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 recent years, designing high performance NLO materials is an interesting topic in nonlinear optics. In this work, the influence of hydrogen atoms substitution with chlorine and bromine atoms of BEDT-TTF (C_{10}H_{8}S_{8}) on nonlinear optical, electronic, optoelectronic and thermodynamic properties is investigated by using ab-initio and density functional theory. The proposed materials exhibit good nonlinear optical response. Results obtained with B3LYP/cc-pVDZ method shown a better fit to experimental data than RHF/cc-pVDZ in terms of geometric parameters (bond lengths and bond angles). First and second hyperpolarizabilities (β and γ) values show that the proposed materials have very good optoelectronic and nonlinear optical properties. Energies gap, $E_{g}$ show that the molecules may have semi-conductors properties and hence have applications in the field of optoelectronic devices.

Keywords BEDT-TTF · hyperpolarizability · Nonlinear optical properties · Optoelectronic properties · doping
1 Introduction

In the last few decades, the developing of nonlinear optical (NLO), electronic and optoelectronic materials have become an interesting topic and attracting great interest, because they find many 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 (Shakerzadeh et al. 2016). Research on designing new high performance NLO materials is being an intriguing issue for scientist (Shakerzadeh et al. 2016).

The discovery of bis(ethylenedithio) tetrathiafulvalene abbreviated as BEDT-TTF or simply ET in 1980 (Demiralp et al. 1995) (Fig. 1), we find in the literature others organic conductors, which are designed, studied and synthesized by others authors (Imamura et al. 1999). The works of Demiralp et al. (1997), have been showed that about 30 organic superconductors based on BEDT-TTF have been synthesized with critical temperature $T_c$ up to 12.8 K. Previously in the literature, the detailed of infrared and Raman spectra of BEDT-TTF have been reported by the works of Kozlov et al. (1987), Eldridge et al. (1995) and Liu et al. (1997). In addition, the works of Wallis and Griffiths (2005) revealed others molecules from the chirality of substituted BEDT-TTF derivatives. Moreover, gives opportunities to prepare multifunctional materials. All these works have contributed much to understand this family of molecules. Despite some progress made in our previous work on this BEDT-TTF molecule and its derivatives doping with boron atoms (Olinga et al. 2021). The NLO, electronic, optoelectronic and thermodynamics properties are still not fully understood. In these last decades many works (Sundaraganesan et al. 2007; Moreira et al. 2015; Costa et al. 2016), have shown that the ab-initio and the density functional theory (DFT) have become a powerful tools in order to predict and study some important properties of molecules such as electronic structure, linear and nonlinear optics properties, thermodynamics and optoelectronics properties. The aim of this research article is to propose organic molecules, which can have potential applications in organic electronic. In this article, we study the semi-conductor nature of bis(ethylenedithio)tetrathiafulvalene and some of its derivatives by doping it with some halogen atoms (chlorine and bromine atoms), which may having application in quantum dots and other material. Our main objectives are to use ab-initio and DFT quantum mechanical calculations to decipher the electronic structure, dipole moments, average polarizability, hyperpolarizabilities, first and second hyperpolarizabilities, 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 with its doped-systems. In this work, we reported the theoretical calculations (ab-initio and DFT) in gas phase using Hartree–Fock (HF) and B3LYP (Becke-3-Lee–Yang–Parr) methods with the same cc-pVDZ basis set in the ground state. This paper is organized in four sections. The calculation method is presented in Sect. 2. In Sect. 3, the results and discussion are presented. The conclusion is given in Sect. 4.

Fig. 1 Molecular structure of BEDT-TTF molecule
2 Computational details and theoretical framework

2.1 Computational details

Our calculations were performed using Gaussian 09W calculation code (Frisch et al. 2009). Before investigating the electronic structure, the molecules have been constructed using Gauss View 6.0.16 modeling software (Dennington and Keith, 2016). 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 hybrid 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 (Sundaraganesan et al. 2007; Becke 1988; Lee et al. 1988).

2.2 Theoretical framework

In order to investigate the relationships among molecular structures and nonlinear optical and optoelectronic properties, the dipole moment, the polarizabilities, first and second hyperpolarizabilities of BEDT-TTF molecule and its derivatives (chlorinated and brominated structures) are calculated using RHF/cc-pVDZ and B3LYP/cc-pVDZ methods.

