

# The theoretical investigation of one of the derivatives of 1, 2-dithienylcyclopentene as a molecular switch

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**Abstract** The structural and electronic properties of a three-state molecular switch—an active device in a nano-electronic circuit—were studied using the B3LYP/6-31G\* method. Due to its chemical stability, high conductivity upon doping, and non-linear optical properties, polythiophene is among the most widely studied conjugated organic polymers, both experimentally and theoretically. The aim of the present work was to theoretically study a very complex case: a three-state switch synthesized and experimentally investigated by Nishida et al. (Org Lett 6:2523–2526, 2004). An initial set of test calculations showed B3LYP level of theory and 6-31G\* basis set to be the most appropriate for our purpose, i.e., the study of the structure, charge and spin distributions, as well as electrical characteristics such as electric polarizability, HOMO-LUMO gap (HLG) and electric dipole moment, for one of the 1,2-dithienylcyclopentene derivatives. Also, natural bond orbital analyses were performed to calculate local charges and charge transfers in order to study the capability of the molecule as a molecular switch. The results reported here are of general significance, and demonstrate that it is possible to use certain structural and electrical properties to understand and design electro-photochromic compounds showing a switching function in cases where stable forms can be exchanged by light or electron transfer.

**Keywords** Molecular switch · DFT-B3LYP · Natural bond orbital · 1,2-Dithienylcyclopentene · Charge distribution

## Introduction

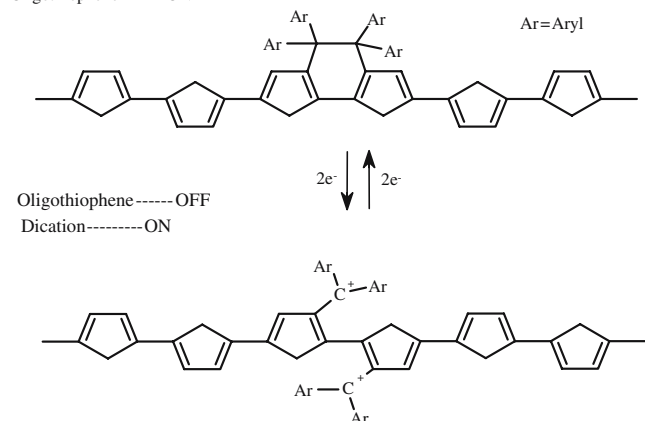
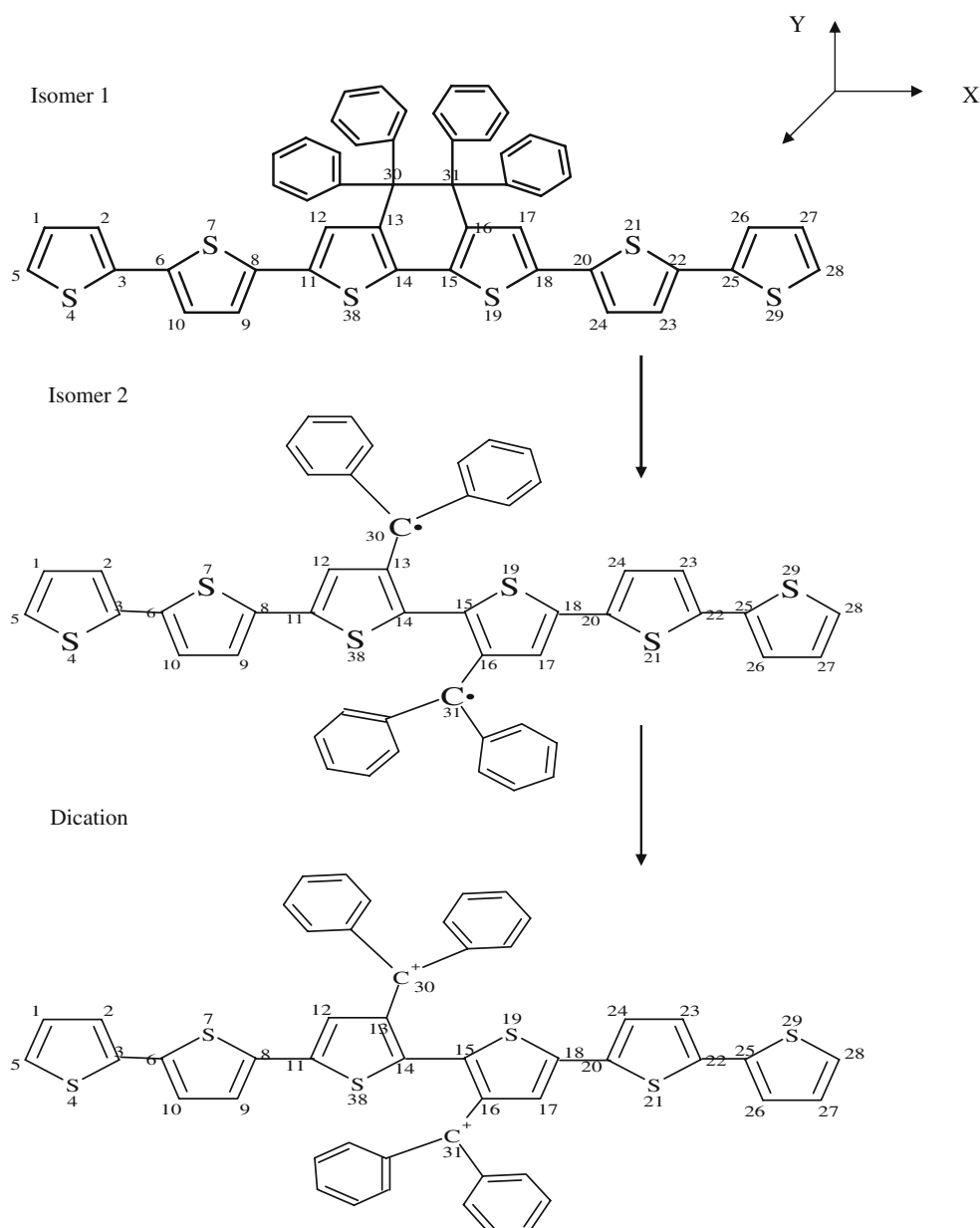
