10}H_8S_8$



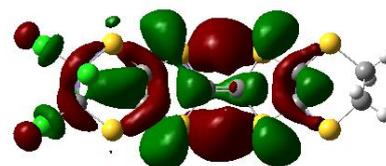
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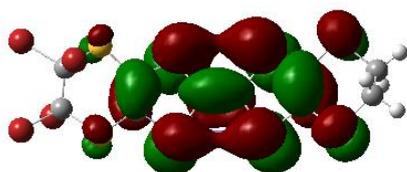
$C_{10}H_4S_8Cl_4$



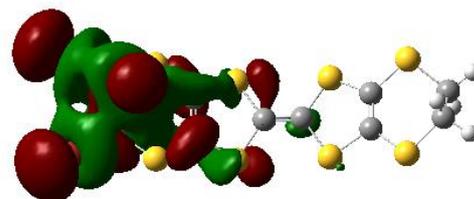
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$C_{10}H_4S_8Br_4$



$E_g = 9.26 \text{ eV}$

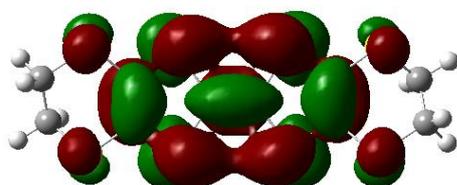


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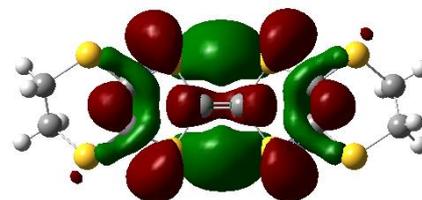
**LUMO**

**Fig 3** : LUMO and HOMO molecular orbital diagrams of the studied molecular structures using RHF/cc-pVDZ

$C_{10}H_8S_8$



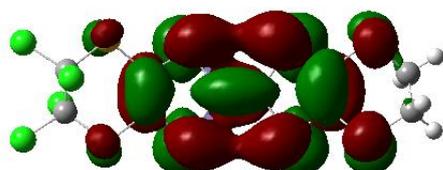
$E_g = 3.81 \text{ eV}$



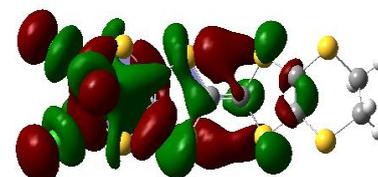
**HOMO**

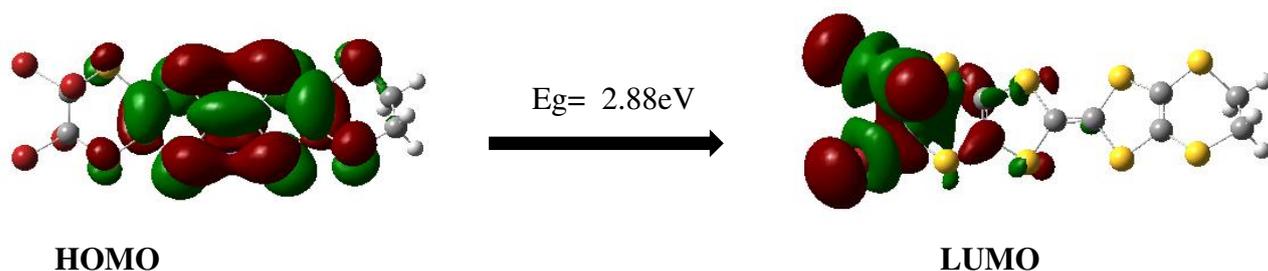
**LUMO**

$C_{10}H_4S_8Cl_4$



$E_g = 3.62 \text{ eV}$





**Fig 4** : LUMO and HOMO molecular orbital diagrams of the studied molecular structures using B3LYP/cc-pVDZ

## 2.4. Optoelectronic properties

Optoelectronic parameters properties such as : the polarization density(P), the electric field (E), electric susceptibility ( $\chi$ ), dielectric constant ( $\epsilon$ ), and the magnitude of the displacement vector (D), refractive index ( $\eta$ ) were calculated and listed in **Table 4**. These parameters values were computed using the equations given in the literature [31-33]. We observed that our computed results are very different when we move from undoped molecule to doped. Moreover, this difference is slightly between the uncorelated to the electron-correlated level of theory. Therefore, high values of the electric field E, the electric susceptibility  $\chi$ , refractive index n and low value of dielectric constant  $\epsilon$  of doped systems find applications in optoelectronic materials. In fact, in renewable energy, photovoltaic and photonic devices.

