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Investigation of The Geometric, Electronic, Vibrational, And Thermodynamic Properties of the BEDT-TTF Molecule Using the DFT Method

B. Kh. Atadjanov

Karakalpak Research Institute for Natural Sciences of Karakalpak Branch of the Uzbekistan Academy of Sciences, Republic of Uzbekistan, Nukus

Zh. A. Zhaksimuratov

Karakalpak Research Institute for Natural Sciences of Karakalpak Branch of the Uzbekistan Academy of Sciences, Republic of Uzbekistan, Nukus

Kh. Sh. Adilova

Karakalpak Research Institute for Natural Sciences of Karakalpak Branch of the Uzbekistan Academy of Sciences, Republic of Uzbekistan, Nukus

Kh. S. Primov

Karakalpak Research Institute for Natural Sciences of Karakalpak Branch of the Uzbekistan Academy of Sciences, Republic of Uzbekistan, Nukus

B. Zh. Narymbetov

Karakalpak Research Institute for Natural Sciences of Karakalpak Branch of the Uzbekistan Academy of Sciences, Republic of Uzbekistan, Nukus

U. K. Ernazarov

Karakalpak Research Institute for Natural Sciences of Karakalpak Branch of the Uzbekistan Academy of Sciences, Republic of Uzbekistan, Nukus

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Abstract: In this work, the geometric, electronic, vibrational, and thermodynamic properties of the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecule, used as an important donor in the chemistry of organic molecular conductors, were investigated within the framework of density functional theory (DFT). The calculations were performed using the ORCA 6.0 program at the PBE0/def2-TZVP level with the D3BJ dispersion correction. The absence of negative vibrational frequencies in the optimized structure indicates that it corresponds to a local minimum on the potential energy surface. For the frontier molecular orbitals, the HOMO and LUMO energies were −4.955 and −0.955 eV, respectively, while the Kohn–Sham HOMO–LUMO energy difference was ≈4.01 eV. Mulliken charges and Mayer bond orders showed the delocalized character of the electron density in the molecular core. In the calculated IR spectrum, the modes in the regions of 810.93, 1323.38, and 1583.55 cm^{-1} were identified as characteristic vibrations. At a temperature of 298.15 K and a pressure of 101.325 kPa, the Gibbs free energy was −3570.00008156 Eh. The obtained results characterize the features of the electronic structure of the neutral BEDT-TTF molecule in the isolated state and provide a theoretical basis for discussing its donor nature at the molecular level.

Keywords: BEDT-TTF, DFT, PBE0, HOMO–LUMO, IR spectrum, Gibbs free energy.

Introduction: Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) is one of the most extensively studied electron-donor molecules among tetrathiafulvalene derivatives, and its radical cation salts form a large family of low-dimensional organic conductors, metals, and superconductors. In BEDT-TTF-based crystals, the electronic properties depend strongly not only on the donor molecule itself, but also on the relative arrangement of donor molecules in the crystal, their dimerization, and intermolecular transfer integrals [1–4]. Therefore, an accurate description of the equilibrium geometry and electronic structure of an isolated BEDT-TTF molecule provides a fundamental theoretical model for understanding complex systems in the crystalline state.

From a conformational point of view, the BEDT-TTF molecule is not strictly limited to a planar structure. For the neutral donor, a boat-like deformation and a conformation close to C_2 symmetry have previously been discussed using theoretical and vibrational analyses [5]. In addition, extensive identification of the normal vibrational modes of BEDT-TTF has been carried out based on IR and Raman spectra, as well as isotope substitution studies [6,7]. These data are important for establishing the relationship between the calculated vibrational frequencies and the actual structural features of the molecule.

The DFT approach has been effectively applied to describe the structural and electronic properties of BEDT-TTF and its charge-transfer salts. In particular, molecular and periodic DFT calculations have revealed the electronic state of the donors and the influence of their mutual arrangement in the crystal on their properties [2,3]. At the same time, a comprehensive consideration of the geometry, frontier orbitals, atomic charges, bond orders, IR modes, and thermodynamic functions of an isolated neutral BEDT-TTF molecule at the same level of theory allows the obtained results to be interpreted in an interconnected manner.