Molecular-scale electronics is developing rapidly because of advances in the synthesis of suitably tailored organic structures, bringing us closer to the ultimate miniaturization of nanoelectronic devices [2–5]. A dominant trend in the design of electronic and photonic devices in recent decades has been a decrease in their dimensions. According to Moore's rule [6], which predicts an exponential decrease in the average size of the constituent elements of these devices, one may expect them to reach the order of molecular dimensions within a short time. Thus, the design of molecular scale electronic devices based on premises deduced from parameters of individual molecules has been of interest to many researchers [7–15].

In recent years, the activity of many research groups has been focused on molecular switches, since they have important applications in nanotechnology, biomedicine and the design of computer chips [16–20]. Such systems are based on the reversible changes in one or more molecular properties, such as conductivity, magnetism or absorption [21]. Molecular switches are the active components of molecular electronic devices capable of inducing chemical and physical changes in response to external stimuli such as electrical current, light, magnetic fields and biological impulses. It has been discovered experimentally that some molecular wires can exhibit electrical bistability, and switch between strongly and weakly conducting states, either spontaneously or in response to a change in applied bias voltage [9, 22–25].

Photochromic molecules such as diarylethenes and electro-photochromic molecules such as oligothiophenes are good examples of bistable molecular systems used for switching purposes [1, 26]. Upon exposure to radiation of a

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Oligothiophene -----ON

**Fig. 1** Model of a thiophene wire incorporating a redox active unit**Fig. 2** Molecular structures of isomers 1 and 2 of 1,2-dithienylcyclopentene and its dication

specific wavelength, or upon applying an oxidant, these systems undergo reversible photochemical reactions, reverting to their original state when irradiated with light of a longer wavelength, or when stored in the dark or with a suitable reductant [1, 27, 28].

