



AB initio investigation on molecular behaviour of building blocks of organic superconductors : 4,5-ethylenedithio-1,3-dithiole-2-thione and 4,5-ethylenedithio-1,3-dithiole-2-one

P Rani and R A Yadav*

*Spectroscopy Laboratory, Department of Physics,
Banaras Hindu University, Varanasi -221 005, India*

Dedicated to Prof J R Durig

Molecular behaviour of the building blocks of organic superconductors namely, [4,5-ethylenedithio-1,3-dithiole-2-thione (EDT-DTT), 4,5-ethylenedithio-1,3-dithiole-2-one (EDT-DTO)] and their cations and anions using density functional theory method B3LYP/6-311++G** method. The effect of addition and removal of electron on the molecular geometries, frontier MOs, ionization potential, electron affinity and other electronic properties have been investigated. The calculated frontier MO energies suggest that charge transfer occurs within the molecules. Electrical properties such as dipole moment, mean polarizability, polarizability anisotropy and first hyperpolarizability have been determined. The present calculations suggest that addition of an electron in the EDT-DTT molecule involves larger geometry modifications as compared to the removal of an electron from it, which results in the chair-like conformation. EDT-DTO and EDT-DTT has been found to have better charge transfer properties as compared to EDT-DTO and EDT-DTT is found to be better hole transporter as compared to the electron transporter. © Anita Publications. All rights reserved.

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1 Introduction

Bis (ethylenedithio) tetrathiafulvalene (BEDT-TTF) is a π -electron donor molecule of a class of relatively high-temperature atmospheric-pressure organic superconductors and has played an essential role in the field of organic conductors over the last few decades [1]. BEDT-TTF and its charge transfer salts have received much attention as these show a wide range of electrical conductivity from insulators and semiconductors to metals and superconductors [1-3]. The conductivities of such compounds are closely related to the electron-molecular vibration couplings [4]. 4,5-ethylenedithio-1,3-dithiole-2-thione (EDT-DTT) and 4,5-ethylenedithio-1,3-dithiole-2-one (EDT-DTO) molecules are two important precursors in the synthesis of the BEDT-TTF molecule and therefore, it is necessary to understand their conducting properties.

The parameters on which conducting properties depend are ionization potential, electron affinity, frontier MOs and HOMO-LUMO energy gap. Chemical concepts like electronegativity and hardness are important in understanding various physicochemical processes. The concept of electronegativity was first proposed by Pauling [5] to describe the power of an atom in a molecule to attract electrons towards itself and has been widely used to deal with chemical phenomena. Hardness is used as a tool to understand the chemical reactivity and other molecular properties of a system [6]. It was found that stability of molecules is related to hardness [7,8]. Parr *et al* [9] have defined electrophilicity index which is a convenient parameter to assess the electrophilicity power of an atom or molecule. These parameters are helpful in understanding the characteristics of organic molecules. Density functional theory (DFT) [10,11] has been found to be successful in analyzing these parameters.

Electrical properties such as dipole moment and polarizability of molecules are of considerable interest in a number of fields, such as in non-linear optics and the theory of molecular interactions. The electrical properties of organic molecules are affected by the nature of the conjugated bonds, the strength of the donor and acceptor groups and the molecular conformations. *ab initio* calculations are excellent

Corresponding author :

e-mail: rayadav@bhu.ac.in, ray1357@gmail.com; *Tel.:* +91 5422368593; *Mobile :* +919452497623 (R A Yadav)

alternative methods to predict electrical properties of the organic molecules such as molecular dipole moment, polarizability, and hyperpolarizability [12-16].

The charge transport phenomena in π -conjugated organic molecules have attracted a lot of interest because of their wide ranged applications in a number of electronics processes. Most of the organic molecule based systems are found to be hole conductors rather than electron conductors. The carrier mobility of organic molecular crystals is governed by two parameters, (i) the electronic coupling (transfer integral) between adjacent molecules, which needs to be maximized and (ii) the reorganization energy which needs to be small for efficient transport and can be understood within the Marcus theory formalism of electron transfer [17-20]. The reorganization energy corresponds to the sum of geometry relaxation energies in going from the neutral-state geometry to the charged-state geometry and vice versa.

Therefore, in the present article we have studied the charge transport phenomena in the EDT-DTT and EDT-DTO molecules in order to understand their conducting behaviour, for which detailed analysis of their geometrical and electronic structures has been carried out. The present investigation also includes the study of electronic, thermodynamical and electrical properties of EDT-DTT and EDT-DTO along with their corresponding radical cations and anions.

2 Computational details

The theoretical calculations presented in this work have been carried out using the Gaussian 03 suite of programs [21, 23]. The computations have been performed using the DFT methods [10] at the B3LYP/6-311++G** level. The geometries were optimized by minimizing the energies with respect to all the geometrical parameters without imposing any molecular symmetry constraints. All the optimized geometries and frontier MOs were viewed with the help of the Gauss View software [24].

3 Result and Discussions

3.1 Geometrical Parameters

The optimized geometrical parameters of the EDT-DTT along with its radical cation (EDT-DTT⁺) and anion (EDT-DTT⁻) and EDT-DTO along with its radical cation (EDT-DTO⁺) are collected in Table 1 while their labeling schemes are shown in Fig 1. It could be seen that there are little deviations in the computed geometrical parameters from those reported in the X-ray diffraction data [18], and these differences are probably due to the I₂ molecule which is attached with S atom at the site of S10. The computed bond length and bond angles are in reasonable agreement with the corresponding experimental values and also completely consistent with Liu's calculation. Radical anion of the EDT-DTO molecule is found to be unstable. The calculations predict that the EDT-DTT and EDT-DTO molecules and their corresponding radical cations have non-planar structures with C₂ point group symmetry, whereas radical anion of the EDT-DTT molecule has non-planar structure with C₁ point group symmetry. It can be seen from the Table 1 that the conversion of neutral molecules into their corresponding radical cations and anion results into significant changes in the magnitudes of the bond lengths and angles.

As a result of cationic radicalization of EDT-DTT and EDT-DTO, the geometry modifications occur mainly in the C-S/O, C₄-C₅ and C₂=S₁₀/O₁₀ bond lengths and C₅-S₆-C₇ and C₄-S₉-C₈ bond angles. In addition, significant changes are noticed in the C₅-C₄-S₉, S₉-C₄-S₃, C₄-C₅-S₆, S₆-C₅-S₁, C₈-C₇-S₆, S₆-C₇-H₁₃/H₁₄, S₉-C₈-H₁₁/H₁₂, C₅-S₁-C₂, C₄-S₃-C₂, S₁-C₂-S₃, S₁-C₂-S₁₀/O₁₀ and S₃-C₂-S₁₀/O₁₀ bond angles due to anionic radicalization of EDT-DTT. For both the neutral molecules, the dihedral angles S₉-C₄-C₅-S₆, S₉-C₄-C₅-S₁, S₃-C₄-C₅-S₆, S₉-C₄-S₃-C₂, S₆-C₅-S₁-C₂, S₃-C₄-C₅-S₁, C₄-C₅-S₁-C₂, C₅-C₄-S₃-C₂, C₅-S₁-C₂-S₃, C₄-S₃-C₂-S₁, C₅-S₁-C₂-S₁₀/O₁₀ and C₄-S₃-C₂-S₁₀/O₁₀ are either 0° or ±180°, indicating that S₉, S₆, C₄, C₅, S₃, S₁, C₂ and O₁₀/S₁₀ are in the same plane, while for their radical cations only dihedral angles C₅-S₁-C₂-S₃, C₄-S₃-C₂-S₁, C₅-S₁-C₂-S₁₀/O₁₀ and C₄-S₃-C₂-S₁₀/O₁₀ are either 0° or ±180°, indicating that C₄, C₅, S₃, S₁, C₂ and O₁₀/S₁₀ are in the same plane. Major changes are found in the dihedral angles for the radical anion of EDT-DTT

molecules. Variation in the dihedral angles shows that the two C atoms and the four H atoms of the terminal CH₂ groups of all the studied molecules are not in the same plane. Thus, it has been found that one of the two CH₂ groups lies above and the other one lies below the molecular plane containing S₉, S₆, C₄, C₅, S₃, S₁, C₂ and O₁₀/S₁₀ atoms in the neutral molecules and their radical cations. However, in case of the radical anion of the EDT-DTT molecule, the dihedral angle S₃-C₄-S₉-C₈ (-130°) and S₁-C₅-S₆-C₇ (146°) indicate that both the CH₂ groups are lying only on one side of the molecular plane consisting of S₉-C₄-S₃ and S₁-C₅-S₆ atoms. The dihedral angles C₄-S₃-C₂-S₁₀ (176.6°) and C₅-S₁-C₂-S₁₀ (-176.6°) suggest that the C₂ and S₁₀ atoms are lying on one side of the molecular plane consisting of the S₉-C₄-S₃ and S₁-C₅-S₆ atoms. Thus, the CH₂ group and the C₂ and S₁₀ atoms are on the opposite side of the molecular plane and form chair configuration for the EDT-DTT radical anion. Detailed description of the optimized molecular geometries as a result of radicalization has been discussed earlier [25]. It can be seen from the Table 1 that modifications in the geometrical structures are smaller in EDT-DTT as compared to those in EDT-DTO due to removal of an electron. Addition of an electron in the EDT-DTT molecule involves larger geometry modifications as compared to the removal of an electron from the EDT-DTT molecule.

Table 1. Geometrical parameters^a of EDT-DTT, EDT-DTT⁺, EDT-DTT⁻, EDT-DTO and EDT-DTO⁺