**Table 4** : Average of the polarizability  $\langle \alpha \rangle$ , Polarization density(P), the electric field (E), electric susceptibility ( $\chi$ ), dielectric constant ( $\epsilon$ ), and refractive index ( $\eta$ ) of the molecules  $C_{10}H_8S_8$  (ET),  $C_{10}H_4S_8Cl_4$  (Cl<sub>4</sub>ET) and  $C_{10}H_4S_8Br_4$  (Br<sub>4</sub>ET) obtained at RHF and B3LYP methods with cc-pVDZ

| Properties  | $C_{10}H_8S_8$ |        | $C_{10}H_4S_8Cl_4$ |        | $C_{10}H_4S_8Br_4$ |        |
|---|----------------|--------|--------------------|--------|--------------------|--------|
|   | RHF            | B3LYP  | RHF                | B3LYP  | RHF                | B3LYP  |
| $\mu(Cm) \times 10^{-30}$                               | 3.25           | 4.70   | 16.34              | 15.4   | 14.31              | 13.78  |
| $\langle \alpha \rangle (C^2m^2J^{-2}) \times 10^{-41}$ | 392.79         | 437.75 | 461.09             | 515.58 | 502.18             | 562.79 |
| $V(m^3) \times 10^{-30}$                                | 154.85         | 176.56 | 191.10             | 204.34 | 198.16             | 204.34 |
| $E(V.m^{-1}) \times 10^9$                               | 0.83           | 1.07   | 3.54               | 2.93   | 2.85               | 2.45   |
| $P(C.m^{-2}) \times 10^{-3}$                            | 20.99          | 26.62  | 85.52              | 75.36  | 72.21              | 67.44  |
| $\chi$  | 2.86           | 2.81   | 2.73               | 2.85   | 2.86               | 3.11   |
| $\epsilon_r$  | 3.86           | 3.81   | 3.73               | 3.85   | 3.86               | 4.11   |
| $\epsilon \times 10^{-12}$                              | 34.18          | 33.73  | 33.01              | 34.06  | 34.18              | 36.39  |
| $n$   | 1.96           | 1.95   | 1.93               | 1.96   | 1.96               | 2.03   |

## 2.5. Thermodynamic properties

The various thermodynamic parameters presented in **table 5** such as Total electronic energy (Eelec), Zero vibrational point energy (ZPVE), Gibbs free energy (G), Thermal energy (E), Entropy (S), Enthalpy (H), constant volume calorific capacity (Cv) were calculated at an ambient temperature of 298.15 K and a pressure of 1 atm. Our results show that structures doped with chlorine and bromine have a lower total energy than the undoped molecule (C<sub>10</sub>H<sub>8</sub>S<sub>8</sub>). On the other hand, the variation of the thermodynamic properties such as entropy, enthalpy and specific heat change slightly. This difference observed when going from the HF to the DFT is certainly due to the effect of correlation of the electrons. Therefore, we are able to conclude that there is an influence of doping with chlorine and bromine on the entropy of molecular structures, which confirms that the charge dynamics of the doped molecules are higher than its original molecule at the same temperature. This result further demonstrates that these doped materials have a high chemical reactivity and a high thermal resistivity. A better agreement with work reported by Mveme et al [18].