In BEDT-TTF-based organic conductors, the donor properties of the molecule are determined by the π-electron system of the central tetrathiafulvalene core. The large number of sulfur atoms creates conditions for the distribution of orbital density over a wider region. Therefore, geometric relaxation, the state of the C=C and C–S bonds, as well as the energies of the frontier orbitals are considered as interrelated parameters. The study of the isolated molecular state provides a convenient theoretical basis for the subsequent evaluation of changes in its salts and crystalline forms.

In previously conducted studies, the structure of BEDT-TTF, normal vibrational modes, and electronic properties in charge-transfer salts have been analyzed using various methods [1–7]. An interconnected analysis of the geometry, HOMO–LUMO states, atomic charges, bond orders, IR spectrum, and thermodynamic functions obtained at the same level of theory makes it possible to present the electronic structure of the molecule in an integrated manner. In the present work, this approach was applied.

The aim of the present work is to provide an interconnected analysis of the equilibrium geometry of the neutral BEDT-TTF molecule, frontier molecular orbitals, Mulliken charges and Mayer bond orders, IR-active vibrational modes, as well as thermodynamic functions under standard conditions, based on the available results of quantum chemical calculations.

METHODS

The initial three-dimensional model of the BEDT-TTF molecule was created using the Avogadro software. All quantum chemical calculations were performed using the ORCA 6.0 program package [8]. The geometry was fully optimized using the PBE0 hybrid functional [9] and the def2-TZVP basis set [10]. To account for long-range dispersion interactions, the D3 dispersion correction with Becke–Johnson damping was applied [11,12].

After geometry optimization, the vibrational frequencies were calculated. The absence of negative (imaginary) frequencies was taken as a criterion for verifying that the optimized structure corresponds to a local minimum on the potential energy surface. To characterize the electronic structure, the HOMO and LUMO energies, Mulliken atomic charges, as well as Mayer valences and bond orders were analyzed [13]. The frequencies and intensities of the IR-active modes were calculated. Thermochemical quantities were obtained from the ORCA output data at a temperature of T = 298.15 K and a pressure of P = 101.325 kPa.

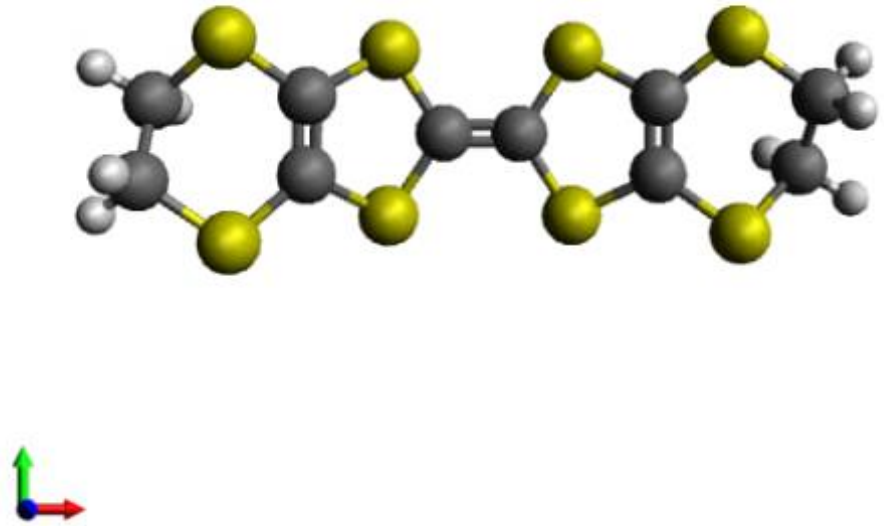


Fig. 1. Initial model of the BEDT-TTF molecule.

RESULTS AND DISCUSSION

Geometry and Conformational Features: During geometry optimization, relaxation of the BEDT-TTF framework relative to the initial structure was observed. Changes in the coordinates of the central tetrathiafulvalene moiety and the peripheral ethylene groups indicate a deviation of the molecule from a strictly planar model. The calculated equilibrium structure exhibits a boat-like deformation, which is consistent with the C_2-type conformation previously proposed for neutral BEDT-TTF based on theoretical vibrational analysis [5].