Definition	EDT-DTT		EDT-	EDT-	EDT-	EDT-	EDT-DTTI ₂ ^c		
	Calc.	Present Liu ^b B3LYP /6-311+ /6-31G**+G**	EDT-DTT ⁺ Calc	EDT-DTT ⁻ Calc	EDT-DTO Calc	EDT-DTO ⁺ Calc	Exp. X-ray Diff.	Calc B3LYP HF/3-21G**3-21G*	
r(C ₄ -C ₅)	1.351	1.355	1.405	1.352	1.348	1.411	1.34	1.356	1.328
r(C ₄ -S ₉)	1.774	1.755	1.733	1.770	1.776	1.727	1.744	1.769	1.762
r(C ₄ -S ₃)	1.770	1.771	1.741	1.775	1.772	1.742	1.742	1.766	1.760
r(C ₅ -S ₆)	1.774	1.755	1.733	1.771	1.776	1.727	1.736	1.768	1.762
r(C ₅ -S ₁)	1.770	1.771	1.741	1.778	1.772	1.742	1.748	1.769	1.760
r(C ₇ -C ₈)	1.526	1.529	1.516	1.520	1.526	1.515	1.57	1.543	1.539
r(C ₇ -S ₆)	1.832	1.834	1.839	1.863	1.831	1.837	1.76	1.835	1.813
r(C ₇ -H ₁₃)	1.093	1.095	1.092	1.095	1.093	1.092	-	-	-
r(C ₇ -H ₁₄)	1.090	1.092	1.091	1.091	1.090	1.091	-	-	-
r(C ₈ -S ₉)	1.832	1.834	1.839	1.841	1.831	1.837	1.79	1.837	1.813
r(C ₈ -H ₁₁)	1.090	1.095	1.091	1.091	1.090	1.091	-	-	-
r(C ₈ -H ₁₂)	1.093	1.092	1.092	1.094	1.093	1.092	-	-	-
r(S ₁ -C ₂)	1.760	1.763	1.768	1.826	1.801	1.823	1.699	1.747	1.731
r(S ₃ -C ₂)	1.760	1.763	1.768	1.824	1.801	1.823	1.714	1.747	1.732
r(S ₁₀ /O ₁₀ -C ₂)	1.644	1.645	1.627	1.697	1.197	1.180	1.663	1.666	1.638
α(C ₅ -C ₄ -S ₉)	128.8	128.8	128.0	122.6	128.7	127.7	127.9	129.1	128.9
α(C ₅ -C ₄ -S ₃)	116.3	116.3	116.1	116.9	117.5	117.6	115.2	115.9	116.4
α(S ₉ -C ₄ -S ₃)	115.0	-	115.91	120.0	113.8	114.7	-	-	-
α(C ₄ -C ₅ -S ₆)	128.8	128.8	128.0	126.4	128.7	127.7	127.3	128.9	128.9
α(C ₄ -C ₅ -S ₁)	116.3	128.8	116.1	116.5	117.5	117.6	-	-	-
α(S ₆ -C ₅ -S ₁)	115.0	-	115.9	117.1	113.8	114.7	-	-	-
α(C ₈ -C ₇ -S ₆)	113.1	113.1	113.2	115.1	113.0	113.0	114.8	112.3	112.4
α(C ₈ -C ₇ -H ₁₃)	110.1	-	110.2	109.7	110.2	110.3	-	-	-

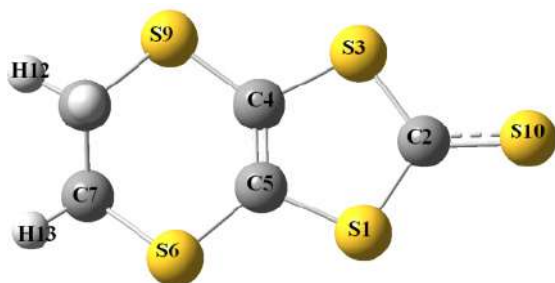
$\alpha(C_8-C_7-H_{14})$	111.3	-	112.6	110.1	111.2	112.7	-	-	-
$\alpha(S_6-C_7-H_{13})$	103.7	-	103.2	106.8	103.8	103.4	-	-	-
$\alpha(S_6-C_7-H_{14})$	109.7	-	108.6	106.0	109.7	108.4	-	-	-
$\alpha(H_{13}-C_7-H_{14})$	108.6	-	108.6	108.9	108.6	108.5	-	-	-
$\alpha(C_7-C_8-S_9)$	113.1	113.1	113.2	112.9	113.0	113.0	114.4	112.3	112.4
$\alpha(C_7-C_8-H_{11})$	111.3	-	112.6	111.5	111.2	112.7	-	-	-
$\alpha(C_7-C_8-H_{12})$	110.1	-	110.2	109.5	110.2	110.3	-	-	-
$\alpha(S_9-C_8-H_{11})$	109.7	-	108.6	107.2	109.7	108.4	-	-	-
$\alpha(S_9-C_8-H_{12})$	103.7	-	103.2	106.7	103.8	103.4	-	-	-
$\alpha(H_{11}-C_8-H_{12})$	108.6	108.5	108.6	108.8	108.6	108.5	-	-	-
$\alpha(C_5-S_6-C_7)$	100.5	100.5	102.5	104.3	100.7	103.1	98.1	100.2	100.4
$\alpha(C_4-S_9-C_8)$	100.5	100.5	102.5	96.3	100.7	103.1	99.7	100.2	100.4
$\alpha(C_5-S_1-C_2)$	97.8	97.8	97.7	93.6	96.5	96.2	97.5	96.7	96.8
$\alpha(C_4-S_3-C_2)$	97.8	97.8	97.7	93.6	96.5	96.2	97.8	97.2	96.9
$\alpha(S_1-C_2-S_3)$	111.9	112.0	112.3	107.8	111.9	112.3	113.2	113.5	113.5
$\alpha(S_1-C_2-S_{10}/O_{10})$	124.0	-	123.8	122.5	124.0	123.8	-	-	-
$\alpha(S_3-C_2-S_{10}/O_{10})$	124.0	-	123.8	122.9	124.0	123.8	-	-	-
$\delta(S_9-C_4-C_5-S_6)$	-1.6	-	2.4	7.2	-1.3	4.5	-	-	-
$\delta(S_9-C_4-C_5-S_1)$	179.1	-	-177.5	-171.7	179.3	-175.8	-	-	-
$\delta(S_3-C_4-C_5-S_6)$	179.1	-	-177.5	178.5	179.3	-175.8	-	-	-
$\delta(S_3-C_4-C_5-S_1)$	-0.2	-	2.5	-0.4	-0.1	3.8	-	-	-
$\delta(C_5-C_4-S_9-C_8)$	14.7	-	11.7	41.0	14.6	10.4	-	-	-
$\delta(S_3-C_4-S_9-C_8)$	-166.0	-	-168.3	-130.0	-166.0	-169.2	-	-	-
$\delta(C_5-C_4-S_3-C_2)$	0.2	-	-1.8	20.6	0.0	-2.7	-	-	-
$\delta(S_9-C_4-S_3-C_2)$	-179.3	-	178.2	-167.9	-179.4	177.0	-	-	-
$\delta(C_4-C_5-S_6-C_7)$	14.7	-	11.8	-32.5	14.6	10.4	-	-	-
$\delta(S_1-C_5-S_6-C_7)$	-166.0	-	-168.3	146.4	-166.0	-169.2	-	-	-
$\delta(C_4-C_5-S_1-C_2)$	0.2	-	-1.8	-20.0	0.0	-2.7	-	-	-
$\delta(S_6-C_5-S_1-C_2)$	-179.3	-	178.2	161.0	-179.4	177.0	-	-	-
$\delta(S_6-C_7-C_8-S_9)$	72.7	-	69.7	51.1	72.6	69.4	-	-	-
$\delta(S_6-C_7-C_8-H_{11})$	-51.37	-	-54.0	-69.7	-51.2	-53.9	-	-	-
$\delta(S_6-C_7-C_8-H_{12})$	-171.8	-	-175.3	169.9	-171.7	-175.4	-	-	-
$\delta(H_{13}-C_7-C_8-S_9)$	-171.8	-	-175.3	171.6	-171.7	-175.4	-	-	-
$\delta(H_{13}-C_7-C_8-H_{11})$	64.28	-	61.0	50.9	64.4	61.3	-	-	-
$\delta(H_{13}-C_7-C_8-H_{12})$	-56.28	-	-60.3	-69.6	-56.1	-60.2	-	-	-
$\delta(H_{14}-C_7-C_8-S_9)$	-51.38	-	-54.0	-68.6	-51.2	-53.9	-	-	-
$\delta(H_{14}-C_7-C_8-H_{11})$	-175.38	-	-177.6	170.6	-175.1	-177.2	-	-	-
$\delta(H_{14}-C_7-C_8-H_{12})$	64.28	-	61.0	50.2	64.4	61.3	-	-	-
$\delta(C_8-C_7-S_6-C_5)$	-49.4	-	-47.6	-0.2	-49.4	-47.3	-	-	-
$\delta(H_{13}-C_7-S_6-C_5)$	-168.7	-	-166.8	-122.3	-168.9	-166.6	-	-	-

$\delta(\text{H}_{14}\text{-C}_7\text{-S}_6\text{-C}_5)$	75.5	-	78.1	121.7	75.3	78.3	-	-	-
$\delta(\text{C}_7\text{-C}_8\text{-S}_9\text{-C}_4)$	-49.4	-	-47.6	-70.7	-49.4	-47.3	-	-	-
$\delta(\text{H}_{11}\text{-C}_8\text{-S}_9\text{-C}_4)$	75.5	-	78.1	52.5	75.3	78.3	-	-	-
$\delta(\text{H}_{12}\text{-C}_8\text{-S}_9\text{-C}_4)$	-168.7	-	-166.8	168.9	-168.8	-166.6	-	-	-
$\delta(\text{C}_5\text{-S}_1\text{-C}_2\text{-S}_3)$	-0.0	-	0.5	31.6	-0.0	0.8	-	-	-
$\delta(\text{C}_5\text{-S}_1\text{-C}_2\text{-S}_{10}/\text{O}_{10})$	180.0	-	-179.5	-176.6	180.0	-179.2	-	-	-
$\delta(\text{C}_4\text{-S}_3\text{-C}_2\text{-S}_1)$	-0.0	-	0.5	-31.8	-0.0	0.8	-	-	-
$\delta(\text{C}_4\text{-S}_3\text{-C}_2\text{-S}_{10}/\text{O}_{10})$	180.0	-	-179.5	176.6	180.0	-179.2	-	-	-

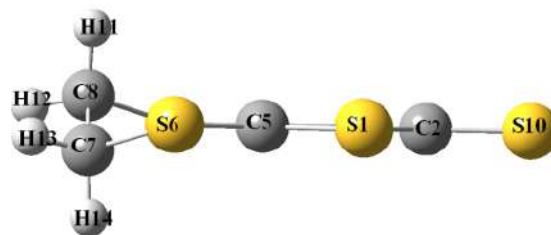
a: bond lengths in Å, bond angles and dihedral angles in degrees (°).

b: data taken from the ref. [26].

