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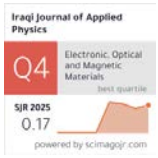

Optimized Properties of Electronic Structure of BEDT-TTF Molecules

The objective of this paper is to report a study on the electronic properties of BEDT-TTF, one of the most important organic semiconductors, by means of density functional theory (DFT) techniques in the DMol3 code. The optimized molecular structure was used to perform this calculation, and three exchange–correlation functionals (LDA-PWC, GGA-PBE, hybrid B3LYP) were employed to access the frontier molecular orbitals (HOMO and LUMO). Sensitivity differences were significant in the energy gap, and the B3LYP model was closer to reality and superior for electronic stability as well as reactivity prediction. According to the computations, due to its narrow band gap and a large π–conjugated system, the compound should have high electronic conduction performance, which has also been proved in solid-state physics for those organic superconducting salts. The study demonstrates the significance of theoretical modeling in understanding electron transport mechanisms and influencing future development of new derivatives for organic electronic applications.

Keywords: Organic semiconductors; Density functional theory; BEDT-TTF; Frontier molecular orbitals

1. Introduction

Bis(ethylenedithio)tetrathiafulvalene, or BEDT-TTF for short, is a chemical compound that exhibits metallic conduction and has the molecular formula $C_{10}H_8S_8$ with molar mass 384.7 g/mol [1]. The compound belongs to tetrathiafulvalene (TTF) based donor in the planar conjugated system, and modified with two ethylenedithio groups [2], as shown in Fig. (1).

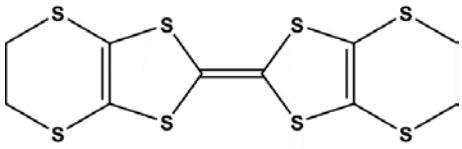

Fig. (1) Chemical structure of the BEDT-TTF molecule

BEDT-TTF is a key organic molecule and has been well-studied in the context of molecular electronics (particularly with respect to organic conductors, superconductors [3]). It was first prepared in the late 1970s and early 1980s and quickly become known for its propensity to produce charge transfer salts with unusual electrical and magnetic characteristics [4]. Metallic and superconducting properties at low temperatures of these salts are unusual features for organic substances [5] and, therefore, the discovery of these new materials is a crucial step in creating organic electronic materials.

BEDT-TTF is well known as an electron-donor molecule that forms a charge-transfer salt with various inorganic anions [6]. These salts generally crystallize in a laminar arrangement, most suitable of the BEDT-TTF being conducting layers, and those of anion were insulating layers [7]. The anion type and generator molecules configuration have great influence on the electronic character of these materials, that can be insulating on top of semiconducting to conducting and even superconducting states [8].

BEDT-TTF has been a revolutionary discovery and development in the history of organic electronics. Its capability to produce a variety of charge-transfer complexes has made it an important model compound for the study of organic superconductivity, low-dimensional conductors and molecular magnetism. Thus, BEDT-TTF-based materials are highly valuable for molecular electronics, sensors and devices that utilize controllable electronic and magnetic properties [9].

The study of the frontier molecular orbitals (HOMO/LUMO) and the energy gap is especially useful for elucidating the electronic characteristics in conducting organic materials like BEDT-TTF. The location of these orbitals contributes to indicating the molecule's electro-donating/accepting character, and when the energy gap is calculated, it gives direct information about electronic activity as well as in making a decision between whether or not a compound may shift from a semiconducting state of matter to that of metal [10]. Furthermore, investigation of global chemical reactivity descriptors offers information about overall stability and reactivity of the molecule [11].

With the spectacular progress in quantum computing during the past decades, theoretical studies have become indispensable tools to interpret structural and electronic properties of chemical compounds. In this context, the Density Functional Theory (DFT) has become one of the most popular and successful formalisms due to its trade-off between computational accuracy and numerical efficiency when compared with conventional wavefunction-based approaches [12]. Achievement in these aspects has allowed to provide optimized geometries, molecular orbital energies (HOMO/LUMO) and electronic band gap

values, at the same time predicting vibrational and thermodynamic traits quite accurately [13]. These advances have had a profound influence on research of organic conductors by making it possible to match theoretical results with experimental spectroscopic and conductivity data, thereby assisting in the understanding electron transport processes and in the design of new substances with improved properties.

In present work, we report the computation and analysis of frontier molecular orbitals (HOMO and LUMO), energy gap (ΔE_g) of BEDT-TTF as well as the assessment of global chemical reactivity descriptors involving ionization potential (IP), electron affinity (EA), hardness (η), softness (S), electronegativity (χ) and electrophilicity index (ω). Such calculations are performed in order to examine the feasibility of BEDT-TTF as a high-performance electron donor for organic semiconductors.