The spatial relaxation observed as a result of geometry optimization indicates a reduction in the internal strain of the molecule and the formation of a stable conformation corresponding to its electronic structure. In particular, the spatial arrangement of the peripheral ethylene groups contributes to the deviation from the plane of the central TTF core. This geometry was used as the primary structure for subsequent calculations of molecular orbitals, atomic charges, and vibrational modes.

When evaluating the geometric characteristics of BEDT-TTF, not only the coordinates of individual atoms but also their overall spatial arrangement relative to one another are important. The boat-like shape of the calculated structure indicates that the molecule is not completely planar and is consistent with the conformation of neutral BEDT-TTF reported in previous theoretical studies [5]. This agreement indicates that the selected PBE0/def2-TZVP-D3BJ approach adequately reproduces the main structural features of the molecule (Table 1).

This result applies only to the optimized isolated molecule. In the crystalline state, the conformation of the molecule may change under the influence of intermolecular interactions, anions, and crystal packing [1–4]. Therefore, the calculated geometry was interpreted not as a single conformation of all BEDT-TTF fragments in the crystal, but as the equilibrium state of the neutral molecule in the gas phase (Table 1).

Table 1. Changes in the coordinates of selected atoms during geometry optimization.

Atom	Initial X	Final X	Initial Y	Final Y	Initial Z	Final Z
C(0)	−10.9731	−11.0169	−1.1512	−1.2901	2.3151	1.5796
C(4)	−1.2684	−1.2703	−0.0009	0.0151	−1.0887	−0.4344

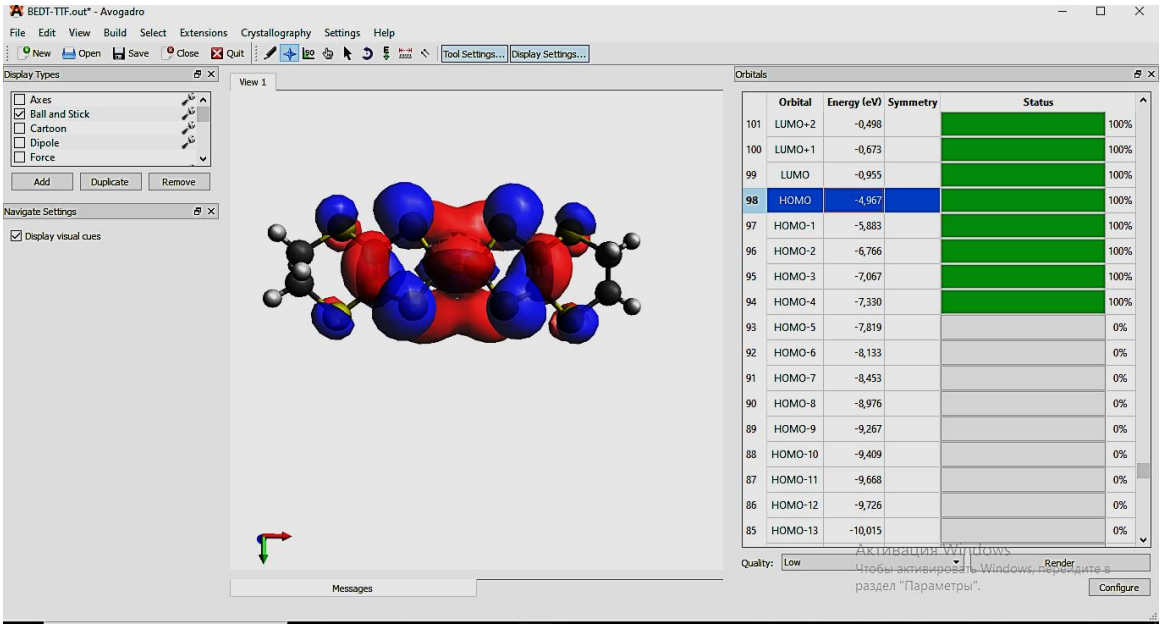
C(6)	−6.2389	−5.7868	−1.2595	−1.2275	−0.1521	0.7352
S(10)	−3.3269	−3.1055	−2.6180	−2.7305	−1.0887	−0.5137
S(14)	−8.8369	−8.1914	−3.2343	−3.2601	0.6540	1.6559