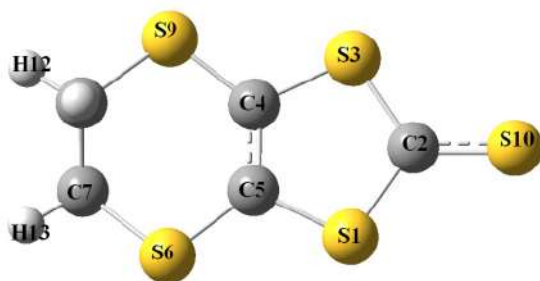
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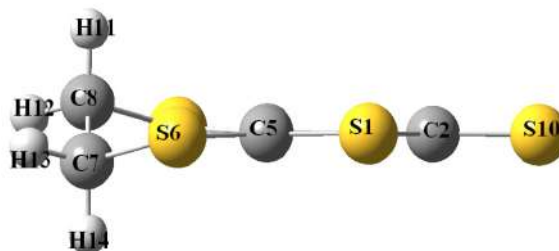
Front view of EDT-DTT



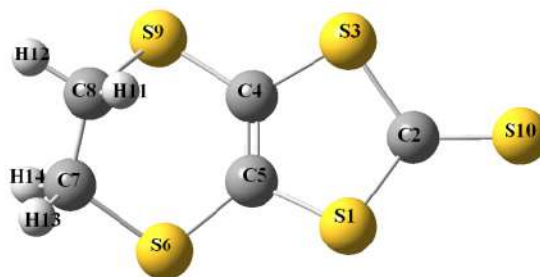
Lateral view of EDT-DTT



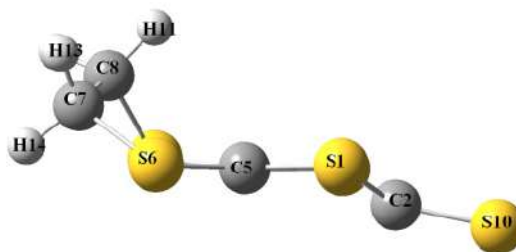
Front view of EDT-DTT⁺



Lateral view of EDT-DTT⁺



Front view of EDT-DTT⁻



Lateral view of EDT-DTT⁻

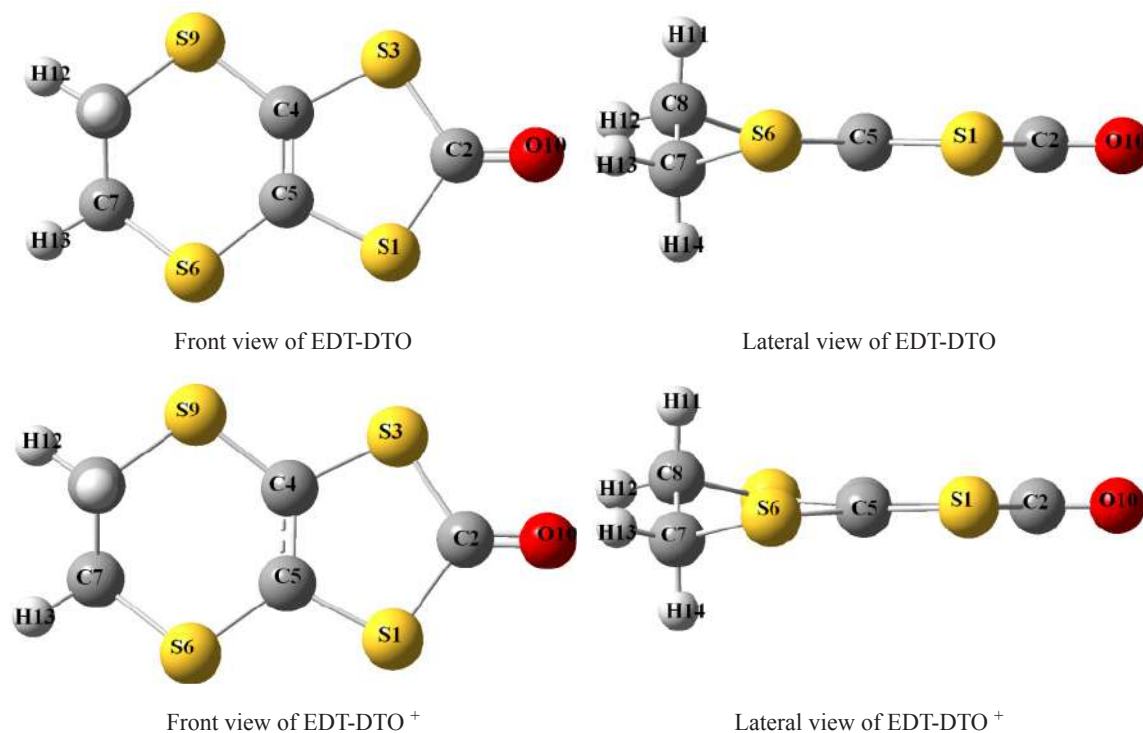


Fig 1. Front and lateral view of all the studied molecules

3.2. Electronic Structures

Table 2 encompasses the energies of the first five HOMOs and LUMOs and their corresponding orbital numbers within the brackets. For the cation and anion species due to removal of the degeneracy one has two sets of energy levels for the α and β electrons with the opposite spins.

Table 2. Energy^d of Frontier MOs for EDT-DTT, EDT-DTT⁺, EDT-DTT⁻, EDT-DTO and EDT-DTO⁺

HOMO / LUMO	EDT-DTT α	EDT-DTT ⁺ α	EDT-DTT ⁺ β	EDT-DTT ⁻ α	EDT-DTT ⁻ β	EDT-DTO α	EDT-DTO ⁺ α	EDT-DTO ⁺ β
LUMO+4	-0.4618 (62)	-4.5084 (62)	-4.8140 (61)	2.8572 (63)	2.8175 (62)	-0.3967 (58)	-4.7925 (58)	-4.9601 (57)
LUMO+3	-0.7040 (61)	-4.8722 (61)	-5.3604 (60)	2.7380 (62)	2.6400 (61)	-0.6264 (57)	-5.0461 (57)	-5.3805 (56)
LUMO+2	-1.1861 (60)	-5.4877 (60)	-5.5862 (59)	2.4961 (61)	2.4542 (60)	-1.1015 (56)	-5.5500 (56)	-5.5133 (55)
LUMO+1	-1.2368 (59)	-5.9933 (59)	-6.3389 (58)	2.2738 (60)	2.2670 (59)	-1.1222 (55)	-5.8140 (55)	-5.9318 (54)
LUMO	-2.1769 (58)	-6.5620 (58)	-8.9457 (57)	1.7064 (59)	1.6909 (58)	-1.3290 (54)	-6.2866 (54)	-9.1343 (53)

HOMO	-5.8690 (57)	-10.5188 (57)	-10.8092 (56)	0.3957 (58)	-1.4705 (57)	-5.9451 (53)	-10.8533 (53)	-11.8761 (52)
HOMO-1	-6.4390 (56)	-10.9227 (56)	-11.2704 (55)	-1.5897 (57)	-1.5059 (56)	-7.3539 (52)	-12.2767 (52)	-12.1711 (51)
HOMO-2	-7.1659 (55)	-11.8614 (55)	-11.7393 (54)	-1.8104 (56)	-2.9903 (55)	-7.7242 (51)	-12.4699 (51)	-12.4919 (50)
HOMO-3	-7.4548 (54)	-12.0854 (54)	-13.4310 (53)	-3.2961 (55)	-3.2722 (54)	-8.0102 (50)	-12.6985 (50)	-13.6043 (49)
HOMO-4	-8.8491 (53)	-13.6702 (53)	-13.8348 (52)	-3.4341 (54)	-4.1549 (53)	-8.7553 (49)	-13.9075 (49)	-14.0599 (48)

d: Energies are measured in eV

Each numerical value within the bracket represents the corresponding orbital number.

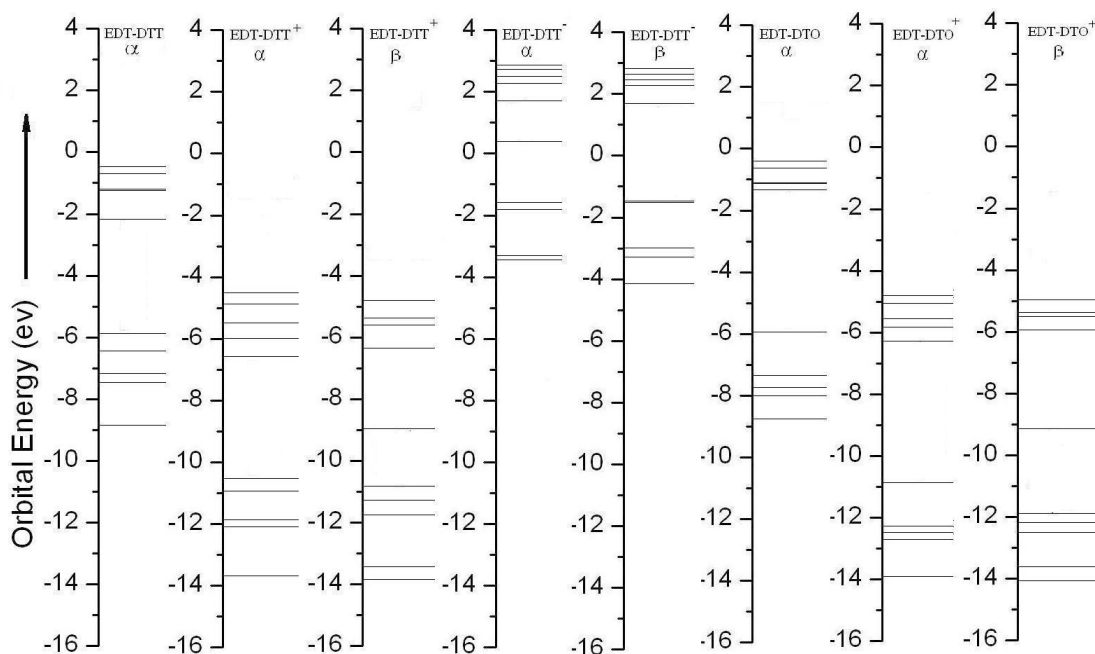


Fig 2. Energy level diagram of first five HOMO and LUMO for all the molecules under study.

The LUMO of EDT-DTT is mainly localized on the pentagon ring and C=O bond with strong π bonding character between C_4-C_5 atom pair, anti-bonding character between C_4-S_3 , S_3-C_2 , C_2-S_1 , S_1-C_5 and C_2-S_{10} atom pairs and has non-bonding character amongst S_9 , S_6 and ethylene group atoms (Fig 2). The HOMO of the EDT-DTT extends over the hexagon and pentagon rings including the C=S bond with strong π bonding character between C_4-C_5 atom pair, weak π bonding character between C_2-S_1 and C_2-S_3 atom pairs and anti-bonding character between C_2-S_{10} , C_4-S_3 , C_5-S_1 , C_5-S_6 and C_4-S_9 atom pairs. For the EDT-DTT⁺ radical, the spatial distribution of HOMO and LUMO for the α electrons is similar to those for its neutral molecule. For the β electrons of EDT-DTT⁺, the spatial structure of its LUMO is same as that of the HOMO of EDT-DTT and EDT-DTT⁺ species with α electrons, while its HOMO is extended on the whole molecule except on the ethylene group and C_4-C_5 atom pair with bonding character between the atoms of the C-S

bond (Fig 3). The HOMO of the EDT-DTT⁻ species with α electrons has strong bonding character between the atoms of pentagon ring and non-bonding character between the atoms of the hexagon ring and ethylene group, while its LUMO is highly delocalized over the entire molecule except on the C-S bond (Fig 4). For the β electrons of EDT-DTT⁻ molecule, the spatial distribution of LUMO is similar to that of its α electron's HOMO, whereas the spatial distribution of its HOMO is highly delocalized over the entire molecule with strong π bonding character between C₄-C₅ atom pair, weak π bonding character between C₂-S₃ and C₂-S₁ atom pair and non-bonding character between C₂ and S₁₀ atoms. The spatial distribution of HOMO and LUMO are found to be the same for the EDT-DTT and EDT-DTO molecules (Fig 5). For the EDT-DTO⁺ molecule, the spatial structure of LUMO for α electrons is highly delocalized and is extended over the entire hexagon and pentagon rings with non-bonding character of carbonyl group, while its HOMO is identical with the HOMO of neutral EDT-DTO molecule. It could be seen from the Fig 6 that for the β electrons of EDT-DTO⁺ molecule, LUMO is identical to the HOMO of its α electrons, while HOMO is localized over the hexagon and pentagon rings with π anti-bonding character and non-bonding character between the carbonyl group, C₈-H₁₂, C₇-H₁₃ and the C=C bond (Fig 6).