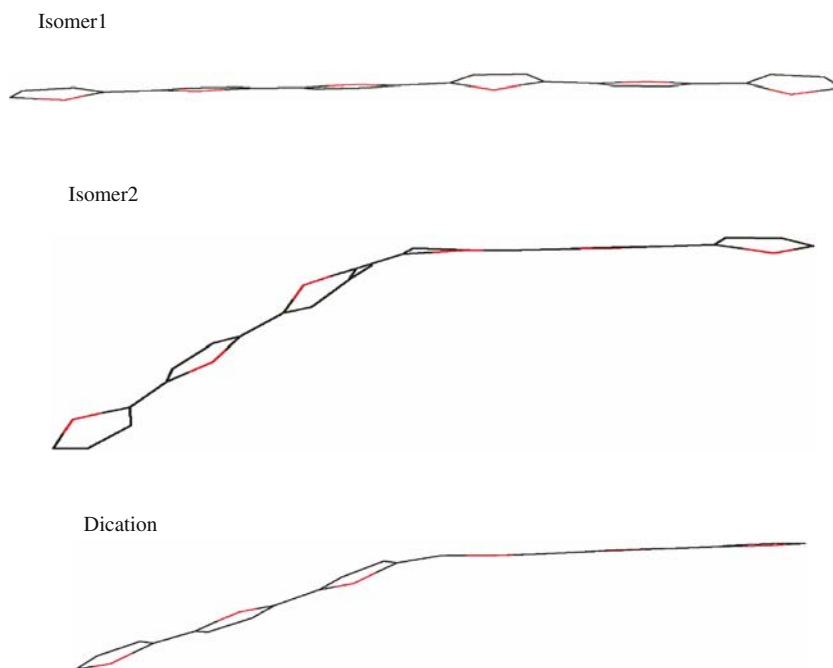
It has been suggested that this intriguing behavior may be due to charging of the molecules and/or changes in molecular geometry (conformation) [24]; however, the complexity of the experimental systems has thus far prevented the development of quantitative exploration of this phenomenon. A variety of theoretical efforts have been presented in recent years, with the aim of understanding such processes and designing more molecular switches.

**Table 1** The dihedral angles of the central bithiophene moieties and the dihedral angles of the neighboring thiophenes in the main chain on the left and right sides of the central bithiophene

	S <sub>38</sub> -C <sub>14</sub> - C <sub>15</sub> -C <sub>19</sub>	S <sub>38</sub> -C <sub>14</sub> - C <sub>15</sub> -C <sub>13</sub>	S <sub>7</sub> -C <sub>6</sub> - C <sub>3</sub> -C <sub>2</sub>	S <sub>29</sub> -C <sub>25</sub> - C <sub>22</sub> -C <sub>23</sub>
Isomer 1	24.32	-1.39	-15.86	16.56
Isomer 2	-158.25	-163.17	-15.64	15.56
Dication	-142.94	167.10	3.00	2.68

Thiophene oligomers are one of the most important materials for making molecular nanowires because of their excellent electron and energy transfer properties through  $\pi$ -conjugation, which can be utilized for the construction of molecular devices. On the other hand, switching such molecular wires via external stimuli is an important theme. For this purpose, switching of the  $\pi$ -conjugation using a conformational change has been considered. Among thiophene oligomers, 1,2-dithienylcyclopentene derivatives have been reported as examples of electro-photochromic compounds showing a switching function, where two stable forms can be exchanged by light or electron transfer (see Figs. 1, 2) [29, 30].

The available experimental data concerning one of the derivatives of 1,2-dithienylcyclopentene has attracted the interest of researchers in this field and focused concentration on its two isomers and cation. The main aim of the present study was to theoretically investigate the electrical conduction properties of the 1,2-dithienylcyclopentene derivative in order to understand its switching behavior in detail, thus providing a useful base from which to design molecular switch candidates.