The polarizability, first and second order hyperpolarizabilities tensors respectively ($\alpha_{xx}$, $\alpha_{xy}$, $\alpha_{yx}$, $\alpha_{yy}$, $\alpha_{yz}$, $\alpha_{zy}$, $\alpha_{zz}$, $\beta_{xxx}$, $\beta_{xyy}$, $\beta_{xzz}$, $\beta_{zxx}$, $\beta_{zyy}$, $\beta_{zzy}$, $\beta_{zzz}$ and $\gamma_{xxxx}$, $\gamma_{yyyy}$, $\gamma_{zzzz}$, $\gamma_{xxyy}$, $\gamma_{xxzz}$, $\gamma_{yyzz}$, $\gamma_{zzxx}$, $\gamma_{zxyy}$, $\gamma_{zzyy}$, $\gamma_{zzzz}$) can be obtained by a frequency job output file of Gaussian. However, $\alpha$, $\beta$ and $\gamma$ values of Gaussian output are in atomic units (a.u). So these conversion factors are used to convert atomic units to SI units in order to calculate optoelectronic properties: $\alpha$: 1.a.u=0.1482×10−24 esu=1.648778×10−41 C2 m2 J−1, $\beta$: 1.a.u=8.6393×10−33 esu=3.206361×10−53 C3 m3 J−2, $\gamma$: 1.a.u=5.0367×10−40 esu=6.23597×10−65 C4 m4 J−3 and 1 Debye=3.336×10−30 C m (coulomb meter) (Olinga et al. 2021; Anu et al. 2020). Therefore, the total molecular dipole moment ($\mu$), the average value of the polarizability $\langle \alpha \rangle$, anisotropy of polarizability $\Delta \alpha$, and the average values of the first and second hyperpolarizabilities $\langle \beta \rangle$ and $\langle \gamma \rangle$ can be calculated using the Eqs. (1), (2), (3), (4), (5) and (6) below (Mveme et al. 2020; Yossa et al. 2020; Anu et al. 2020; Olinga et al. 2021).

In the case of strong fields, the dipole moment is given by the formula below:

$$\mu = \alpha E + \beta E^2 + \gamma E^3 \ldots$$  \hspace{1cm} (1)

where $\alpha$ is the polarizability, $\beta$ is the first order hyperpolarizability and $\gamma$ is the second molecular hyperpolarizability.

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

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

$$\langle \gamma \rangle = \left[ (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz})^2 + (\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})^2 + (\gamma_{zxx} + \gamma_{zxy} + \gamma_{zyy})^2 \right]^{\frac{1}{2}}$$  \hspace{1cm} (4)
The anisotropy of polarizability ($\Delta \alpha$) is given by the Eq. 5 below:

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

(5)

Refractive index ($n$) in semiconductor is given by Eq. 6:

$$n = \sqrt{1 + \chi_e}$$  

(6)

The total dipole moment $\mu_{tot}$ is calculated using the following Eq. 6 (Ejuh et al. 2018a, b):

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

(7)

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 the Eqs. 8–13 (Fankam et al. 2020a, b; Kabe et al. 2020; Midoune and Messaoudi 2020):

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

(8)

Chemical potential ($\mu$) = $\frac{1}{2} (E_{LUMO} + E_{HOMO})$  

(9)

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

(10)

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

(11)

Energy gap ($E_{gap}$) = $E_{LUMO} - E_{HOMO}$  

(12)

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

(13)

The ionization potential (IP) and electron affinity (EA) can be expressed by HOMO and LUMO orbital energies as (see Eq. 14) (Anu et al. 2020).

$$IP = -E_{HOMO} \text{ and } EA = -E_{LUMO}$$  

(14)

The equations below given in the literature (Anu et al. 2020) are used for the calculation of optoelectronic properties:

$$D = \varepsilon E, \quad \varepsilon = \varepsilon_o \varepsilon_r, \quad P = \varepsilon_o \chi E, \quad \chi = \varepsilon_r - 1, \quad P = \frac{\langle \alpha \rangle}{V} \quad \text{and} \quad \mu = \langle \alpha \rangle E$$  

(15)
3 Results and discussion

3.1 Geometrical analysis of studied molecules

3.1.1 Optimized structure

We obtained fully optimized structures of $\text{C}_{10}\text{H}_8\text{S}_8$, $\text{C}_{10}\text{H}_4\text{S}_8\text{Cl}_4$ and $\text{C}_{10}\text{H}_4\text{S}_8\text{Br}_4$ using B3LYP method by employing the cc-pVDZ basis set. In Fig. 2, we have the ground state optimized geometric of the molecules (ET, Cl4ET and Br4ET): structure undoped (a), doped (b) and (c) respectively. Energies values of these optimized molecules are $-3571.49$ a.u for ET, $-5409.91$ a.u for Cl4ET and $-13,865.66$ a.u for Br4ET.