The energy level diagram of the first five HOMOs and LUMOs for all the studied species has been shown in the Fig 7. As shown in the Table 2, the present study indicated that the LUMO+1 and LUMO+2 are nearly degenerate for both the neutral molecules. Also the EDT-DTT⁻ species has nearly degenerate HOMO and HOMO-1 for the β electrons.

3.3 Charge transport properties

In π -conjugated systems, strong coupling exists between the geometric and electronic structures which controls the transport properties [28, 29]. Addition and removal of electron usually leads to marked geometry relaxations, which in turn modifies the electronic structure [30]. As a result efficiency of the charge transport and ultimately the performance of electronic devices are controlled to a large extent by the reorganization energies due to hole-vibration or electron-vibration interactions [31]. Thus, for different molecular structures, charge transfer rates are essentially dependent on their reorganization energies. For an efficient charge transport process, the magnitude of the reorganization energy should be low and therefore, such molecules are expected to be good conductors.

The reorganization energy for electron ($\lambda_{\text{electron}}$) and hole (λ_{hole}) carriers is calculated using the following formulae [32-34],

$$\lambda_{\text{electron}} = (E_{-}^{*} - E_{-}) + (E_{\text{anion}}^{*} - E) \quad (1)$$

$$\lambda_{\text{hole}} = (E_{+}^{*} - E_{+}) + (E_{\text{cation}}^{*} - E) \quad (2)$$

where, E is the optimized ground state energy of the neutral molecule, E_{-} (E_{+}) is the optimized energy of the anionic (cationic) molecule, E_{anion}^{*} (E_{cation}^{*}) is the energy of the neutral molecule in anionic (cationic) geometry and E_{-}^{*} (E_{+}^{*}) is the energy of the anionic (cationic) molecule in neutral geometry.

Addition of an electron to the EDT-DTO molecule results into its unstable anion and hence for the EDT-DTO molecule only λ_{hole} could be estimated. For the EDT-DTT molecule the reorganization energy for the hole and electron are calculated to be -19.8643×10^{-6} and -17.1432×10^{-6} eV, respectively, whereas for the EDT-DTO molecule the reorganization energy for the hole is -9.7961×10^{-6} eV.

For the EDT-DTT molecule, the reorganization energy for the electron is larger than that for the holes. This could be explained in terms of the geometrical changes that occur in different optimized structures of EDT-DTT. From the Fig 1, it could be clearly seen that the neutral and cationic species possess planar geometries, except for the ethylene group, whereas the anionic species possesses a non-planar chair-like conformation. Thus, addition of an electron to the neutral EDT-DTT molecule results in the chair-like geometry leading to large geometry modifications while enhance the electron reorganization energy more than that for the holes. Similarly, removal of an electron from both the neutral molecules involves smaller

modifications in the geometrical structure of EDT-DTT as compared to that of EDT-DTO and therefore, results in the smaller hole reorganization energy for EDT-DTT as compared to that for EDT-DTO. Thus, EDT-DTT has better charge transfer properties as compared to EDT-DTO and hence, the EDT-DTT molecule is a better hole transporter than the electron transporter.

3.4 Electronic Properties

For the cations and anions there are two sets of energy levels for α and β electrons with opposite spins. The present calculations predict an alpha MO for the HOMO and a beta MO for the LUMO for the anions and cations. All the computed electronic quantities are collected in Table 3.

Table 3. Electronic Properties^e of EDT-DTT, EDT-DTT⁺, EDT-DTT⁻, EDT-DTO and EDT-DTO⁺

Parameters	EDT-DTT	EDT-DTT ⁺	EDT-DTT ⁻	EDT-DTO	EDT-DTO ⁺
E_{HOMO}	-5.8690	-10.5188	0.3957	-5.9451	-10.8533
E_{LUMO}	-2.1769	-8.9457	1.6909	-1.3290	-9.1343
Energy gap (ΔE)	3.6921	1.5731	1.2952	4.6161	1.7190
Ionization potential (IP)	5.8690	10.5188	-0.3957	5.9451	10.8533
Electron affinity (EA)	2.1769	8.9457	-1.6909	1.3290	9.1343
Chemical potential (μ)	-4.0230	-9.7323	1.0433	-3.6371	-9.9938
Electronegativity (χ)	4.0230	9.7323	-1.0433	3.6371	9.9938
Chemical hardness (η)	1.8461	0.7866	0.6476	2.3081	0.8595
Chemical softness (s)	0.5417	1.2713	1.5442	0.4333	1.1635
Electrophilicity index (ω)	4.3834	60.2070	0.8404	2.8657	58.1012
ΔN_{max}	2.1792	12.3734	1.6110	1.5758	16.9530

e: All the parameters are measured in eV

The higher the value of E_{HOMO} more is the tendency of the molecule to donate the electrons, while the lower the value of E_{LUMO} more is the tendency of the molecule to accept the electrons. Energies of the HOMO and LUMO are essential for governing many chemical reactions and determining electronic band gaps in solids [35-37]. In the present case, the energy of the HOMO seems to be almost unaffected, while the energy of the LUMO increases by 0.8479 eV due to replacement of the S_{10} atom by an O atom in the EDT-DTT molecule. This means that both the neutral molecules have the same tendency to donate the electrons, however, the EDT-DTT molecule has more tendency to accept the electrons as compared to the EDT-DTO molecule. The EDT-DTT molecule has lower LUMO energy, indicating that it has better charge transfer properties [38]. It has also been found that the EDT-DTT⁻ species lose electron more easily as compared to its neutral molecule which in turn lose electron more easily with respect to its cationic species. Similarly, the neutral EDT-DTO molecule lose electron more easily as compared to its cationic radical. Both the cationic radicals have more tendencies to accept electrons as compared to their corresponding neutral molecules. In case of the radicals, the energies of the HOMO and LUMO decrease for the corresponding cations of both the molecules but their energies increase for the EDT-DTT⁻ molecule.

The energy difference, $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, measures the kinetic stability of the molecule [39, 40] and its large value implies high kinetic stability and low chemical reactivity as it is energetically unfavorable to (i) add electrons to a high lying LUMO, and (ii) remove electrons from a low lying HOMO and so to form the activated complex of any potential reaction [41]. The present study suggests that the energy gap of the EDT-DTO is greater than that of EDT-DTT by 0.9240 eV and therefore, the EDT-DTO is found to be kinetically more stable and chemically less reactive as compared to the EDT-DTT molecule. The energy gaps of the cations are less than their corresponding neutral molecules and hence, the cations have less kinetic stabilities and high chemical reactivity as compared to the neutral molecules. It is also found that the anionic

radical of EDT-DTT is kinetically least stable and chemically most reactive as compared to its neutral and cationic species.

A molecule with high ionization potential (IP) means that it does not lose electron easily [39, 42]. A molecule with greater electron affinity (EA) tends to take electron easily [39, 42]. Employing Koopmans' approximation [43], the ionization potential and electron affinity could be calculated using the relations,

$$IP = -E_{\text{HOMO}} \quad (3)$$

$$EA = -E_{\text{LUMO}} \quad (4)$$

As both the neutral molecules have the same tendency to lose electrons, these molecules have the same ionization potential, but EDT-DTT would take electrons more easily as compared to the EDT-DTO molecule and therefore, it would have greater electron affinity. In case of the radicals, magnitudes of the IP and EA increase for the corresponding cations of both the neutral molecules, but their values decrease for the EDT-DTT. The negative value of electron affinity for the EDT-DTT⁻ molecule indicates its very low tendency to take electron.

Chemical potential (μ) and electronegativity (χ) can be calculated using the relations,

$$\mu \approx -1/2 (IP + EA) \quad (5)$$

$$\chi \approx 1/2(IP + EA) \quad (6)$$

The magnitude of the chemical potential is calculated to be higher for EDT-DTO as compared to the EDT-DTT molecule and reverse is found for the case of electronegativity. It could be noticed that cations have decreased chemical potentials as compared to the parent molecules suggesting that the charge transfer will take place from the neutral molecule towards the radical cation, causing increase in the corresponding electronegativity. However, for EDT-DTT, the chemical potential is predicted to be positive and electronegativity to be negative which could be due to the fact that the EDT-DTT⁻ is thermodynamically more stable as compared to its neutral and cationic species.

The chemical hardness (η) [44] is a measure of the resistance to charge transference and chemical softness (S) [10] is defined as the reciprocal of the hardness. These two properties can be calculated using the relation given by,

$$\eta \approx 1/2(IP - EA) \quad (7)$$

$$S \approx 1/\eta \quad (8)$$

Hard molecules have large HOMO – LUMO gaps and soft molecules have small HOMO – LUMO gaps [45]. From the Table 2, it is found that the EDT-DTT has a lower value of the chemical hardness and thus, the fraction of the transferred electrons is larger for EDT-DTT as compared to the EDT-DTO. A molecule with higher value of chemical hardness is expected to have higher stability and hence, to be more aromatic [7,46], suggesting that EDT-DTO molecule to be more aromatic as compared to EDT-DTT. The magnitude of the chemical hardness is calculated to be larger for the neutral molecule as compared to the cation, which in turn are larger than that of EDT-DTT⁻.

The electrophilicity index (ω) is a measure of energy lowering due to maximal electron flow between donor and acceptor and can be calculated using the formula given below,

$$\omega \approx \mu^2/2\eta \quad (9)$$

When two molecules react with each other, the one with the higher electrophilicity index acts as an electrophile. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge (ΔN) from the surrounding [47]. As can be seen from the Table 2 the EDT-DTT can accept a maximum electronic charge of 2.1792 eV, while the EDT-DTO can accept charge of 1.5758 eV resulting in a higher electrophilicity index of the EDT-DTT molecule as compared to EDT-DTO, suggesting that EDT-DTT is more electrophilic in nature with respect to EDT-DTO. The electrophilicity indices of

both the cations increase drastically, while their magnitudes decrease for the EDT-DTT⁻ as compared to the neutral molecule. The value of maximum electronic charge ($\Delta N_{\text{max}} \approx -2\mu/\Delta E$), that a system could accept. shows the relation EDT-DTT⁺ > EDT-DTT > EDT-DTT⁻ and EDT-DTO⁺ > EDT-DTO.

3.5. Thermodynamical Properties

The various thermodynamical properties of the studied molecules are collected in Table 4. The total energy of the EDT-DTT is -2173.567 a.u. obtained at B3LYP/3-21G** and -2168.906 a.u. obtained at Hf/3-21G* level has been reported from the data [26] which seem to be in reasonably good agreement with present study. It is found that the total energy of the EDT-DTT molecule is less than that of the EDT-DTO molecule by 322.9563 Hartrees suggesting that the EDT-DTT molecule is thermodynamically more stable than EDT-DTO. The thermodynamical stability for EDT-DTT is in the order anionic form > neutral form > cationic form, whereas for the EDT-DTO molecule it is in the order cationic form > neutral form. The magnitudes of the zero point vibrational energy (ZPVE) and the thermal energy correction increase slightly by 1.4023 and 1.1910 Kcal/Mol, respectively, due to the replacement of S₁₀ atom in the EDT-DTT by an O atom. Their magnitudes are almost equal for the neutral and cationic species of both the molecules. It is also found that for the anionic radical of EDT-DTT the magnitude of ZPVE and thermal energy correction decreases by 1.3551 and 1.0190 Kcal/Mol, respectively, as compared to its neutral molecule.