**Fig. 3** Comparison of planarity of the main chain (thiophene rings only are shown) in the three species (isomers 1 and 2, and the dication)

## Computational procedures

As in all complex systems, identifying the minimum-energy configuration is quite difficult because of the presence of several local minima on the energy surface. Initially, structures of the two isomers and dication were fully optimized using additional step procedures at the AM1 level of semi empirical method as initial guesses and hybrid density functional B3LYP [31] level of theory using the 3–21g\* and 6–31g\* basis set as implemented in the program package Gaussian98 (G98w) [32]. Polarizability calculations were carried out using both Gaussian98 and Gaussian03 [33]. Moreover, natural bond orbital (NBO) [34] analysis were performed at the same level using Gaussian03 to obtain local charges and charge transfers in the isomers and dication.

Many modern programs use density functional theory (DFT). DFT is very attractive for calculation of finite systems because even the lowest level of DFT—the local spin density approximation (LSDA)—includes some electron correlation. This is extremely important in the design of organic molecular systems, which have extended  $\pi$ -systems [35].

Compared to ab initio methods, DFT-B3LYP calculation is more powerful in the prediction of electron properties and optimized geometries of 1,2-dithienylcyclopentene and its isomers. However, this method is time consuming since it involves evaluation of the two-electron integral. Hence, we used B3LYP/6-31G\* as the method of choice for the present work. Analysis of electrical properties was based on atomic charges, charge transfers, electric dipole moment and polarizability tensor elements.

**Table 2** The B3LYP/6-31G\* calculated values of dipole moments (Debye) and energy gaps [HLG (eV)]

	$\mu_x$	$\mu_y$	$\mu_z$	$\mu_{tot}$	HLG(eV)
Isomer 1	0.0057	1.4887	0.3785	1.5361	1.739
Isomer 2	0.1439	0.0131	0.0290	0.1474	2.0874
Dication	-0.0002	-0.0002	2.3144	2.3144	0.594

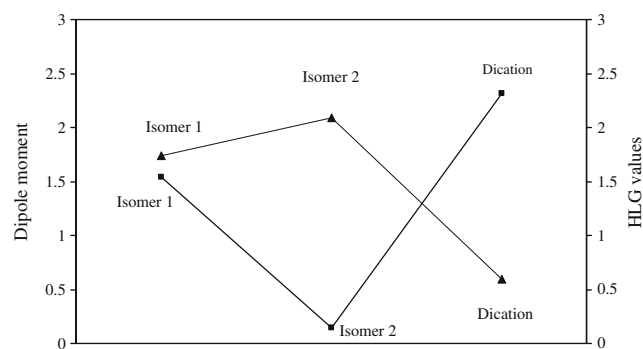
## Results and discussion

### Structural analysis

The electrical conductivity of a molecule depends on many parameters, such as planarity, orientation of the molecule and delocalization in  $\pi$  systems. Thus, here we report our calculation of these parameters, as required to demonstrate the switching behavior of this molecule.

Covalent bond lengths, such as 1.54 Å for  $C_{sp^3}-C_{sp^3}$ , are basic parameters in chemistry [36]. Examples that show marked deviation from standard values have long attracted the attention of chemists [37, 38]. In the course of our study of the molecular systems whose structures are shown in Fig. 2, we have found that the central  $C_{30}-C_{31}$  bond in isomer 1 is fairly long (1.65 Å). X-ray analysis also shows this expansion [1]. This elongation in bond length seems to be caused by two Ar substituents that are located on  $C_{30}-C_{31}$ . Severe steric repulsion between these groups makes this bond the most probable site where a break might happen. Following such a break, spatial rotation in the Cartesian coordination of the molecule turns it into a triplet state diradical molecule (isomer 2). Dication state can then be reached by oxidation of the above rotated isomer.