3.1.2 Geometric properties

The optimized geometric parameters of bis (ethylenedithio) tetrathiafulvalene undoped molecule (a) such as the bond lengths and bond angles obtained by RHF and B3LYP methods with cc-pVDZ as basis set are listed in Table 1 and compared with the experimental results (Guionneau et al. 2000). Based on our calculations, the result of the hybrid functional B3LYP have shown to better fit with experimental data than the HF method given in literature (Guionneau et al. 2000). 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. (2000). 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

![Fig. 2](image-url) 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
Table 1 Geometrical parameters optimized of bis (ethylenedithio) tetrathiafulvalene (BEDT-TTF), bond lengths (Å) and angles (°)

| Parameters | Exp. (Guionneau et al. 2000) | Calculated (cc-pVDZ) | Previous studies |
|------------|-----------------------------|----------------------|-----------------|
|            |                             | B3LYP               | RHF             |                |
| Bond lengths (Å) |                   |                     |                 |
| 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           |
|            | 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               | –               |
| Bond angles (°) |                   |                     |                 |
| 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–C3   | 113.01                     | 116.83              | 116.95          |
|            |                             | 117.22              | 117.0           |
| S2–C4–C3   | 99.75                      | 97.79               | 99.09           |
|            |                             | 100.74              | 100.7           |
| S2–C3–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              | 123.0           |
| H0–C3–H1   | –                          | 108.70              | 108.58          |
|            |                             | 108.58              | 123.0           |
| 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              | 96.0            |
| H0–C3–C3   | –                          | 111.94              | 110.21          |
|            |                             | 110.36              | 96.0            |
| H1–C3–C3   | –                          | 109.49              | 110.51          |
|            |                             | 110.36              | 117.0           |
| H2–C3–C3   | –                          | 110.28              | 111.31          |
|            |                             | 110.36              | 117.0           |
correlation makes them longer (Allen 2002). 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. (1999) and by Demiralp et al. (1997), except for the C3–S3 bond length, which is slightly greater.

The bond angles (°) 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.

### 3.2 Nonlinear optical properties (NLO)

The NLO properties of organic semi-conductors attract much attention in current global research, because these materials have wide applications in photonic technologies, modern communication technologies, optical signal processing and data storage (Saji et al. 2020; Spiridon et al. 2015; Bouchouit et al. 2004). It is important to understand the relationship of molecular structure with the NLO properties. The calculation of the first-order hyperpolarizability ($\beta$) and second hyperpolarizability ($\gamma$) of our molecules are determined theoretically. These both parameters allowed us to measure the NLO activity of the proposed molecules in this work.

The two parameters $\beta$ and $\gamma$, which are the NLO responses of the BEDT-TTF original molecule and the both doped structures, the chlorinated molecule (Cl4ET) and brominated (Br4ET) are carried out using the both Restricted Hartree–Fock (RHF) and DFT/B3LYP methods with the same basis set cc-pVDZ in the gas phase. In addition, we notice that, higher values of first and second molecular hyperpolarizabilities, dipole moment and polarizability are very important for more NLO properties.

Table 2 show our calculated results from the Eqs. (2), (3), (4), (5) and (7) given above. In this Table 2, the first molecular and second hyperpolarizabilities ($\beta$ and $\gamma$) values of all the considered molecules are listed. Also, we observed that all the values of the dipole moment ($\mu$) are different from zero, which leads to believe that these molecules are polar. In addition, these dipole moment values decrease from the uncorrelated method (HF) to the B3LYP method, which takes into account the correlation of electronic exchanges of the considered systems. We have observed the highest first molecular hyperpolarizability $\beta$ for C$_{10}$H$_8$S$_8$Br$_4$ ($\beta_{\text{mol}} = 10.494.1467 \times 10^{-33}$ e.s.u), the molecule functionalized by the bromine atom. While, the lowest first molecular hyperpolarizability is observed for C$_{10}$H$_8$S$_8$ ($\beta_{\text{mol}} = 973.45 \times 10^{-33}$ e.s.u), undoped molecule. In addition, first molecular hyperpolarizability value of C$_{10}$H$_8$S$_8$Cl$_4$ is $\beta_{\text{mol}} = 4156.79 \times 10^{-33}$ e.s.u. In order to compare these $\beta$ values off all the considered molecules with the Urea ($\beta_o = 928 \times 10^{-33}$ e.s.u.) (Olinga et al. 2021). Urea is used as reference molecule to study the nonlinear optical properties of the...
compound (Saji et al. 2020; Muthu et al. 2002; Fonkem et al. 2019). Based on our results, we observed that first hyperpolarizabilities values of brominated and chlorinated molecules are 11 and 4.5 times greater than those of Urea respectively. The highest values of hyperpolarizabilities of the both doped molecules (Cl4ET and Br4ET) indicates that the proposed materials can be good NLO molecules. Likewise, the undoped ET molecule does not exhibit nonlinear behavior. We can conclude that doping improves some particular properties such as nonlinear optical properties. Also, high performance NLO materials depend on the large first molecular hyperpolarizability value. These NLO active materials find application in modern communication technology and data storage, some works in the literature confirm it (Sahraoui et al. 2009).