Table 4. Thermo-dynamical Properties^f of EDT-DTT, EDT-DTT⁺, EDT-DTT⁻, EDT-DTO and EDT-DTO⁺

Parameters	EDT-DTT	EDT-DTT ⁺	EDT-DTT ⁻	EDT-DTO	EDT-DTO ⁺
Total energy(E)	-2184.0424 (-2173.5671) ^c (-2168.9058) ^c	-2183.7659	-2184.0722	-1861.0862	-1860.8090
Zero point vibrational energy(ZPVE)	50.2811	50.1533	48.9260	51.6834	51.7466
Contribution to the thermal energy correction (TE)	56.7160	56.5350	55.6970	57.9070	57.9430
Constant volume molar heat capacity(C _V)	36.7580	36.9690	38.1520	35.9300	35.8950
Entropy (S)	103.1330	102.8670	106.5200	100.9290	101.3340

^f: E are measured in Hartrees, ZPVE & TE are measured in Kcal/Mol and C_V & S are measured in Cal/Mol-Kelvin.

- Total energy for the EDT-DTT₂ (-15945.867 a.u. and -159444.747 a.u. by the calculation at B3LYP/3-21G** and HF/3-21G* respectively) has been reported from the ref. [27].

The molecules with larger molecular mass need more heat than the smaller ones [48]. The molecular mass of EDT-DTT is more than EDT-DTO and thus, the heat capacity of EDT-DTT is calculated to be greater than that of EDT-DTO. Addition of an electron in the EDT-DTT molecule increases the magnitude of the molar heat capacity by 1.3940 cal/Mol-Kelvin, while the removal of an electron from both the neutral molecules does not affect its magnitude. According to the similarity principle [49], higher the similarity among the systems, higher the value of the entropy will be and higher the stability will be. Replacement of the S₁₀ atom by an O atom in the EDT-DTT molecule decreases the magnitude of entropy suggesting that EDT-DTT is more stable as compared to the EDT-DTO molecule. In case of the radical, the entropy is found to be unaffected due to the cationic radicalization, whereas its magnitude enhances due to the anionic radicalization.

3.6. Electrical Properties

The computed dipole moment (δ), mean polarizability (α), polarizability anisotropy ($\Delta\alpha$) and first hyperpolarizability (β_{total}) are collected in Table 5. The dipole moment is most widely used quantity to

describe the polarity of a molecule [50]. On account of more electronegative character of oxygen atom, the magnitude of the dipole moment of EDT-DTO is less than that of the EDT-DTT suggesting EDT-DTT to be more polar in nature as compared to EDT-DTO. Addition of an electron in the EDT-DTT molecule doubles the polarity of the molecule. On removal of an electron from the EDT-DTT molecule, the magnitude of dipole moment decreases, whereas EDT-DTO shows the opposite tendency.

Table 5. Electrical properties^c of EDT-DTT, EDT-DTT⁺, EDT-DTT⁻, EDT-DTO and EDT-DTO⁺

Parameters	EDT-DTT	EDT-DTT ⁺	EDT-DTT ⁻	EDT-DTO	EDT-DTO ⁺
Dipole moment (δ)	6.3745	5.1146	12.2527	5.6503	6.3676
Mean Polarizability (α)	4.3434	4.1738	2.0258	3.8568	3.5975
Polarizability anisotropy ($\Delta\alpha$)	7.1889	5.9499	1.4055	6.7527	5.6268
First hyperpolarizability (β)	20.3331	18.3059	16.7560	10.3929	14.7073
Total hyperpolarizability (β_{total})	7.9766	10.7216	5.2163	2.4169	9.6922

^c: α , $\Delta\alpha$, β and β_{total} are measured in a.u. and δ is measured in Debye. For α and $\Delta\alpha$, 1 a.u. = $1.6488 \times 10^{-41} \text{ C}^2\text{m}^2\text{J}^{-1}$ and for β , 1 a.u. = $3.2064 \times 10^{-53} \text{ C}^3\text{m}^3\text{J}^{-2}$

The dipole polarizability is a molecular property that represents the response of the molecular charge distribution to the action of an external electric field. The mean polarizability (α) and polarizability anisotropy ($\Delta\alpha$) were calculated from the polarizability components by [51],

$$\alpha = \frac{1}{3} (\alpha_x + \alpha_y + \alpha_z) \quad (10)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} \{(\alpha_y - \alpha_x)^2 + (\alpha_z - \alpha_y)^2 + (\alpha_z - \alpha_x)^2\}^{1/2} \quad (11)$$

Similar to the dipole moment, the magnitude of mean polarizability (α) and polarizability anisotropy ($\Delta\alpha$) decrease due to the substitution of O atom at the S₁₀ site of the EDT-DTT, which could be due to the high electronegativity of O atom. The magnitude of the mean polarizability is found to be almost the same for the neutral and the cationic species of both the molecules, whereas it reduces to half of its value for EDT-DTT. Polarizability anisotropy is found to decrease slightly due to cationic radicalization of both the molecules but decreases drastically as a result of anionic radicalization.

First hyperpolarizability is represented by a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced into 10 components [52]. The output file from the Gaussian 03 provides the 10 components of this matrix as β_{xxx} , β_{xyy} , β_{xyy} , β_{yyy} , β_{xzz} , β_{xzz} , β_{yzz} , β_{yzz} , β_{zzz} and β_{zzz} . The values of the first hyperpolarizability from the Gaussian 03 output file could be computed as explained in Ref [53]. The magnitude of the first hyperpolarizability (β) is given by,

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (12)$$

Magnitude of the first hyperpolarizability reduces to half of its value due to the substitution of O atom at the S₁₀ site of the EDT-DTT molecule because of the electronegative character of the O atom. Addition and removal of an electron in the EDT-DTT molecule decreases the magnitude of β_{tot} , whereas removal of an electron in the EDT-DTO molecule increases its magnitude.

Another quantity of interest in this study is the total hyperpolarizability, which is also known as intrinsic quadratic hyperpolarizability, and it can be calculated using the formula given by [54],

$$\beta_{total} = (\beta_{xxx}^2 + \beta_{yyy}^2 + \beta_{zzz}^2)^{1/2} \quad (13)$$

The total hyperpolarizability is calculated to be 7.9766 a.u. for the neutral EDT-DTT molecule which, reduces by 5.5597 a.u. for the EDT-DTO molecule. As a result of cationic radicalization the magnitude

of β_{total} increases, while it decreases with the anionic radicalization of the neutral molecules.

4 Conclusions

From the present investigations it could be concluded that the EDT-DTT and EDT-DTO molecules and their corresponding radical cations possess non-planar structures with C_2 point group symmetry, whereas radical anion of the EDT-DTT molecule possesses non-planar structure with C_1 point group symmetry. Radical anion of the EDT-DTO molecule is found to be unstable. Addition of an electron in the EDT-DTT involves larger geometry modifications as compared to the removal of an electron from the EDT-DTT molecule, which results in the chair-like conformation. From the present study, one can conclude that EDT-DTT has better charge transfer properties as compared to EDT-DTO and EDT-DTT is a better hole transporter than the electron transporter. The EDT-DTT molecule has higher tendency to accept electrons as compared to EDT-DTO, however, both of these molecules have the same tendency to donate electrons. The present study predicted that the energy gap of the EDT-DTO molecule is greater than that of the EDT-DTT molecule and hence, it is found to be kinetically more stable and chemically less reactive as compared to the EDT-DTT molecule. For the EDT-DTT⁻ molecule, chemical potential is predicted to be positive and electronegativity to be negative, which might be due to the fact that it is thermodynamically more stable as compared to their neutral and cationic species. The EDT-DTO molecule is found to be more aromatic as compared to EDT-DTT and reverse is found in the case of electrophilicity index. The magnitude of the dipole moment of EDT-DTO is less than that of the EDT-DTT molecule, suggesting the EDT-DTT molecule to be more polar as compared to EDT-DTO. Addition of an electron in the EDT-DTT molecule doubles the polarity of the molecule. Polarizability anisotropy is found to decrease slightly due to cationic radicalization of both the molecules but decreases drastically as a result of anionic radicalization of EDT-DTT.