Frontier Molecular Orbitals: In the PBE0/def2-TZVP-D3BJ calculation, the HOMO energy was −4.96 eV (−0.1825 Eh), whereas the LUMO energy was −0.955 eV (−0.0351 Eh). Accordingly, the energy difference between the frontier Kohn–Sham orbitals, ΔE(HOMO–LUMO), was ≈4.01 eV (0.1474 Eh). This value was considered an important parameter characterizing the electronic structure of the neutral BEDT-TTF molecule at the selected level of theory.

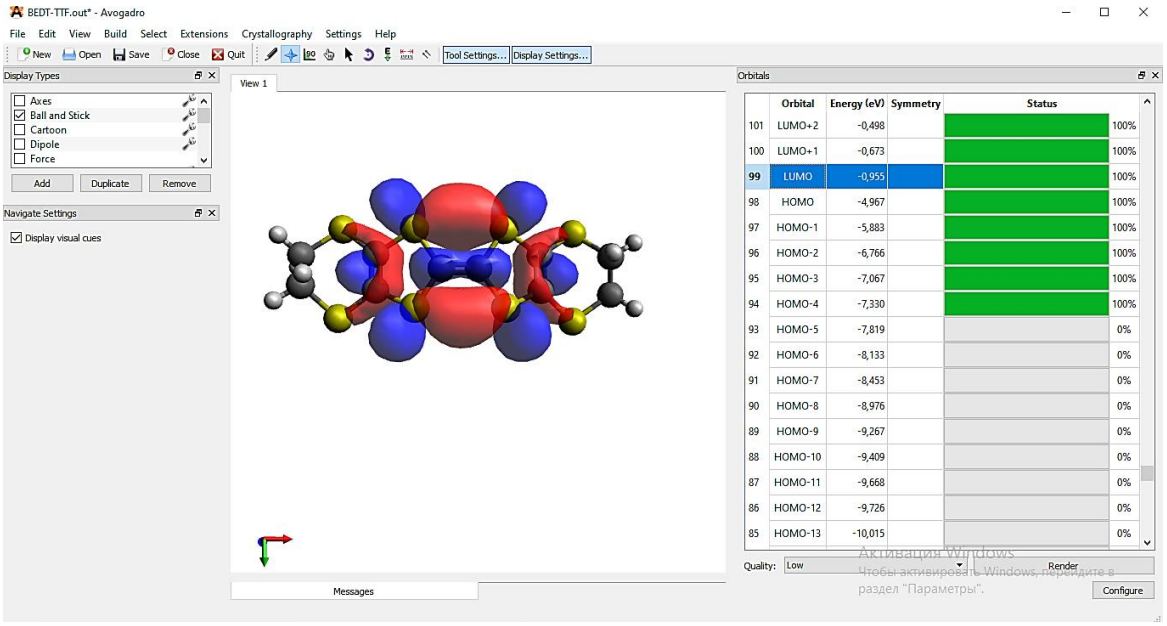
Frontier molecular orbitals are important for explaining chemical activity and electron-donating properties. The HOMO energy of −4.96 eV characterizes the energy position of the orbital capable of donating electrons, whereas the LUMO energy of −0.955 eV reflects the state of the lowest-lying vacant orbital. The difference of ≈4.01 eV between them provides information about the electronic excitability of the neutral molecule under the selected calculation conditions.

In the HOMO image, the broad distribution of electron density over the central π-system and in the region of the sulfur atoms shows that the donor center in the BEDT-TTF molecule is not limited to a single atom or a single bond. This delocalization is also manifested in the subsequent Mulliken and Mayer analyses. Thus, the results of the orbital and population analyses complement each other and show that the central TTF fragment represents an electronically interconnected system.