The dihedral angles of the central bithiophene moieties,  $S_{38}-C_{14}-C_{15}-C_{19}$  and  $S_{38}-C_{14}-C_{15}-C_{13}$ , for the isomers and dication are reported in Table 1. Also, the main chain of these species is depicted in Fig. 3. The data presented in Table 1 and Fig. 3 show the deviation from coplanarity at

**Fig. 4** The HOMO–LUMO gap (HLG) and dipole moments of isomers 1 and 2, and the dication (▲ and ■ represent HLG and dipole moment values respectively) using B3LYP/6–31G\* level of theory**Table 3** Elements of the electric polarizability tensor (bohr<sup>3</sup>) calculated by G03 at DFT 6-31g\* level of theory for the optimized structures

Gaussian 03						
B3LYP/6-31g*						
	$\alpha_{xx}$	$\alpha_{xy}$	$\alpha_{yy}$	$\alpha_{xz}$	$\alpha_{yz}$	$\alpha_{zz}$
Isomer 1	1,430.053	121.422	989.325	-0.95	3.21	574.098
Isomer 2	1,128.266	-41.740	921.109	-1.68	5.849	566.854
Dication	2,533.061	327.998	1,005.481	-0.005	-0.001	586.056

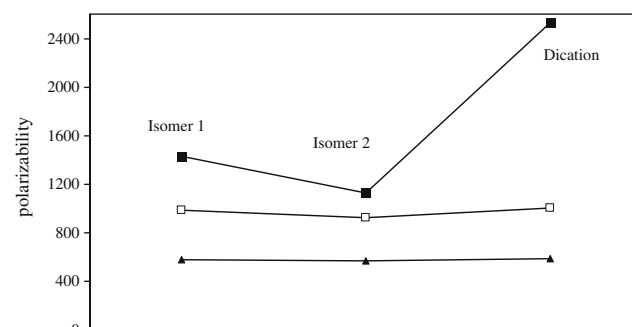
the center of the bithiophene moieties for all these species. These deviations are due to the effects of the phenyl groups located on  $C_{30}$  and  $C_{31}$ . Nevertheless, a detailed analysis shows that the thiophene chains next to the central bithiophene moieties are planer in the dication. However, in the case of isomers 1 and 2 we see a remarkable deviation from planarity (see Table 1 and Fig. 2).

### Electronic properties

#### HOMO-LUMO gap

The energy gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), known as the HOMO–LUMO gap or simply HLG, is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity [14, 39].

The energy gaps were determined by simply taking the differences in energy between HOMO and LUMO energy levels. For  $\pi$ -conjugated systems such as polyenes and the heterocyclic  $\pi$ -conjugated oligomers (e.g., the oligothiophene considered here), the lowest allowed excitations correspond to singlet  $\pi \rightarrow \pi^*$  transitions and provide an estimate for  $\lambda_{max}$  in the UV/VIS absorption spectra [40].

**Fig. 5** Diagonal components of polarizability tensor (■, □ and ▲ represent  $\alpha_{xx}$ ,  $\alpha_{yy}$  and  $\alpha_{zz}$ , respectively) calculated using the B3LYP/6–31G\* method in the Gaussian 03 program package. As can be seen,  $\alpha_{xx}$  exhibits most variation