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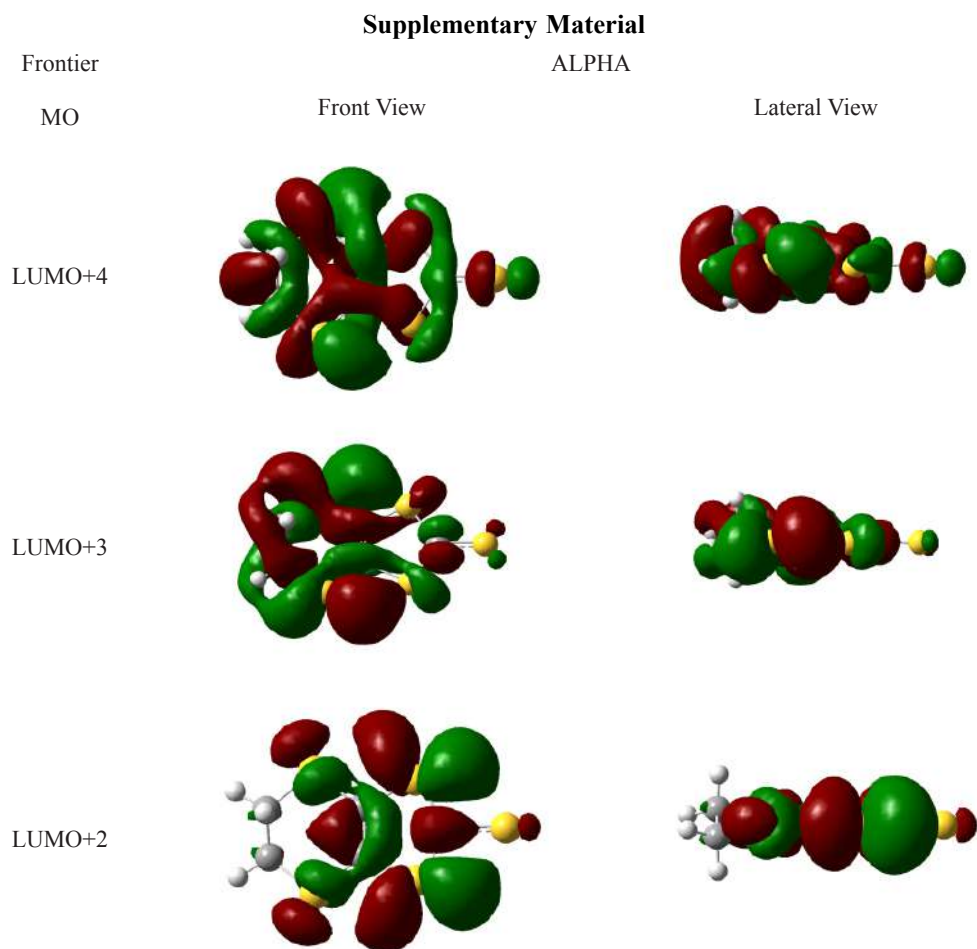
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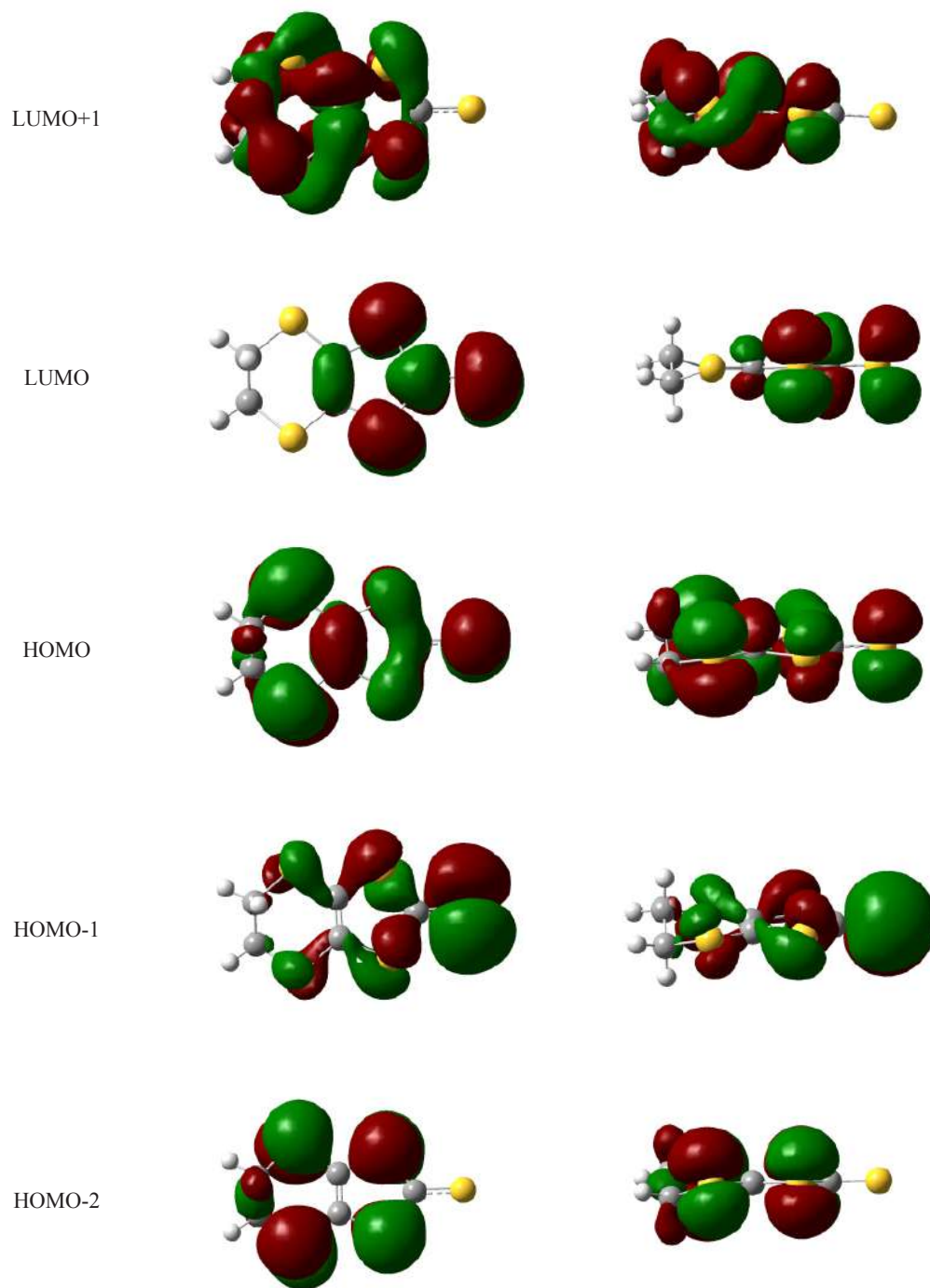
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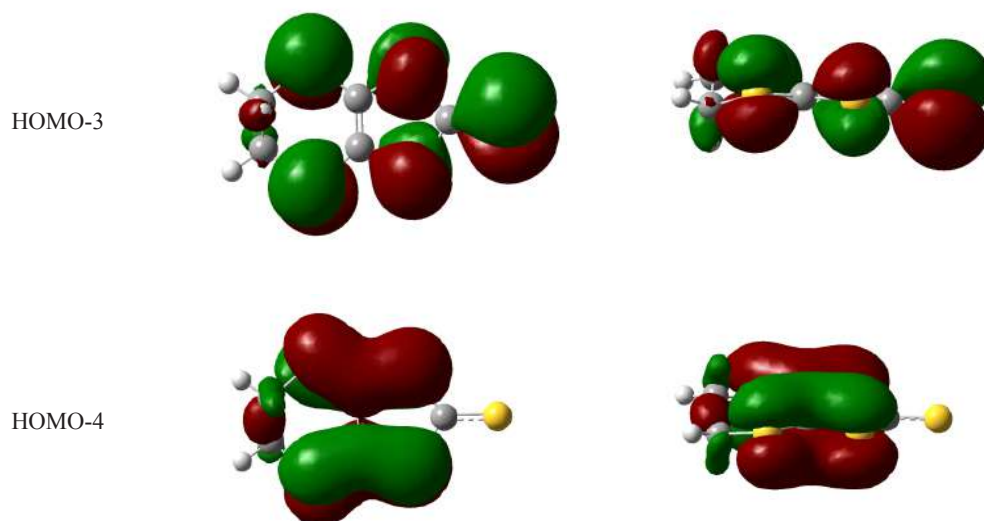
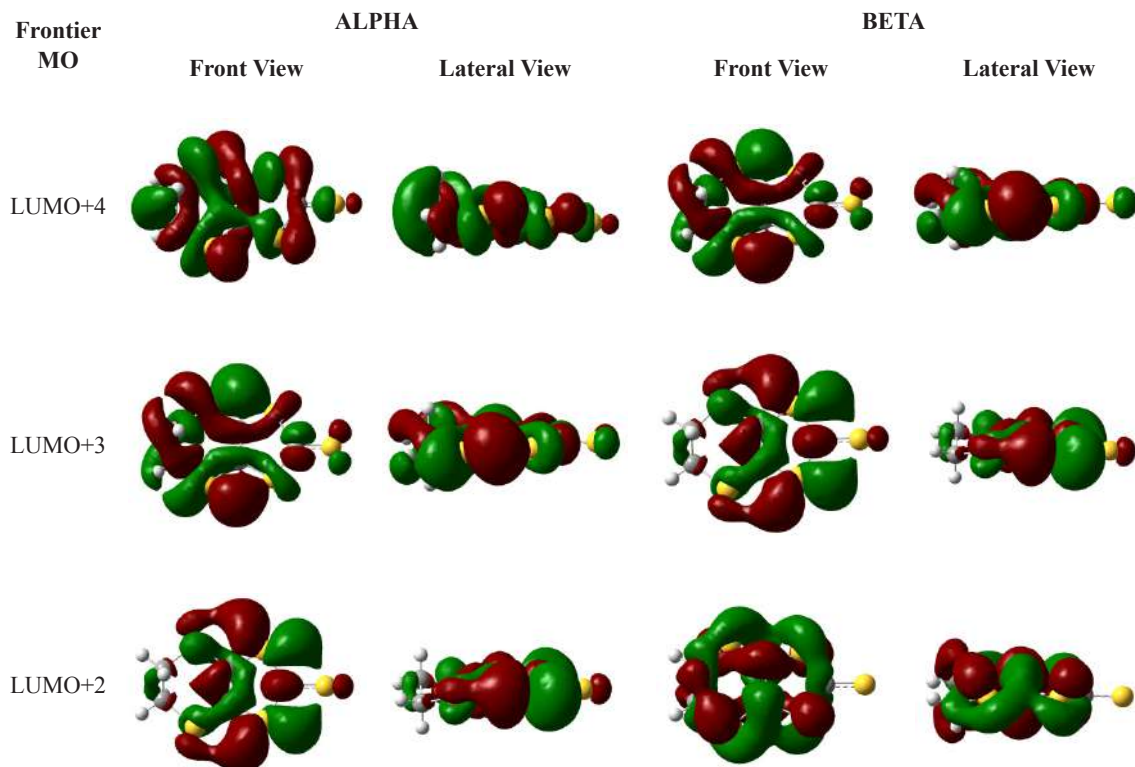