**Table 5:** Total electronic energy (Eelec), Zero vibrational point energy (ZPVE), Gibbs free energy (G), Thermal energy (E), Entropy (S), Enthalpy (H), constant volume calorific capacity (Cv), of the molecules C<sub>10</sub>H<sub>8</sub>S<sub>8</sub> (ET), C<sub>10</sub>H<sub>4</sub>S<sub>8</sub> Cl<sub>4</sub> (Cl4ET) and C<sub>10</sub>H<sub>4</sub>S<sub>8</sub> Br<sub>4</sub> (Br4ET) obtained using Hartree-Fock and B3LYP with CC-pVDZ basis set at T=298.15K.

| Properties                                 | C <sub>10</sub> H <sub>8</sub> S <sub>8</sub> |          | C <sub>10</sub> H <sub>4</sub> S <sub>8</sub> Cl <sub>4</sub> |          | C <sub>10</sub> H <sub>4</sub> S <sub>8</sub> Br <sub>4</sub> |           |
|--|---|----------|---|----------|---|-----------|
|  | RHF   | B3LYP    | RHF   | B3LYP    | RHF   | B3LYP     |
| Eelec (a.u)                                | -3563.51                                      | -3571.49 | -5399.14  | -5409.91 | -13850.69   | -13865.66 |
| ZPVE (kcal/mol)                            | 107.66  | 99.09    | 81.60   | 74.16    | 79.69   | 72.40     |
| E <sub>0</sub> (kcal/mol) x10 <sup>3</sup> | -2236.03                                      | -2241.05 | -3387.93  | -3394.70 | -8691.34  | -8700.76  |
| E (kcal/mol) x10 <sup>3</sup>              | -2236.02                                      | -2241.04 | -3387.91  | -3394.69 | -8691.32  | -8700.75  |
| H (kcal/mol) x10 <sup>3</sup>              | -2236.02                                      | -2241.04 | -3387.91  | -3394.69 | -8691.32  | -8700.75  |
| G (kcal/mol) x10 <sup>3</sup>              | -2236.06                                      | -2241.08 | -3387.96  | -3394.74 | -8691.37  | -8700.80  |
| Ethermal (kcal/mol)                        | 118.87  | 111.11   | 95.63   | 89.253   | 94.59   | 88.37     |
| Cv (cal/mol.k <sup>1</sup> )               | 64.68   | 69.38    | 79.82   | 85.22    | 81.92   | 87.20     |
| S(cal/mol.k <sup>1</sup> )                 | 144.18  | 148.47   | 166.17  | 173.61   | 176.75  | 184.62    |

### 3. Conclusion

In summary, the non linear optical, electronic, optoelectronic and thermodynamic properties of undoped and doped BEDT-TTF have been studied. Our goal was to investigate the effect or influence of doping with halogen like chlorine and bromine on the original molecule. The results obtained from the B3LYP and RHF methods using cc-pVDZ basis set show that BEDT-TTF has a weak nonlinear optical (NLO) behavior. However, substituted hydrogen by chlorine and bromine show more interesting properties such as high hyperpolarizability ( $\beta$ ) makes the molecule to find applications in NLO. In fact, we presented for the first time the result on the substitution of BEDT-TTF with chlorine and bromine. New systems obtained are a good candidate to find application in renewable energy, emerging technologies. The HOMO-LUMO energy gap obtained lead us to believe that BEDT-TTF and its derivatives are good semiconductor materials that can be used in photovoltaic cells, light emitting diode (LED) and field effect transistor (FET). Finally, thermodynamic parameters computed are in agreement with the work of other researchers.

### Declaration of Competing Interest

The authors declare that there is no conflict of Interest in regard with this work.