**Table 4** Natural bond orbital (NBO) charges on desired atoms calculated at DFT-B3LYP/6-31G\* level of theory

<b>Isomers</b> <b>Atoms</b>	<b>Isomer 1</b>	<b>Isomer 2</b>	<b>Dication</b>
<b>C 1</b>	-0.27817	-0.27300	-0.26400
<b>C 2</b>	-0.26164	-0.25622	-0.21238
<b>C 3</b>	-0.25639	-0.24146	-0.26375
<b>S 4</b>	0.47901	0.45368	0.50350
<b>C 5</b>	-0.45251	-0.43295	-0.38463
<b>C 6</b>	-0.24440	-0.22650	-0.17232
<b>S 7</b>	0.48112	0.45703	0.48153
<b>C 8</b>	-0.24474	-0.23004	-0.25696
<b>C 9</b>	-0.25616	-0.24422	-0.20708
<b>C 10</b>	-0.25541	-0.25285	-0.24638
<b>C 11</b>	-0.24155	-0.19813	-0.18558
<b>C 12</b>	-0.24857	-0.23640	-0.22561
<b>C 13</b>	-0.03729	-0.06340	-0.09789
<b>C 14</b>	-0.23471	-0.19068	-0.19724
<b>C 15</b>	-0.23550	-0.19014	-0.19731
<b>C 16</b>	-0.03733	-0.06357	-0.09783
<b>C 17</b>	-0.24879	-0.23625	-0.22529
<b>C 18</b>	-0.24242	-0.19815	-0.18547
<b>S 19</b>	0.50729	0.38826	0.50280
<b>C 20</b>	-0.24589	-0.22964	-0.25675
<b>S 21</b>	0.48375	0.45652	0.48145
<b>C 22</b>	-0.24536	-0.22639	-0.17211
<b>C 23</b>	-0.25572	-0.25273	-0.24625
<b>C 24</b>	-0.25664	-0.24431	-0.20702
<b>C 25</b>	-0.25650	-0.24155	-0.26356
<b>C 26</b>	-0.26166	-0.25625	-0.21230
<b>C 27</b>	-0.27822	-0.27307	-0.26398

**Table 4** (continued)

<b>C 28</b>	-0.45261	-0.43285	-0.38450
<b>S 29</b>	0.47936	0.45366	0.50343
<b>C 30</b>	-0.05052	-0.00658	0.15567
<b>C 31</b>	-0.05055	-0.00663	0.15620
<b>C 32</b>	-0.01909	-0.08031	-0.10686
<b>C 33</b>	-0.03631	-0.06942	-0.10661
<b>C 34</b>	-0.23699	-0.21352	-0.17219
<b>C 35</b>	-0.23832	-0.23379	-0.22743
<b>C 36</b>	-0.23720	-0.22786	-0.15098
<b>C 37</b>	-0.24103	-0.23334	-0.22628
<b>S 38</b>	0.50543	0.38821	0.50284
<b>C 39</b>	-0.22850	-0.20881	-0.17219
<b>C 40</b>	-0.22507	-0.20695	-0.17562
<b>C 41</b>	-0.23668	-0.23197	-0.22543
<b>C 42</b>	-0.23763	-0.22528	-0.15993
<b>C 43</b>	-0.23832	-0.23611	-0.23376
<b>C 44</b>	-0.24154	-0.20302	-0.17631
<b>C 45</b>	-0.03591	-0.06946	-0.10660
<b>C 46</b>	-0.22885	-0.20887	-0.17211
<b>C 47</b>	-0.24108	-0.23346	-0.22631
<b>C 48</b>	-0.23720	-0.22785	-0.15087
<b>C 49</b>	-0.23821	-0.23372	-0.22746
<b>C 50</b>	-0.23688	-0.21345	-0.17210
<b>C 51</b>	-0.01875	-0.08042	-0.10686
<b>C 52</b>	-0.22487	-0.20684	-0.17556
<b>C 53</b>	-0.23671	-0.23171	-0.22547
<b>C 54</b>	-0.23786	-0.22523	-0.15987
<b>C 55</b>	-0.23845	-0.23613	-0.23379
<b>C 56</b>	-0.24152	-0.20316	-0.17622

See Fig. 2 for numbering scheme

Values of HLG ( $=E_{\text{LUMO}}-E_{\text{HOMO}}$ ) for the two isomers and the dication are reported in Table 2, and the variation in HLG is plotted in Fig. 4.

Figure 4 shows that the HLG value increases in going from isomer 1 to isomer 2 and decreases when the dication state is reached. Since HLG is a measure of electrical conductivity, the decreasing trend in the HLG value means that electrical conductivity increases when the dication state is obtained.

In isomer 2, the gap between valence and conduction band is greater than in the other species, therefore expect least conduction in this isomer.

### Electric polarizability

Polarizability is a measure of the ability of a molecule to respond to an electric field. When a molecule is subjected to an external electric field, some of its electrons (certainly from valence orbital HOMO) acquire sufficient energy to move along the direction of the field [41].