One the other hand, another important NLO parameter have also computed, second molecular hyperpolarizability $\gamma$. This second molecular hyperpolarizability is a

| Properties          | ET    | Cl4ET | Br4ET |
|---------------------|-------|-------|-------|
| $\mu$ (Debye)       | 0.9747| 1.4128| 4.8996| 4.6169| 4.2882| 4.1329|
| $\alpha_{xx}$       | 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|
| $\alpha_{zx}$       | 0.113  | -1.09  | 11.449 | 7.367  | 15.346 | 9.915  |
| $\alpha_{zx}$       | -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|
| $\langle\alpha\rangle$ (e.s.u) $10^{-24}$ | 35.305 | 41.387 | 41.444 | 46.343 | 45.138 | 50.586 |
| $\Delta\alpha$ (e.s.u) $10^{-24}$ | 33.344 | 41.387 | 35.152 | 44.144 | 36.15  | 46.505  |
| $\beta_{xx}$        | 0.116  | 0.0465 | 118.88 | -545.69| 39.166 | -1157.53|
| $\beta_{xy}$        | -3.892 | -9.337 | 8.1138 | 16.63  | 21.52  | 35.895  |
| $\beta_{yy}$        | -9.435 | -24.498| 22.72  | 41.173 | 6.307  | 1.265   |
| $\beta_{yy}$        | 45.937 | -61.544| -3.77  | -7.14  | -7.976 | -11.02  |
| $\beta_{yy}$        | -9.385 | -22.04 | 38.078 | -0.40  | 35.247 | 10.23  |
| $\beta_{yz}$        | -8.903 | -23.83 | 12.754 | 26.85  | 20.104 | 13.78  |
| $\beta_{yz}$        | 26.344 | -34.33 | -15.25 | -23.53 | -4.709 | -14.6   |
| $\beta_{zz}$        | 9.041  | 24.477 | 31.405 | 23.59  | -5.004 | -57.76  |
| $\beta_{zz}$        | -16.52 | 27.681 | 4.51   | -3.522 | 15.225 | 8.958   |
| $\beta_{zz}$        | 42.98  | -46.254| 23.885 | 10.42  | 29.13  | 26.098  |
| $\beta_{mol}$ (e.s.u) $10^{-33}$ | 716.07 | 973.45 | 1.550.116 | 4.156.79 | 670.68 | 10.494.146 |
| $\gamma_{xxxx}$     | -10.415.57 | -10.749.27 | -19.500.14 | -19.576.25 | -21.198.062 | -21.458.38 |
| $\gamma_{yyyy}$     | -2020.349 | -1933.936 | -2451.884 | -2392.982 | -2761.941 | -2694.634 |
| $\gamma_{zzzz}$     | -510.6174 | -468.9096 | -1325.644 | -1277.296 | -1840.5061 | -1763.904 |
| $\gamma_{xyxy}$     | -5445.823 | -5359.195 | -8757.757 | -8635.595 | -10.303.284 | -10.200.624 |
| $\gamma_{xxzz}$     | -4791.572 | -4874.253 | -8271.113 | -8351.552 | -9757.749 | -9929.2706 |
| $\gamma_{yyzz}$     | -878.3672 | -807.6564 | -1313.541 | -1265.545 | -1554.5574 | -1510.5374 |
| $\gamma$ ($10^{-61}$ C$^4$ m$^4$ J$^{-3}$) | -3.00046 | -3.01668 | -5.19033 | -5.17474 | -5.91301 | -5.93047 |
microscopic property of the molecule, and is defined as the sum of electronic contributions and a contribution coming from the orientation of the permanent dipole momentum in the electric field. The Eq. 4, which is given in literature (Anu et al. 2020), is used to carry out these second hyperpolarizabilities of all the considered molecules and their values are grouped in Table 2. The results show the negative values of second hyperpolarizabilities. The theoretical values of the second hyperpolarizabilities for Cl4ET and Br4ET obtained in gas phase using B3LYP/cc-pVDZ are $-5.17474 \times 10^{-61}$ C⁴ m⁴ J⁻³ and $-5.93047 \times 10^{-61}$ C⁴ m⁴ J⁻³ respectively. These negative values of $\gamma$ are the fact the contributions to gamma are due to the pi-electrons. With these large values of gamma, and the comparison of these computed results with others recently published (Fankam et al. 2020a, b, Ejuh et al. 2020) allowed us to confirm that these proposed materials are a good candidate for NLO applications. Due to the large values of the hyperpolarizabilities $\beta$ and $\gamma$ of our doped systems, compared to the organic reference molecule Urea, and based on the work of other authors. Such as Speridon et al. (2015), Kulyk et al. (2017) and El Kouari et al. (2015), we believe that these considered materials have potential applications in the field of optoelectronic devices such as data storage, optical communication, optical switching.