2. Theoretical Background

Frontier molecular orbital (FMO) theory represents the basis for understanding extended conjugated systems and their response to light. The two critical FMOs out of the viewport are the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). The HOMO refers to the highest occupied energy level of the electrons and that of LUMO is the lowest unoccupied molecular orbital upon excitation [14,15] - as shown in Fig. (2) [16].

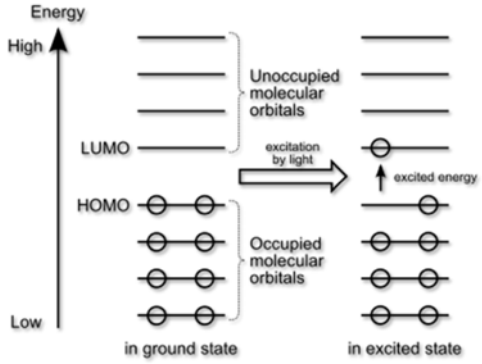

Fig. (2) Schematic representation of a molecule illustrating the HOMO and LUMO

The circles represent an electron in an orbital; here the HOMO absorbs light of high enough frequency to fill the LUMO. The energy difference of the two orbitals is of pivotal importance for molecule stability, reactivity and optical performance [17]. The band gap is vital for the study of many phenomena, such as conduction, optical properties and chemical reactivity. Usually, the compound with a higher energy gap is more thermodynamically stable since the HOMO-LUMO electron transition energy becomes energetically less favored. On the contrary, smaller energy gap indicates higher reactivity and electron mobility, so a better material with elect and photo application escalation [18].

Chemical reactivity parameters constitute a set of quantitative descriptors that characterize the chemical behavior of molecules based on their electronic properties. Among the most significant of these parameters are:

(1) Ionization Potential (IP), which is a fundamental property in the study of chemical reactivity, representing the minimum energy required to remove an electron from a neutral atom or molecule, thereby forming a positively charged ion [19]. It can be calculated as:

$$IP=-E_{HOMO} \quad (1)$$

where E_{HOMO} is the energy of the highest occupied molecular orbital.

(2) Electron Affinity (EA), is an important measure that helps us to understand the reactivity of atoms and molecules, as it indicates their tendency toward attracting more electrons. Quantitatively, it is the amount of energy required to remove one electron from a neutral atom, or the energy released when an electron is added to a neutral atom to form a negative ion. Electron affinity can be calculated from the LUMO energy by means of Density Functional Theory (DFT) combined with Koopmans' theorem. By this theorem, the negative of energy should approximately be the electron affinity [20,21]:

$$EA=-E_{LUMO} \quad (2)$$

where E_{LUMO} is the energy of the lowest unoccupied molecular orbital

(3) Chemical Hardness (η), is a key parameter in theoretical and computational chemistry that offers insights into the molecular reactivity and stability. This quantity is usually referred to as a species ability of resisting the variation in its electron density [22], with an equation derived from Density Functional Theory (DFT) (watch out). Strictly, chemical hardness is to be considered as the first derivative of the E w.r.t. neutron number at constant external potential (HALF-neutron):

$$\eta = \frac{IP-EA}{2} \quad (3)$$

(4) Chemical Softness (S), on the other hand, is a measure of molecular reactivity and provides the information about how easily charge can be transferred in a molecule. In DFT, softness is also closely related to how a molecule responds to changes in electron density which implies how reactive the molecule would be [23]. From a mathematical point of view, chemical softness is the reciprocal allocation of chemical hardness and information concerning electron spread:

$$S = \frac{1}{\eta} \quad (4)$$

(5) Chemical Potential (μ), is the basis of understanding chemical reaction and thermodynamic process in many fields (physical chemistry, materials science etc.) [24]. It is the variation of the free energy of a system after adding an infinitesimal amount of

matter [25]. In the limit of heavy negative doping, the chemical potential can be well-approximated by ionization potential and electron affinity:

$$\mu = \frac{IP+EA}{2} \quad (5)$$

(6) Electronegativity (χ), is a central concept in chemistry, describing the tendency of an atom within a molecule to attract electrons, which influences chemical bonding and reactivity. Introduced by Linus Pauling nearly a century ago [26], it can be defined mathematically as:

$$\chi = -\mu = \frac{\mathrm{IP+EA}}{2} \quad (6)$$

(7) Electrophilicity (ω) quantifies a molecule's or atom's ability to accept electrons during a chemical reaction [27]. It is expressed as:

$$\omega = \frac{\mu^2}{2\eta} \quad (7)$$

where μ is the chemical potential and η is the chemical hardness. Maynard et al. and Parr et al. provided a unified definition of electrophilicity, highlighting its dual nature through kinetic and thermodynamic pathways [28]