The electron density of the HOMO is predominantly distributed along the π-system, which includes the tetrathiafulvalene core and the sulfur atoms. Such a distribution is consistent with the electron-donor nature of the BEDT-TTF molecule. In turn, the redistribution of electron density in the LUMO state demonstrates the molecular basis of orbital changes in excited states or states associated with electron acceptance. The results obtained for the neutral molecule characterize the structure of its frontier orbitals (Fig. 2).



(a)



(b)

Fig. 2. HOMO (a) and LUMO (b) orbitals of the BEDT-TTF molecule.

Mulliken Charges and Mayer Bond Orders:

Mulliken population analysis shows a relatively high negative charge on the peripheral aliphatic carbon atoms, whereas the charge on the central C(4) and C(5) atoms is close to zero. In the calculated data, a negative charge of up to −0.0646e was recorded on the outer sulfur atoms. This charge distribution shows that, in the neutral BEDT-TTF molecule, the electron density is distributed unevenly among the atoms, while the sulfur-containing fragments make a significant contribution to the formation of the electronic state.

Although the magnitude of Mulliken charges depends on the basis set and the population analysis scheme, it is useful for identifying relative differences between atoms within the same computational approach. In the present calculation, the differences in charges between the carbon and sulfur atoms indicate that the molecular core is characterized by an electronically heterogeneous environment. This result is consistent with the electron density distribution in the frontier orbitals.

Bond orders also characterize these features of the electronic structure from another perspective. The difference in the values for the central C=C bond and the C=C bonds in the side fragments shows that the electronic environment of the bonds is not identical. A Mayer bond order greater than 1 for the C–S bonds indicates the presence of partial multiple-bond character in these bonds and strong electronic interaction with the π-system (Table 2).

Table 2. Mulliken Charges and Mayer Valence Indicators for Selected Atoms

Atom	Element	Mulliken Charge, e	Mayer Valence	Bonded Valence
C(0), C(2)	$C(sp^3)$	−0.1838	3.9156	3.9156
C(1), C(3)	$C(sp^3)$	−0.2494	4.0398	4.0398
C(4), C(5)	$C(sp^2)$	+0.0007	3.8562	3.8562
C(6), C(8)	$C(sp^2)$	−0.0081	4.0430	4.0430

The Mayer bond orders for the central C(4)–C(5) bond were 1.5131, for the C=C bonds in the side rings — 1.6331, and for the central C–S bonds — approximately 1.14. The lower bond order of the central bond compared with the local C=C bond, as well as the C–S bond orders above unity, are consistent with the delocalized character of the π-electron density along the molecular core. This shows that the bonds in the BEDT-TTF core are not formed as strictly localized double and single bonds, but rather as an interconnected electronic system.

Dipole Moment and Vibrational Characteristics: In the optimized structure, the calculated total dipole moment was 0.5983 D, while the X and Y components were practically close to zero, and the main component was directed along the Z axis (−0.5983 D). This result shows that the optimized conformation deviates from a strictly planar and inversion-symmetric model. The boat-like conformation, close to C_2 symmetry, is also consistent with previously performed vibrational calculations for neutral BEDT-TTF [5].

The small but non-zero value of the dipole moment is associated with the spatial symmetry of the molecule. The practically zero components along the X and Y axes and the concentration of the main contribution along the Z axis show that, in the optimized conformation, the charge distribution is predominantly asymmetric in one spatial direction. This state is logically consistent with the boat-like deformation.

Low-frequency modes are associated with soft structural deformations and relatively free motions of the ethylene groups. At higher frequencies, stretching vibrations of the C–S and C=C bonds predominate. Therefore, the calculated spectrum represents a dynamic manifestation of the features observed in the geometric and electronic analyses.

For the 26-atom BEDT-TTF molecule, 3N−6 = 72 fundamental vibrational modes were obtained, and all of them had positive values; the minimum frequency was 18.90 cm^{-1}. The absence of negative frequencies confirms that the optimized structure corresponds to a stable local minimum on the calculated potential energy surface.

Table 3. Selected intense modes in the IR spectrum.