### 3.3 Electronic properties

Energy gap is defined as the difference between LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital). This property is very important because it allows us to explain clearly the stability and the reactivity of the molecules (Saji et al. 2020; Muthu and Uma Maheswari 2002; Fonkem et al. 2019; Ejuh et al. 2017). Table 3 gives details of HOMO and LUMO and others related parameters such as Ionization potential abbreviated IP, Electron affinity (AE)…. These parameters which can be obtained from the HOMO and LUMO values are calculated using the Eqs. (8), (9), (10), (11), (12), (13) and (14) given above.

The HOMO–LUMO energy gap of bis (ethylenedithio) tetrathiafulvalene (ET) undoped molecule and both doped molecules (Cl₄ET and Br₄ET) in gas phase are computed as 3.81 eV, 3.62 eV and 2.88 eV using B3LYP/cc-pVDZ respectively. In literature, energy

| Table 3 | Calculated Energy values of ET, Cl₄ET and Br₄ET using RHF and B3LYP methods with cc-pVDZ basis set |
|---------|---------------------------------------------------------------------------------|
| Properties                  | ET RHF  | ET B3LYP | Cl₄ET RHF | Cl₄ET B3LYP | Br₄ET RHF | Br₄ET B3LYP |
|EHOMO (ev)                  | −7.07  | −7.49  | −7.44  | −5.14  | −5.11  | −5.11  |
|ELUMO (ev)                  | 2.89   | 2.42   | 1.82   | 1.52   | 2.33   | 2.33   |
|Ionization potential        | 7.07   | 7.49   | 7.44   | 5.14   | 5.11   | 5.11   |
|Electron affinity           | −2.89  | −2.42  | −1.82  | 1.52   | 2.33   | 2.33   |
|Energy gap                  | 9.96   | 9.91   | 9.26   | 3.62   | 2.88   | 2.88   |
|Electronegativity           | 2.09   | 2.53   | 2.81   | 3.33   | 3.67   | 3.67   |
|Chemical potential          | −2.09  | −2.53  | −2.81  | −3.33  | −3.67  | −3.67  |
|Global hardness             | 4.98   | 4.96   | 4.63   | 1.82   | 1.44   | 1.44   |
|Chemical Softness           | 0.20   | 0.20   | 0.22   | 0.55   | 0.69   | 0.69   |
|Refractive index            | 1.96   | 1.93   | 1.96   | 1.96   | 2.03   | 2.03   |
|Electrophilicity index      | 0.44   | 0.65   | 0.85   | 3.05   | 4.68   | 4.68   |
The gap of semiconductor is less than 3 eV ($E_{\text{gap}} < 3$ eV) (Mveme et al. 2020). Therefore, Br$_4$ET brominated molecule is a good semiconductor material. On the other hand, for original molecule ET, its energy gap is more than 3 eV, we can confirm that the molecule is a good dielectric material such as reported in literature (Ejuh et al. 2016, 2017; Veved et al. 2020; Parthasarathi et al. 2004). Based on our results, we can conclude that our proposed materials are very reactive because they have low values of ionization energy. Moreover, the chemical hardness ($\eta$) values obtained describe the chemical stability and reactivity of these compounds. Also, negative chemical potential ($\mu$) values of molecules obtained confirm the stability of the molecules. We can conclude that our new molecules are stable and reactive.

The HOMO–LUMO diagram given in Figs. 3 and 4, show a good charge distribution on the double bond in the ethylene group of the undoped molecule as well as for the doped molecules. In addition, 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. Based on these results, our materials are good candidate to find application in electronic devices.