Fig S1. Spatial distributions of the MOs for EDT-DTT



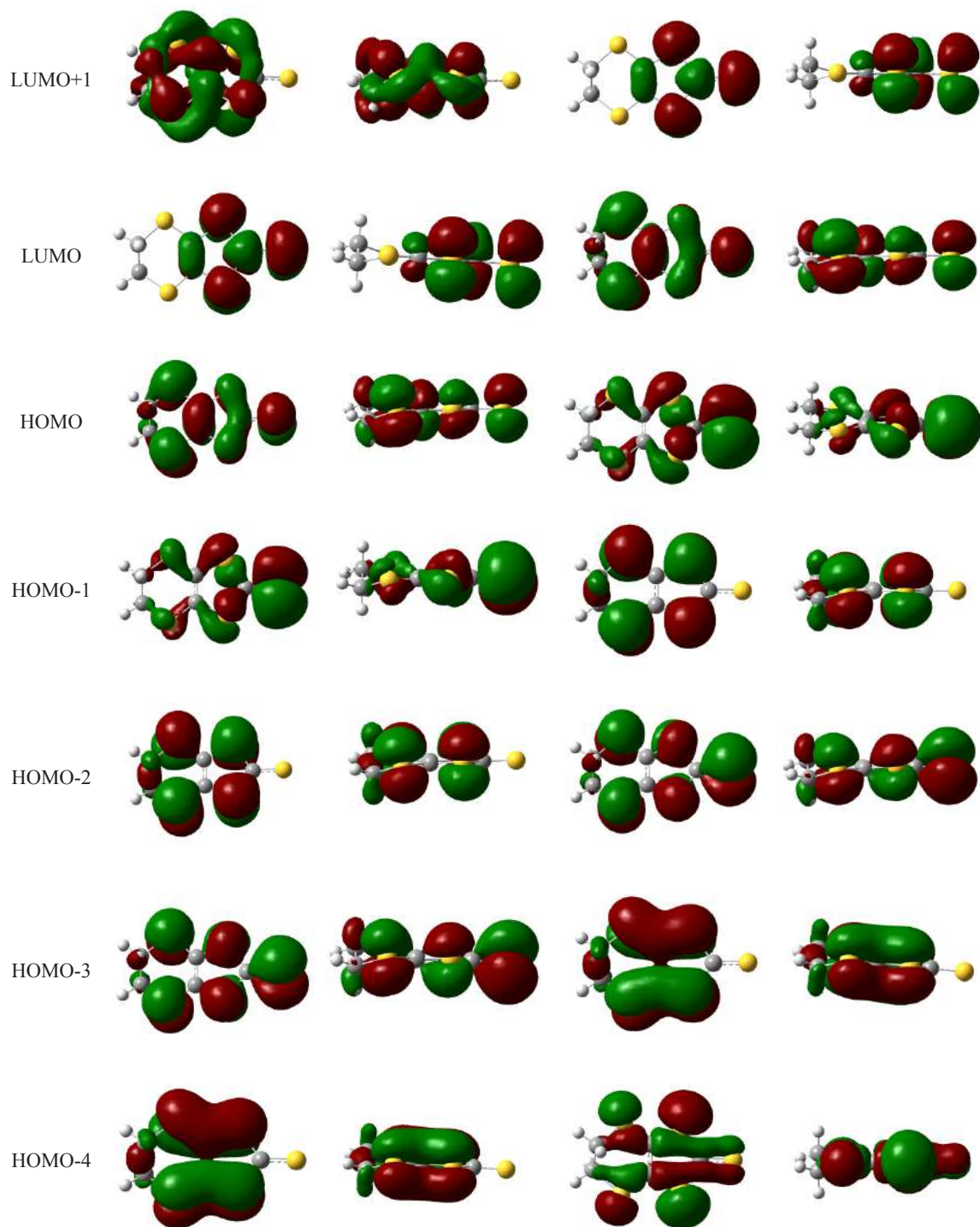
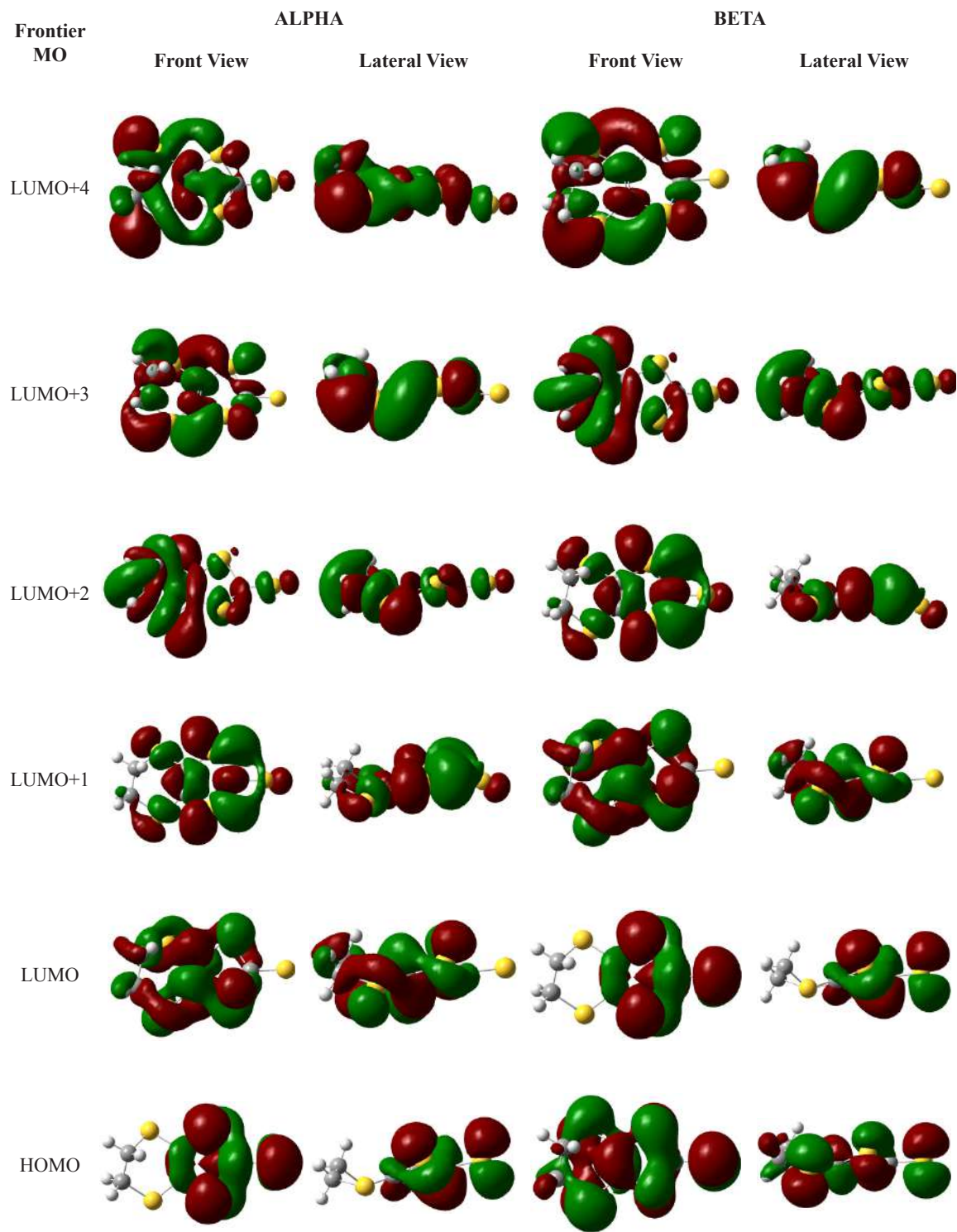


Fig S2. Spatial distributions of the molecular orbital for EDT-DTT⁺



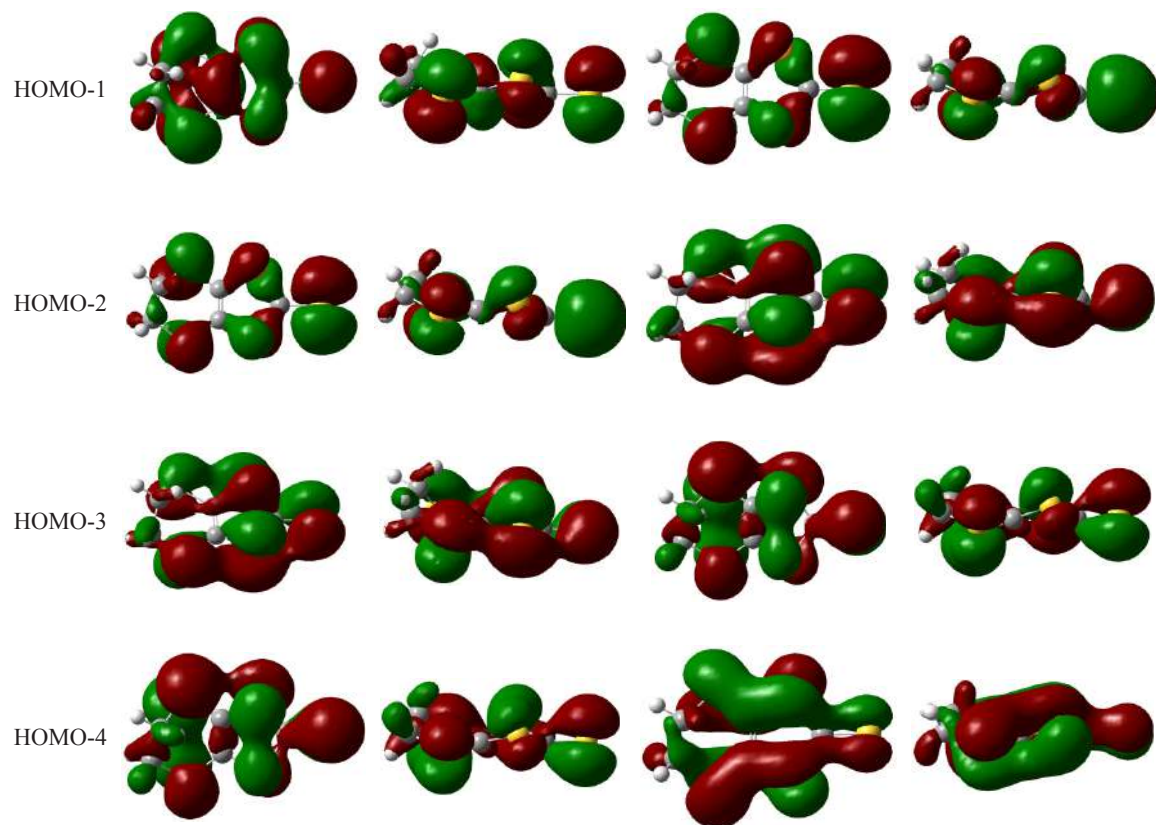
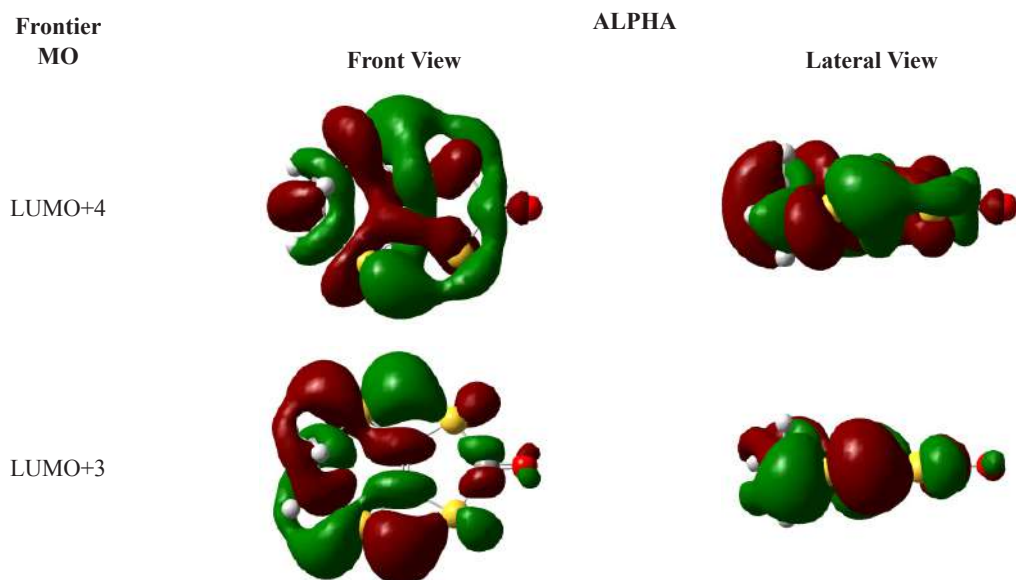
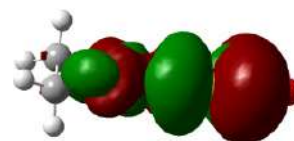
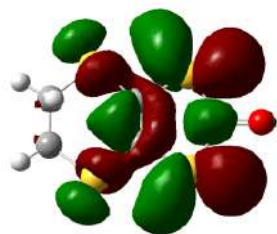


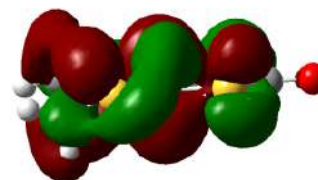
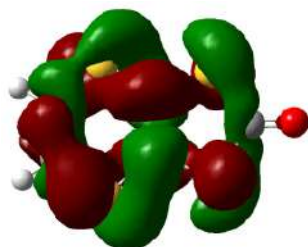
Fig S3. Spatial distributions of the molecular orbital for EDT-DTT⁻