3. Methodology

In this work, the structural, electronic and vibrational properties of the BEDT-TTF molecule were studied by means of a set of DFT calculations carried out using the DMol³ code [9]. All calculations were performed using three exchange correlation functionals, namely (i) LDA-PWC, (ii) GGA-PBE and (iii) hybrid B3LYP functional for comparison of the molecular properties. We performed geometry optimization using very similar numerical settings and slightly adjusted symmetry settings and functional parameters to better describe the electronic structure of BEDT-TTF for each functional. In a stable structure, the observation of positive vibrational frequencies is a criterion [29,30]. Geometry optimization is performed to guarantee the reliability of HOMO–LUMO gap analysis and charge distribution calculations, inhibiting distortion in theoretical consideration. Thus, geometry optimization is regarded as an indispensable step in any trustworthy evaluation of molecular properties. The optimized, balanced, and stable geometry is given in Fig. (3).

4. Results and Discussion

The main electronic characteristics of the BEDT-TTF molecule that are relevant to the area of organic electronics have been calculated with three methods: LDA-PWC, GGA-PBE and B3LYP. The HOMO and LUMO were analyzed in this study, and we compared our results with previous reported data.

The data expose some interesting trends among the methods. Notably, although the lowest energy of HOMO orbitals by B3LYP is at -4.723 eV, GGA-PBE yields the highest one at that level of -4.122 eV (see table 1). LDA-PWC is in between with -4.254 eV. The same trend is observed for the LUMO energies: while the highest are obtained with B3LYP (-1.229 eV), the lowest ones with LDA-PWC (-2.084 eV) according to table (1).

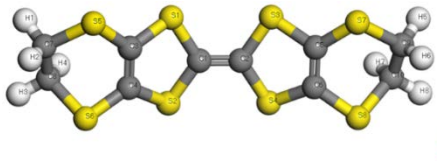

Fig. (3) Geometry-optimized BEDT-TTF molecule obtained using the DMol³ program

Table (1) HOMO and LUMO energies and the corresponding energy gap of the BEDT-TTF molecule calculated using LDA-PWC, GGA-PBE, and B3LYP functionals

Molecular Orbital (eV)	LDA-PWC	GGA-PBE	B3YLP	Previous Work [31]
HOMO Energy	-4.245	-4.122	-4.723	-4.77
LUMO Energy	-2.084	-1.949	-1.229	-0.96
Energy Gap	2.161	2.173	3.494	3.81

Notice that the LDA-PWC and GGA-PBE functionals underestimate much the energy gap (2.161 eV and 2.173 eV, respectively) when compared to B3LYP (3.494 eV) and reference value (3.81 eV). The energy gap is strongly correlated with properties such as molecular reactivity and conductivity; therefore, the functional choice will ultimately be pivotal to these property predictions. These results suggest LDA-PWC and GGA-PBE might not be appropriate for accurate electronic structure calculations of the BEDT-TTF molecule even if they are computationally efficient. By comparison, as a hybrid functional, B3LYP performed better than BP. Thus to study BEDT-TTF or related instead systems a careful choice of XC functionals with the DFT is necessary in order to obtain trustworthy results.

Quantum chemical descriptors based on the HOMO and LUMO energy levels permit a quantitative determination of the electronic nature of the molecule. Herein, we studied the ionization potential (IP), electron affinity (EA), chemical hardness (η), chemical softness (S), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) of the BEDT-TTF molecule as they are computed in the context of varied functionals-LDA-PWC and GGA-PBE- B3LYP DFT Approximations.

The ionization potentials (IP), as given by the negative of HOMO energy, show that B3LYP predicts the largest value (4.723 eV) and very close to the reported one [38] 4.77 eV, while GGA-PBE and LDA-PWC give lower values 4.122 eV for IP-GGA and 4.245 eV for IP-LDA in units of eV. For the electron affinity, given by the negative LUMO energy), all methods provide larger values compared to the prior work (0.96 eV). LDA-PWC has the largest EA (2.084

eV), while lowest value is obtained with B3LYP functional (1.229eV) as shown in table (2).