### 3.4 Optoelectronic properties

Optoelectronic properties of the molecules (ET, Cl$_4$ET and Br$_4$ET), such as the polarization density ($P$), the electric field ($E$), electric susceptibility ($\chi$), dielectric constant ($\varepsilon$), the displacement vector magnitude ($D$) and the refractive index ($\eta$) are calculated in gas phase and listed in Table 4. These parameters values are computed using the Eq. 15 given above.
We observed that our computed optoelectronic properties are very different when we move from undoped to doped molecule. Moreover, this difference is slightly between the uncorrelated to the electron-correlated level of theory. Therefore, high values of the electric field...
E, the electric susceptibility $\chi$, refractive index ($\eta$) and low value of dielectric constant $\varepsilon$ of doped systems find applications in optoelectronic materials. Such as charge storage, optoelectronic and photonic devices etc.

3.5 Thermodynamic properties

Thermodynamic properties of the molecules (ET, Cl4ET and Br4ET), 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) are calculated at room temperature of 298.15 K and a pressure of 1 atm. These results reveal that molecules doped with chlorine and bromine have a lower total energy than the undoped molecule (C10H8S8). On the other hand, the variation of the thermodynamic properties such as entropy, enthalpy and specific heat depend on the effect of correlation of electrons taking in to account in the both level of theory used to compute these standard thermodynamics parameters. This difference is observed when going from the HF/cc-pVDZ to the B3LYP/cc-pVDZ. 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 works reported by others authors in literature (Ejuh et al. 2018a, b; Tchangnwa Nya et al. 2017; Mveme et al. 2020).

4 Conclusion

Theoretical studies of NLO, electronic, optoelectronic and thermodynamic properties were performed in gas phase using ab-initio and DFT methods to decipher some important properties of considered materials. Our goal was to investigate the effect or influence of

| Properties     | C10H8S8 | C10H8S8 Cl4 | C10H8S8 Br4 |
|----------------|---------|-------------|-------------|
|                | RHF     | B3LYP       | RHF         | B3LYP       | RHF       | B3LYP       |
| Eelec (a.u)    | −3563.51| −3571.49    | −5399.14    | −5409.91    | −13,850.69| −13,865.66  |
| ZPVE (kcal/mol)| 107.66  | 99.09       | 81.60       | 74.16       | 79.69     | 72.40       |
| E × 10³ (kcal/mol) | −2236.03| −2241.05    | −3387.93    | −3394.70    | −8691.34  | −8700.76    |
| H × 10³ (kcal/mol) | −2236.02| −2241.04    | −3387.91    | −3394.69    | −8691.32  | −8700.75    |
| G × 10³ (kcal/mol) | −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⁻¹) | 64.68   | 69.38       | 79.82       | 85.22       | 81.92     | 87.20       |
| S (cal/mol k⁻¹)  | 144.18  | 148.47      | 166.17      | 173.61      | 176.75    | 184.62      |
doping with halogen atoms such as chlorine and bromine atoms on the original molecule of BEDT-TTF. 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 atoms show more interesting properties. Also, higher first and second molecular hyperpolarizabilities ($\beta$ and $\gamma$) make these doped molecules to find applications in the field of optoelectronic devices as active NLO materials. In fact, we presented for the first time the result of hydrogen atoms substitution with chlorine and bromine atoms on BEDT-TTF ($C_{10}H_8S_8$). The materials obtained are a good candidate to find application in modern and emerging technologies. The HOMO–LUMO energy gap obtained lead us to believe that BEDT-TTF and its derivatives are good semiconductor materials, which can be used in photovoltaic cells, light emitting diode (LED) and in the field effect transistor (FET). Finally, thermodynamic parameters computed are in agreement with the work of other researchers.