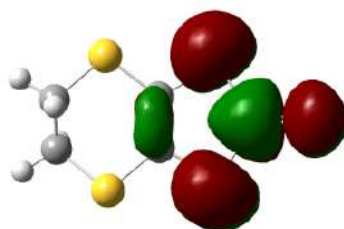
LUMO+2



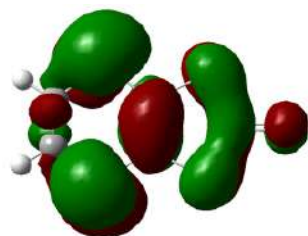
LUMO+1



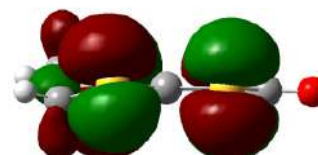
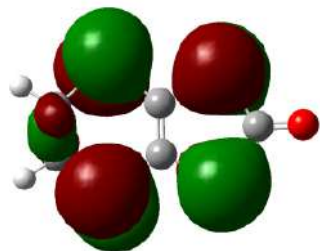
LUMO



HOMO



HOMO-1



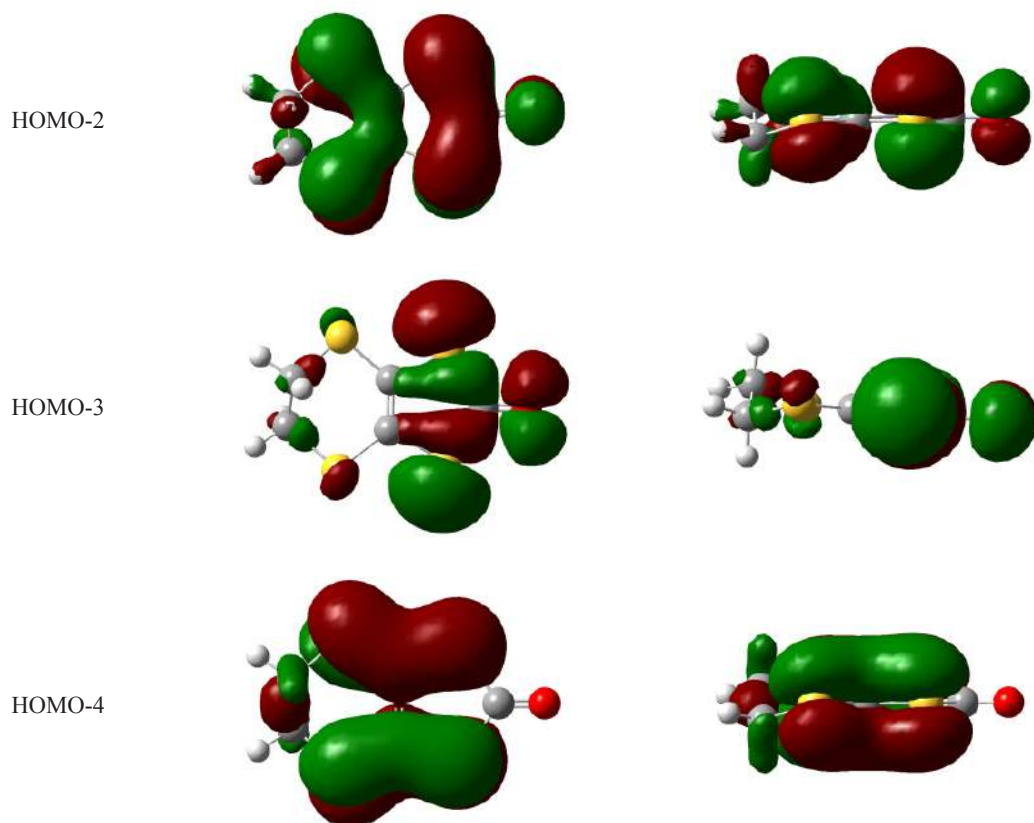
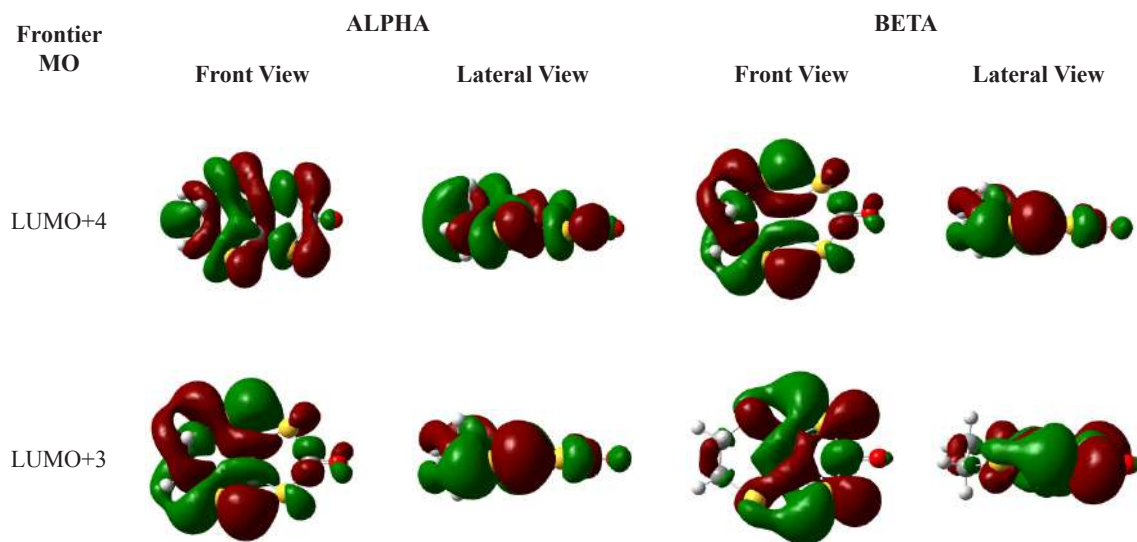
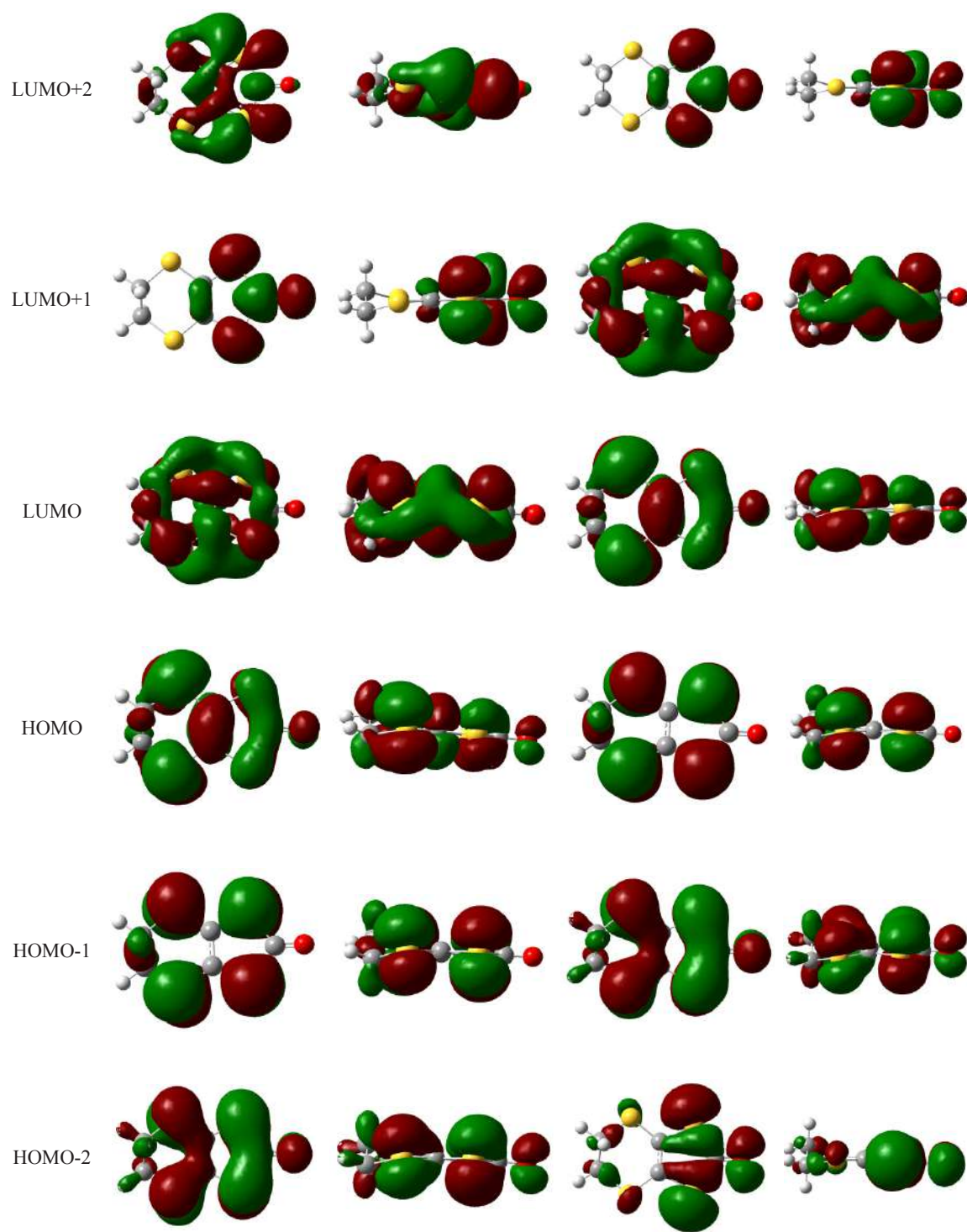


Fig S4. Spatial distributions of the molecular orbital for EDT-DTO molecule





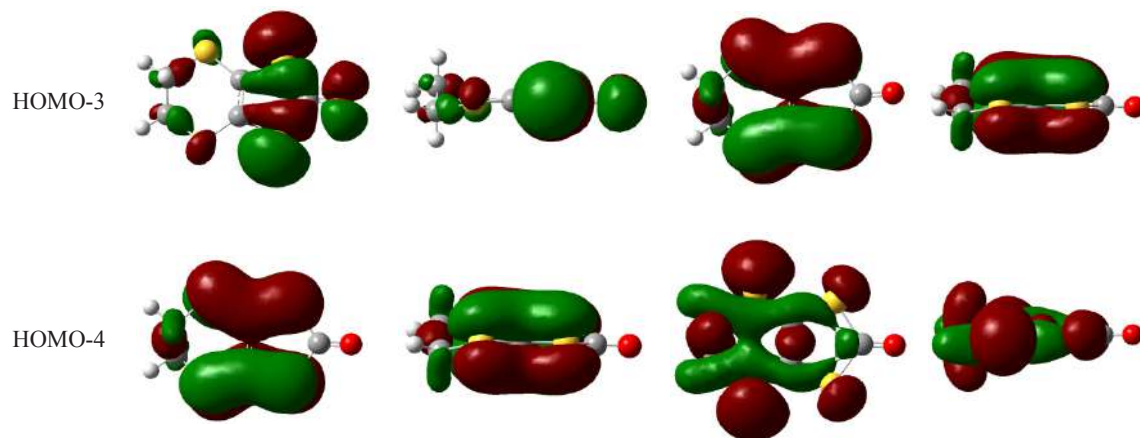


Fig S5. Spatial distributions of the molecular orbital for EDT-DTO⁺ molecule