Mode	Frequency, cm^{-1}	Intensity, km/mol	Main Characteristic of the Vibration
61	1323.38	56.46	In-plane deformation vibration of CH_2 groups
42	810.93	43.80	Asymmetric vibration associated with C–S bonds
72	3077.57	36.23	C–H stretching vibration in ethylene groups
47	934.53	26.45	Mixed C–C/C–S vibration of the ring framework
70	3065.77	22.25	Stretching vibration of aliphatic C–H
68	1583.55	15.22	Stretching vibration of the central C=C double bond

In the calculated IR spectrum, the mode at 1323.38 cm^{-1} exhibited the highest intensity (56.46 km/mol). In the region of 810.93 cm^{-1}, an intense mode associated with C–S bonds was observed, whereas at 1583.55 cm^{-1}, a stretching vibration of the central C=C bond was observed (Table 3). In IR/Raman and isotope studies of BEDT-TTF, vibrations associated with C=C, C–S bonds, and ethylene groups have also been identified as diagnostic modes [6,7]. Therefore, the main modes of the calculated spectrum are in qualitative agreement with the known vibrational characteristics of the BEDT-TTF molecule (Fig. 3).

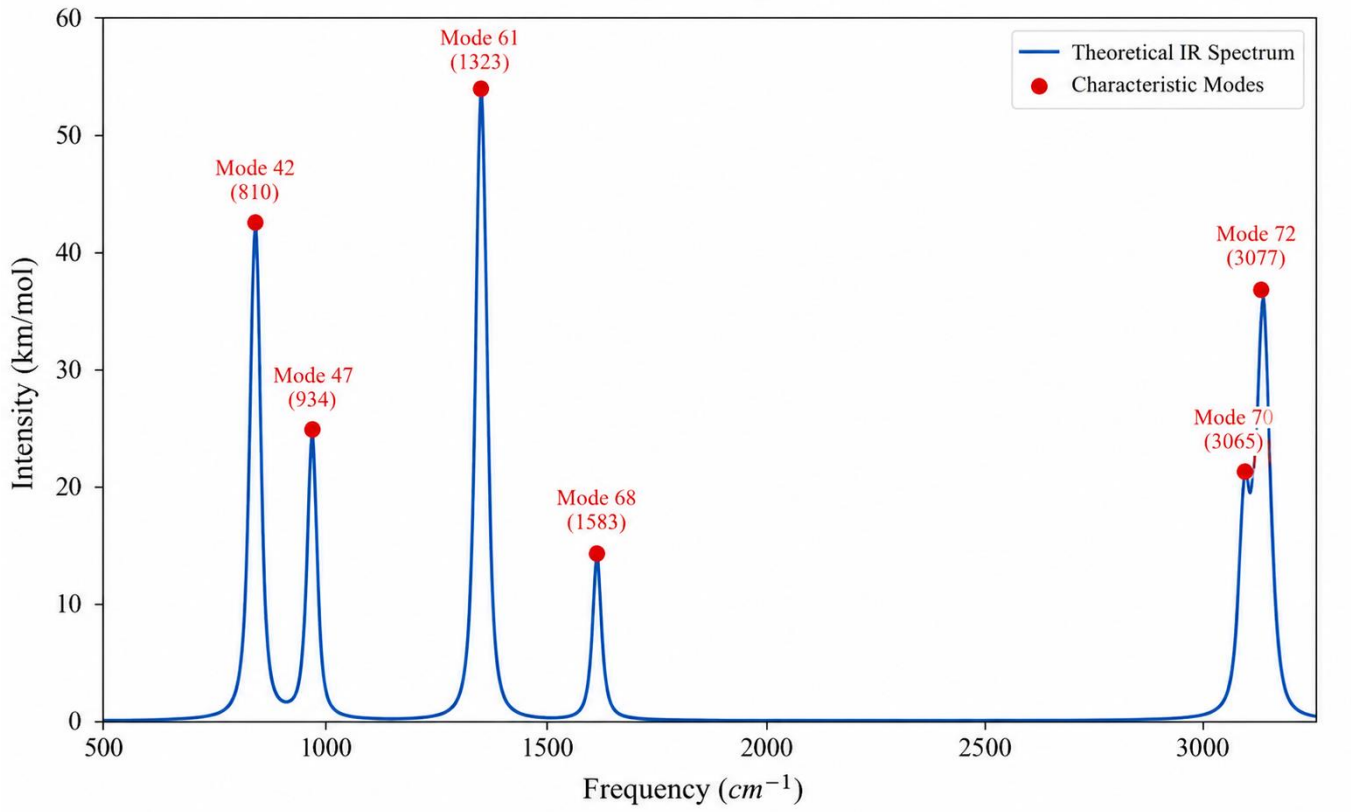


Fig. 3. Calculated IR absorption spectrum of the BEDT-TTF molecule.