To calculate exact polarizability tensor elements, instead of non-post-SCF methods such as RHF and DFT-B3LYP, one should use post-SCF methods such as MPPT, CC, CI, or TD-DFT. Calculations at these high levels of theory are practically impossible for the present molecule with available hardware and software facilities. However, since we are interested in the relative values of polarizability tensor elements of these two isomers and the cation, this does not affect our reasoning. Therefore, polar calculation for the two isomers and cation of the molecule was performed using the Gaussian03 program with B3LYP/6-31G\* level of theory to compute polarizability tensor elements.

Diagonal components ( $\alpha_{xx}$ ,  $\alpha_{yy}$  and  $\alpha_{zz}$ ) and the isotropic component ( $\alpha_{\text{iso}}$ ) of the electric polarizability tensor (in  $\text{a}_0^3$ ) are tabulated in Table 3. The main chain of the molecule, i.e., the thiophene rings expected to conduct the electric current, is in the  $x$  direction of the Cartesian coordinate axes (see Fig. 2). As represented in Table 3 and Fig. 5, there are three important trends for diagonal elements. First,  $\alpha_{yy}$  and  $\alpha_{zz}$  for the three isomers do not differ remarkably, but large differences are seen between  $\alpha_{xx}$  of the two isomers and the cation. Second,  $\alpha_{xx}$  of the cation is very much greater than that of the other species. Third, in comparison to isomers 1 and 2,  $\alpha_{xx}$  of the dication

is markedly higher than  $\alpha_{yy}$  and  $\alpha_{zz}$  of the dication (see Fig. 5). Moreover, Table 3 shows that  $\alpha_{xz}$  and  $\alpha_{yz}$  do not change significantly for the three species, but  $\alpha_{xy}$  for the dication is very much greater than that for the isomers. It is noteworthy that the  $Z$  axis is perpendicular to the plane of the main chain.

In this way, the highest HLG and the lowest  $\alpha_{xx}$  in isomer 2 means that electrical conductivity is lowest in this isomer, and it is clear that the dication state has the greatest conductivity.

### Electric dipole moment

The orientation of the chain of a molecular system is a very important parameter affecting electrical conductivity. Hence, when a molecular system is to be used in an electronic circuit, it is necessary to have some knowledge of the orientation and symmetry of the molecular chain [42]. In this section, we present our calculations of the dipole moments of our molecule.

The calculated values of the electric dipole moment  $\mu$  (in Debye) are presented in Table 2. The analysis shows that the total dipole moment for isomer 2 has the minimum value, meaning that, in this isomer, the orientation of dipole moments in the molecular chain is not in the favorable direction and thus we should not expect much conductivity. The comparison between HLG variation and dipole moment variation plotted in Fig. 4 shows that the dipole moment and HOMO-LUMO gap are inversely correlated.

### Charge density distribution and charge transfer

Natural bond orbital (NBO) analysis provides valuable information on charge, bond type, charge transfer, hybrid direction, resonance weight, bond order and other familiar valence descriptors [34].

The NBO electrical charges on all atoms of the proposed molecule were calculated and are tabulated in Table 4. It can be seen that for each of the three species, positive charges are located on S atoms and all negative charges are located on C atoms. Among all sulfur atoms, the largest positive charges are located on ( $S_{19}$ ,  $S_{38}$ ). Among NBO electrical charges, isomer 2 was observed to have the smallest positive charges on ( $S_{19}$ ,  $S_{38}$ ) compared with the other isomer and the dication.