Table (2) Calculated chemical reactivity parameters of the BEDT-TTF molecule using DFT with LDA-PWC, GGA-PBE, and B3LYP functionals

Parameters	LDA-PWC	GGA-PBE	B3YLP	Ref. [31]
Ionization Potential (IP) (eV)	4.245	4.122	4.723	4.77
Electron Affinity (EA) (eV)	2.084	1.949	1.229	0.96
Chemical Hardness (η) (eV)	1.0805	1.0865	1.747	1.910
Chemical Softness (S) (1/eV)	0.9255	0.9204	0.5724	0.52
Chemical Potential (μ) (eV)	-3.1645	-3.0355	-2.976	-2.86
Electronegativity (χ) (eV)	3.1645	3.0355	2.976	2.86
Electrophilicity Index (ω) (eV)	4.633	4.24	2.535	2.14

These findings highlight the significance of method choice in computational chemistry, in particular for electronic properties prediction of organic molecules. It is worth mentioning that the EA values predicted by B3LYP are lyrics when compared to previously reported results for this tensor. The discrepancies between the methods, as well as comparison with previous work this are likely pointing towards the need for additional studies (possibly even experimental) to properly understand the electronic properties of BEDT-TTF. This work has significance for those investigating organic electronics, and suggests the importance of the computational methods selected when researching these systems.

For the other chemical reactivity parameters (η, S, μ, χ and ω) the lower panels of Fig. (4) show that the chemical hardness (η) equals to $1/2(\varepsilon_H - \varepsilon_L)$, which is a resistance of the electron cloud to distortion indicates that B3LYP run (1.747 eV) and previous study result (1.910 eV) predicts ethylene-dithiolate as more stable molecule while hard GGA-PBE and LDA-PWC predict ridged ethylene dithiolate with higher value compared to B3LYP results. On the other hand, softness (S), which is for hardness inversely proportional and pertains to polarizability, its reverse trend can be seen: LDA-PWC (10.9255 eV^{-1}) and GGA-PBE (10.9204 eV^{-1}) values show higher value of polarizability than B3LYP (10.5724 eV^{-1}) and previous work (10.52 eV^{-1}).

The chemical potential (μ), which is a reflection of the escaping tendency of electrons, is most negative in LDA-PWC (-3.1645 eV) and it can be concluded that it provides a further preference to donate electrons than GGA-PBE (-3.0355 eV), B3LYP (-2.976 eV), and the previous work (-2.86 eV). Correspondingly, the electronegativity (χ), meaning the ability to attract electrons (the negative of μ), behaves in a contradictory manner It increases when going from LDA-PWC (3.1645 eV) that is less potent as an electron-attraction center toward the previous work (2.86 eV) that predicts highest such potency.

The electrophilicity index (ω), an indicator of the electron-accepting fliestadon, concludes that LDA-PWC has the highest value (4.63 eV) and is the most electronegative while GGA-PBE (4.24 eV) < B3LYP (2.535 eV) < present study (2.14 eV). The differences in the descriptors among different DFT methods underline a great importance of the method choice and its comparison with experimental studies. However, the relative trends from this reactivity study still allow new insight into the reactivity of BEDT-TTF.

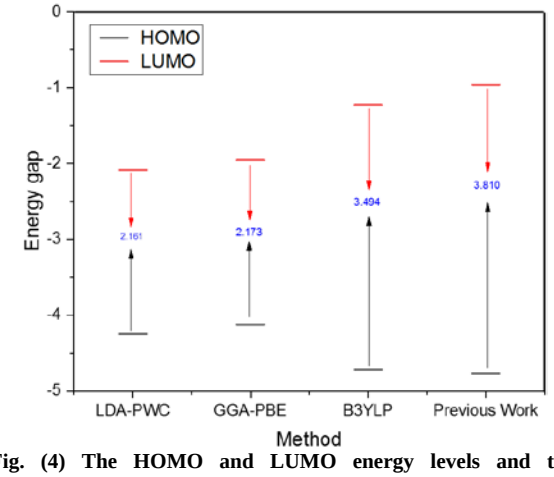

Fig. (4) The HOMO and LUMO energy levels and the corresponding energy gap of the BEDT-TTF molecule calculated using the LDA-PWC, GGA-PBE, and B3LYP functionals

5. Conclusion

Theoretically, the DFT method could be reliable to describe the electronic properties of this class of organic conductor. The calculated HOMO energies of BEDT-TTF agreed with previous reports, and provide further evidence for the molecule's suitability as an electron donor. The energy band gap calculated from B3LYP is the most approximate to the reference (3.81 eV), showing that this functional best describes semiconducting behavior of compound. Further, B3LYP computed IP and EA are in good agreement with available data, endowing the molecule to act as an efficient electron donor. The molecule has a moderate chemical hardness and good softness in addition to high electrophilicity, which contributes to its stability and effectiveness for charge transfer processes. These results all together indicate that BEDT-TTF is a promising electron donor with electronic properties and our calculated gap corresponding to its considerable energy gap as an organic semiconductor for conductive material.

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