References

Allen, F.H.: The Cambridge structural database: a quarter of a million crystal structures and rising. Acta Cryst. B 58, 380 (2002)
Anu, S., et al.: Density functional theory calculations for electronic, optoelectronic and thermodynamic properties of dibenzothiophene metal complexes. Mater. Res. Express 7, 016311 (2020). https://doi.org/10.1088/2053-1591/ab6922
Becke, A.D.: Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A 38, 3098–3101 (1988)
Bouchouit, K., et al.: $\chi^{(2)}$ grating in ru derivative chromophores incorporated within the PMMA polymer matrices. J. Phys. Chem. B 108(39), 14942–14947 (2004)
Costa, S.N., et al.: DFT calculations with van der Waals interactions of hydrated calcium carbonate crystals CaCO$_3$(H$_2$O, 6H$_2$O): structural, electronic, optical, and vibrational properties. J. Phys. Chem. A 120, 5752–5765 (2016)
Demiralp, E., Dasgupta, S., William, A., Goddard, I.I.I.: Electron-transfer boat-vibration mechanism for superconductivity in organic molecules based on BEDT-TTF. J. Am. Chem. Soc. 117, 8154–8158 (1995)
Demiralp, E., Dasgupta, S., William, A., Goddard, I.I.I.: MSX force field and vibrational frequencies for BEDT-TTF (neutral and cation). J. Phys. Chem. A 101, 1975–1981 (1997)
Dennington, R.T., Keith, J.M.: Gauss view, version 6. Semichem Inc, Shawnee Mission (2016)
Ejuh, G.W., Samuel, N., Tchangnwa Nya, F., Ndjakà, J.M.B.: Computational determination of the electronic and nonlinear optical properties of the molecules 2-(4aminophenyl) quinoline, 4-(4-aminophenyl) quinoline, anthracene, anthraquinone and phenanthrene. Mater. Lett. 178, 221–226 (2016). https://doi.org/10.1016/j.matlet.2016.04.097
Ejuh, G.W., Tchangnwa Nya, F., Ottou Abe, M.T., Jean-Baptiste, F.F., Ndjakà, J.M.B.: Electronic structure, physico-chemical, linear and nonlinear optical properties analysis of coronene, 6B-, 6N-, 3B3N-, substituted C24H12 using RHF, B3LYP and wB97XD methods. Opt. Quant. Electron. 49, 382 (2017). https://doi.org/10.1007/s10771-017-2121-2
Ejuh, G.W., Ottou Abe, M.T., Ghiulsain, T., Ndjakà, J.M.B.: Ab initio and DFT studies on the donor–acceptor molecules 1,2,3-trihydroxy-9,10-antraquinone; 1(methylamino)antraquinone; 2-phenyl quinoxaline and 2-(4-aminophenyl) quinoxaline. Mater. Focus 7, 37–44 (2018a). https://doi.org/10.1166/mat.2018.1473
Ejuh, G.W., Ottou Abe, M.T., Tchangnwa Nya, F., Ndjakà, J.M.B.: Prediction of electronic structure, dielectric and thermodynamical properties of flurbiprofen by density functional theory calculation. Karbala J. Mod. Sci. 4, 12–20 (2018b)
Ejuh, G.W., et al.: Theoretical study on the electronic, optoelectronic, linear and non linear optical properties and UV–Vis spectrum of coronene and coronene substituted with chlorine. SN Appl. Sci. 2, 1247 (2020). https://doi.org/10.1007/s42452-020-3028-1
El Kouari, Y., et al.: Computations of absorption spectra and nonlinear optical properties of molecules based on anthocyanidin structure. Opt. Quantum Electron. 47(5), 1091–1099 (2015). https://doi.org/10.1007/s11082-014-9965-4

Eldridge, J.E., Homes, C.C., Williams, J.M., Kini, A.M., Wang, H.H.: The assignment of the normal modes of the BEDT-TTF electron-donor molecule using the infrared and raman spectra of several isotopic analogs. Spectrochim. Acta 51A(6), 947–960 (1995)

Fankam, J.B., Ejuh, G.W., Tchangnwa Nya, F., Ndjaka, J.M.B.: Theoretical investigation of the vibrational spectra and thermodynamic properties of 4,5-dibromo-2,7-dinitro-fluorescein. Opt. Quantum Electron. 52, 292 (2020a). https://doi.org/10.1007/s11082-020-02396-4

Fankam, J.B., Ejuh, G.W., Tchangnwa Nya, F., Ndjaka, J.M.B.: Study of electronic structure, optoelectronic, linear and nonlinear optical properties and chemical descriptors of dibromodinitrofluorescein isomers in gas phase and solvent media using ab initio and DFT methods. Chin. J. Phys. (2020b). https://doi.org/10.1016/j.cjph.2020.05.015

Fonkem, C.C., Ejuh, G.W., Tchangnwa Nya, F., Yossa Kamsi, R.A., Assatse, T., Ndjaka, J.M.B.: A density functional theory (DFT) study of the doping effect on 2-cyano-3-[4 (diphenylamino) phenyl] acrylic acid. Chin. J. Phys. (2019). https://doi.org/10.1016/j.cjph.2019.11.010

Frisch, M.J., et al.: Gaussian 09, revision A 1. Gaussian, Inc., Wallingford CT (2009)

Guionneau, P., Chasseau, D., Judith Howard, A.K., Dayc, P.: Neutral bis(ethylendithio)tetrathiafulvalene at 100 K. Acta Cryst. C 56, 453–454 (2000)

Imamura, Y., Ten-no, S., Yonemitsu, K., Tanimura, Y.: Structures and electronic phases of the bis(ethylendithio)tetrathiafulvalene (BEDT-TTF) salts: a theoretical study based on ab initio molecular orbital methods. J. Chem. Phys. 111, 5986 (1999). https://doi.org/10.1063/1.479894