Thermodynamic Functions: At a temperature of T = 298.15 K and a pressure of P = 101.325 kPa, taking into account zero-point vibrations and thermal corrections, the total internal energy U was −3569.93558293 Eh, the enthalpy H = −3569.93463873 Eh, and the Gibbs free energy G = −3570.00008156 Eh. The entropy contributions in the form of TS were divided into rotational, translational, and vibrational components. When converting the Eh values from the ORCA output data to kcal/mol, the vibrational contribution was 74.851 kJ/mol (17.89 kcal/mol), which is consistent with the total TS value of 171.841 kJ/mol (41.07 kcal/mol).

The combined presentation of the values of the internal energy, enthalpy, and Gibbs free energy makes it possible to more fully characterize the calculated thermodynamic state of the molecule. Enthalpy includes the PV contribution relative to the internal energy, whereas Gibbs free energy also takes the entropic factor into account. Therefore, their mutual differences reflect the combined thermodynamic contributions of vibrational, rotational, and translational motions.

In the calculated results, the total TS contribution, equal to 171.841 kJ/mol (41.07 kcal/mol), indicates that molecular motions make a significant contribution to the entropy (Table 4). Its vibrational component amounted to 74.851 kJ/mol (17.89 kcal/mol), which is particularly associated with the presence of low-frequency modes. When the results are considered together with the geometric and vibrational analyses, it can be seen that the structural flexibility of the BEDT-TTF molecule is also manifested in its thermodynamic description.

Table 4. Thermodynamic Parameters at 298.15 K

Parameter	Value
U	−3569.93558293 Eh
H	−3569.93463873 Eh
TS_{rot}	42.385 kJ/mol (10.13 kcal/mol)
TS_{trans}	54.583 kJ/mol (13.04 kcal/mol)
TS_{vib}	74.851 kJ/mol (17.89 kcal/mol)
TS_{total}	171.841 kJ/mol (41.07 kcal/mol)
G	−3570.00008156 Eh

The significant contribution of vibrational entropy is associated with the presence of low-frequency modes in the range of 18.90–65.95 cm^{-1}. Low-frequency vibrations are sensitive to soft conformational motions of the molecule; consequently, they make a significant contribution to the vibrational component of the thermodynamic functions. The obtained thermodynamic parameters characterize the calculated state of the neutral BEDT-TTF molecule at 298.15 K and 101.325 kPa.

CONCLUSION

Calculations performed at the PBE0/def2-TZVP-D3BJ level made it possible to characterize the geometric, electronic, vibrational, and thermodynamic properties of the neutral BEDT-TTF molecule within a unified framework. The optimized structure has a boat-like conformation, and the positive values of all 72 fundamental vibrational frequencies indicate that it corresponds to a stable local minimum on the potential energy surface. The HOMO and LUMO energies were −4.96 and −0.955 eV, respectively, while the Kohn–Sham energy difference between them was ≈4.01 eV. The frontier orbitals, Mulliken charges, and Mayer bond orders revealed the delocalized character of the electron density in the central tetrathiafulvalene fragment.

In the calculated IR spectrum, the modes in the regions of 810.93, 1323.38, and 1583.55 cm^{-1} were identified as characteristic vibrations associated with the C–S and C=C bonds. At a temperature of 298.15 K and a pressure of 101.325 kPa, the Gibbs free energy was −3570.00008156 Eh, while the total TS value was 171.841 kJ/mol (41.07 kcal/mol).

The obtained results show that the donor π-system, spatial conformation, and vibrational characteristics of the neutral BEDT-TTF molecule are interrelated and provide theoretical data for explaining the electronic structure of BEDT-TTF-based molecular systems.

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