### Acknowledgment

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# Figures

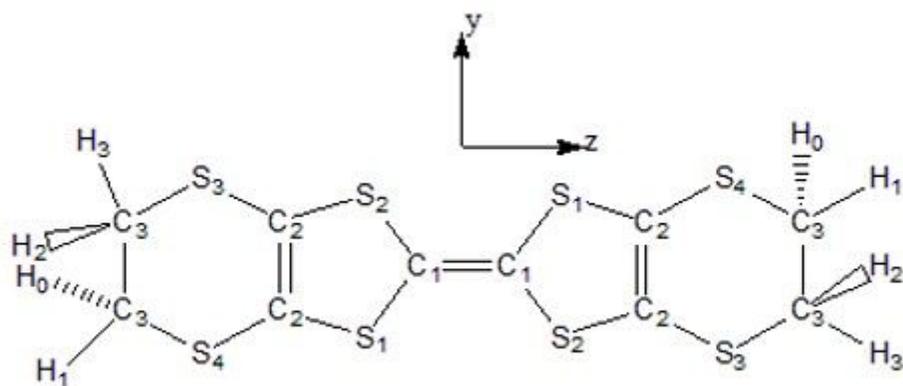


Figure 1

Molecular structure of BEDT-TTF molecule

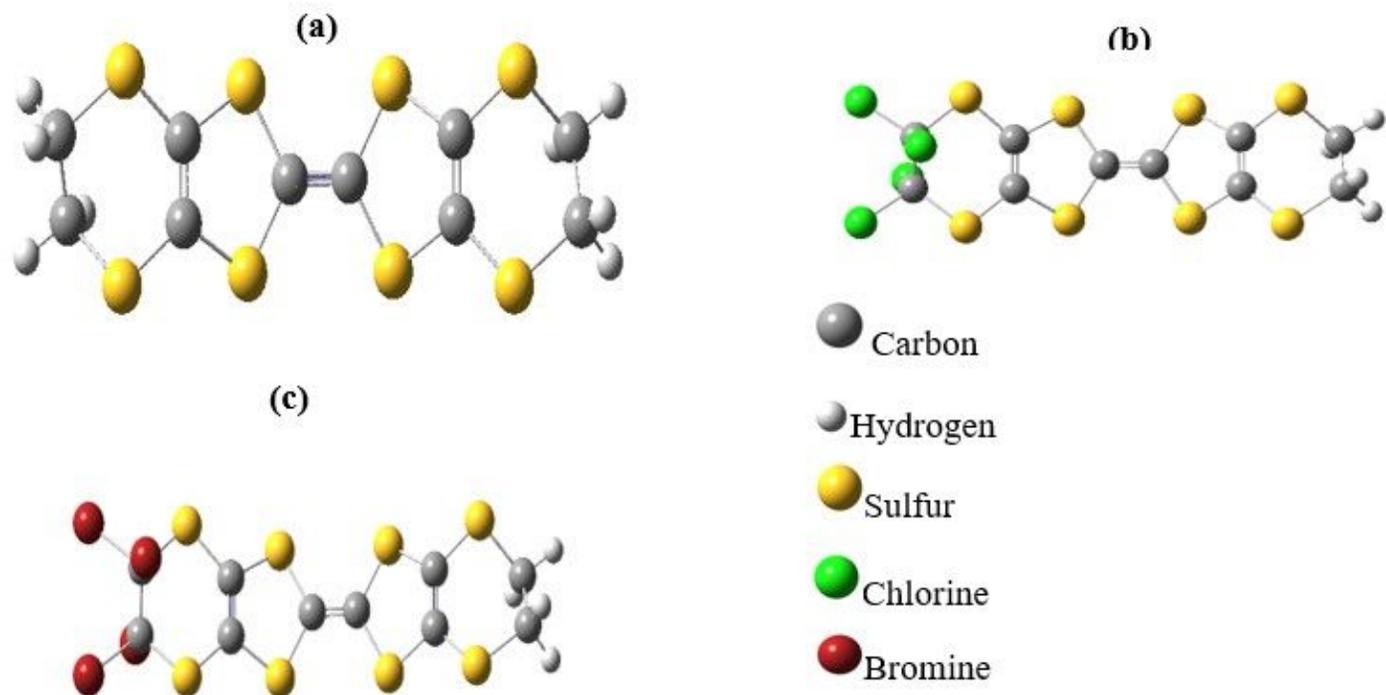
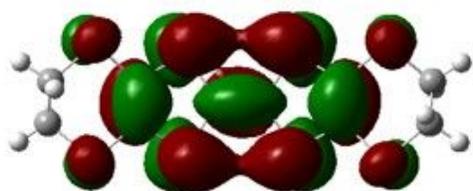
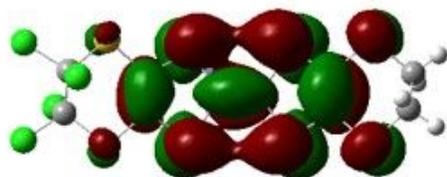
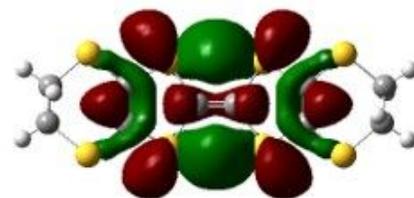