**Table 5** Some of the charge transfer values obtained from NBO calculations

	Desired charge transfer	Isomer 1	Isomer 2	Dication
1	C <sub>13</sub> -C <sub>14</sub> —————C <sub>12</sub> -C <sub>13</sub>	3.43	1.77	2.88
2	C <sub>15</sub> -C <sub>16</sub> —————C <sub>16</sub> -C <sub>17</sub>	3.43	1.77	2.88
3	C <sub>13</sub> -C <sub>14</sub> —————C <sub>15</sub> -C <sub>16</sub>	14.05	3.21	15.31
4	C <sub>15</sub> -C <sub>16</sub> —————C <sub>31</sub> -C <sub>16</sub>	2.30	4.09	3.46
5	C <sub>14</sub> -C <sub>15</sub> —————C <sub>12</sub> -C <sub>13</sub>	2.01	0.92	1.16

In isomer 1, both ( $C_{30}$ ,  $C_{31}$ ) themselves and all substitutions attached to them have negative charges. The negative charges of ( $C_{30}$ ,  $C_{31}$ ), reinforced by the negative charges of the attached substitutions, bring about a higher density, which will in turn lead to the collapse of the bond between these two atoms, namely ( $C_{30}$ ,  $C_{31}$ ). NBO analysis for isomer 2 indicates that the density of negative charges on ( $C_{30}$ ,  $C_{31}$ ) has decreased. Similar analyses for the dication show positive charges on ( $C_{30}$ ,  $C_{31}$ ).

Examination of the local charges of isomer 1 and the dication shows (see Table 4) that most of the carbon atoms of the dication, along the main chain, have less negative charge in comparison to isomer 1, thus the charge distribution is greater for the dication.

Charge transfer was also obtained from NBO calculations (see Table 5). Charge transfers between  $C_{13}$ – $C_{14}$  and  $C_{12}$ – $C_{13}$ , and between  $C_{15}$ – $C_{16}$  and  $C_{16}$ – $C_{17}$ , are the same (charge transfers on both sides of the center biothiophene moieties). These charge transfers are lowest for isomer 2. The third row of Table 5 shows that charge transfers between  $C_{13}$ – $C_{14}$  and  $C_{15}$ – $C_{16}$  for the dication and isomer 1 differ significantly from that of isomer 2. The reader should note that these double bonds are conjugated at the middle of the central biothiophene moieties, the fundamental site of the switching function of the species. Charge transfers between  $C_{15}$ – $C_{16}$  and  $C_{31}$ – $C_{16}$ , which is not along the main chain, are highest for isomer 2. Charge transfers between  $C_{14}$ – $C_{15}$  and  $C_{12}$ – $C_{13}$  are lowest for isomer 2. All these values indicate that isomer 2 experiences local resonance instead of linear resonance. However, isomer 1 and the dication exhibit linear resonance.

## Conclusions

In this paper, the DFT-B3LYP/6-31G\* method has been used successfully to study oligothiophenes containing a redox active hexaarylethane unit, in which C–C bond making/breaking is reversibly induced upon electron transfer. This system shows a remarkable switching function. The results demonstrate that it is possible to investigate and predict the electrical behavior of molecules by using a quantum-chemical calculation.

From the point of view of possible applications in real molecular electronic architecture, the derivative of 1,2-dithienylcyclopentene examined here has been identified as a three-state switch.

Structural analysis shows a favorable linear resonance in the dication in comparison to the isomers. This difference can be assigned to the coplanarity of the main chain as well as to the central location of the biothiophene moieties in the dication.

Analysis of the electronic properties confirmed that isomer 2 has the highest HLG. This is in accordance with

the fact that a higher HLG means a lower conductivity. The lowest HLG value, causing the highest conductivity, is observed in the dication. The results obtained from dipole moment and polarizability calculations demonstrated that isomer 2 has the least conductivity among these three species, according to its low dipole moment and  $\alpha_{xx}$  values. For the above reasons, the dication has the highest conductivity among the three species examined.

NBO analysis also indicated that, in isomer 2, charge transfer between the two sides of the molecule is lower than in the other isomer and dication. The most favorable charge transfer was seen in the dication.

Isomer 2 can be considered as being in the “OFF” state due to its poor electronic properties. The best conductivity was seen in the dication, which can be considered as the “ON” state. Isomer 1 shows a conductivity between that of isomer 2 and the dication.

As a closing remark, we believe that this device, although still at the embryonic stages of development, may open bright horizons in almost all engineering fields through the application of either organic or inorganic molecular chains.

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