Kabé, C., Tchangnwa Nya, F., Ejuh, G.W., Ndjaka, J.M.B.: Comparative study of optoelectronic, thermodynamic, linear and nonlinear optical properties of methyl phenalenyl doped to zinc and copper and their applications. J. Mater. Sci. Mater. Electron. 31, 7898–8790 (2020). https://doi.org/10.1007/s10854-020-03328-4

Kozlov, M.E., Pokhodnya, K.I., Yurchenko, A.A.: The assignment of fundamental vibrations of BEDT-TTF and DFT-d8. Spectrochim. Acta 43A, 323 (1987)

Kulyk, B., et al.: Functionalized azo-based iminopyridine rhenium complexes for nonlinear optical performance. Dyes Pigments 145, 256–262 (2017). https://doi.org/10.1016/j.dyepig.2017.06.012

Lee, C., Yang, W., Parr, R.C.: Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev B 37, 3098–3101 (1988)

Liu, R., Zhou, X., Kasmai, H.: Toward understanding the vibrational spectra of BEDT-TTF, a scaled density functional force field approach. Spectrochim. Acta Part A 53, 1241–1256 (1997)

Mveme, C.D.D., Tchangnwa Nya, F., Ejuh, G.W., Kamsi, R.A.Y., Ndjaka, J.M.B.: Density functional theory study of optoelectronic, nonlinear optical, piezoelectric and thermodynamic properties of poly(3,4-ethylenedioxythiophene), poly(3,4-ethylenedioxythiophene) and their derivative. Opt. Quantum Electron. 52, 373 (2020). https://doi.org/10.1007/s11082-020-02492-5

Olinga, M.G.F., Ottou Abe, M.T., Ntieche, Z., Ejuh, G.W., Ndjaka, J.M.B.: Ab initio investigation of nonlinear optical, electronic, and thermodynamic properties of BEDT-TTF molecule: doping with boron. Heliyon (2021). https://doi.org/10.1016/j.heliyon.2021.e07461

Parthasarathi, R., Padmanabhan, J., Elango, M., Subramanian, V., Chattaraj, P.: Intermolecular reactivity through the generalized philicity concept. Chem. Phys. Lett. 394, 225–230 (2004)

Saji, R.S., Prasana, J.C., Muthu, S., George, J.: Spectroscopic and quantum computational study on naproxen sodium. Spectrochim. Acta Part A Mol. Spectros. 226, 117614 (2020)

Shakerzadeh, E., Tahmasebi, E., Biglari, Z.: A quantum chemical study on the remarkable nonlinear optical and electronic characteristics of boron nitride nanoclusters by complexation via lithium atom. J. Mol. Liq. 221, 443–445 (2016)

Sharaoui, Y.B., et al.: Nonlinear optics and surface relief gratings in alkynyl–ruthenium complexes. J. Opt. A Pure Appl. Opt. 11(2), 024005 (2009). https://doi.org/10.1088/1464-4258/11/2/024005
Spiridon, M.C., et al.: Novel pendant azobenzene/polymer systems for second harmonic generation and optical data storage. Dyes Pigments 114, 24–32 (2015)
Sundaraganesan, N., Illakiamani, S., Meganathan, C., Joshua, B.D.: Vibrational spectroscopy investigation using \textit{ab initio} and density functional theory analysis on the structure of 3-aminobenzotrifluoride. Spectrochim. Acta Part A 67, 214–224 (2007)
Tchangnwa Nya, F., Ejuh, G.W., Ndjaka, J.M.B.: Theoretical study of optoelectronic and thermodynamic properties of molecule 4-[2-(2-N, N-dihydroxy amino thiophene)vinyl] benzanamine: influence of hydroxyl position. Mater. Lett. 202, 89–95 (2017)
Veved, A., Ejuh, G.W., Djongyang, N.: Study of the chemical softness, chemical hardness, chemical stability and interaction energy of the piezoelectric composite: (−CH$_2$−CF$_2$−)$_n$HfO$_2$. Polym. Bull. (2020). https://doi.org/10.1007/s00289-020-03346-6
Wallis, J.D., Griffiths, J.P.: Substituted BEDT-TTF derivatives: synthesis, chirality, properties and potential applications. J. Mater. Chem. 15, 347–365 (2005). https://doi.org/10.1039/b412561b
Yossa, R.A., Ejuh, K.G.W., Nkounga, P., Ndjaka, J.M.B.: Study of the molecular structure, electronic and chemical properties of Rubescin D molecule. Chin. J. Phys. 60, 104–121 (2020)

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