Figure 2

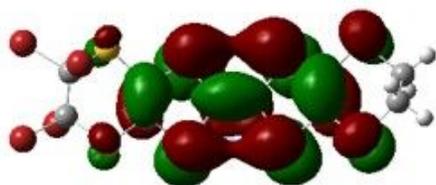
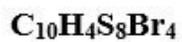
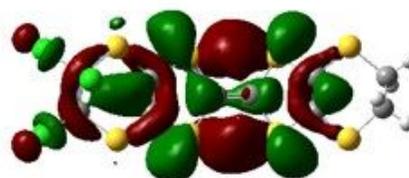
Optimized molecules of (a) bis(ethylenedithio) tetrathiafulvalene (ET), (b) doped to chlorine (Cl<sub>4</sub>ET) and (c) doped to bromine (Br<sub>4</sub>ET) with B3LYP/cc-pVDZ basis set.



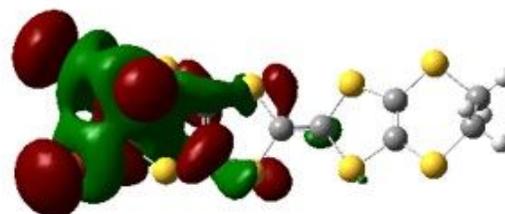
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$E_g = 9.91 \text{ eV}$



$E_g = 9.26 \text{ eV}$

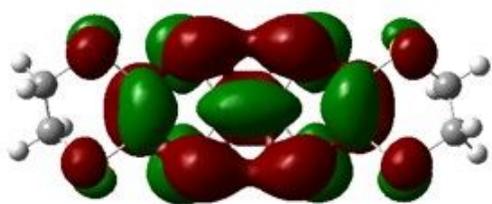


**HOMO**

**LUMO**

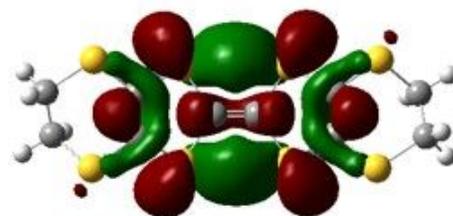
**Figure 3**

LUMO and HOMO molecular orbital diagrams of the studied molecular structures using RHF/cc-pVDZ

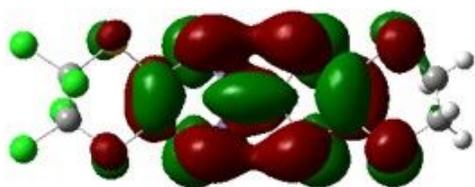


HOMO

$E_g = 3.81 \text{ eV}$

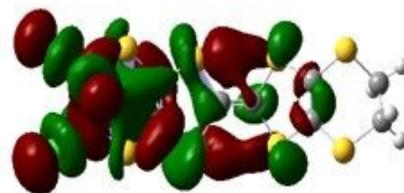


LUMO



HOMO

$E_g = 3.62 \text{ eV}$



LUMO

$E_g = 2.88 \text{ eV}$

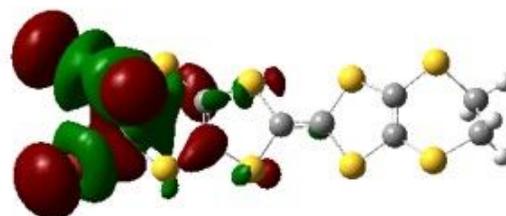


Figure 4

LUMO and HOMO molecular orbital diagrams of the studied molecular structures using B3LYP/cc-pVDZ