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Analysis of Biphenylene and Benzo{3,4}cyclobuta{1,2-c} thiophene Molecular Orbital Structure using the Hückel Method

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Abstract: *The Hückel method is an old fashion method to predict the molecular orbital and energies of π electrons in a conjugated molecule. Although Hückel's theory's approximations are relatively crude, its general results are still reasonable compared to the advanced computing method and experimental results for many molecules. This paper describes the Hückel calculation of biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene using the HuLis software. The benzo{3,4}cyclobuta{1,2-c}thiophene is a derivative of biphenylene, in which case one of the benzene rings is replaced by a thiophene ring. This change produces new electronic properties that are interesting to study. This work focused on calculating those molecules on energy levels diagrams, linear combination coefficient of molecular orbitals, molecular orbital shape, energy gap, resonance energy, bond-order, bond length, and charge distribution (π electron population). Besides, we calculate the harmonic oscillator measure of aromaticity (HOMA) parameter to study the Hückel method's validity.*

Keywords*: Hückel, HuLis, biphenylene, benzo{3,4}cyclobuta{1,2-c}thiophene, HOMA*

1. Introduction

The first impression when hearing the molecular orbitals is the difficulty with the mathematical function involved. The Hückel theory, first proposed by Erich Hückel in 1930 [1–4], offers a relatively simple calculation with quite useful information for π electron system of a conjugated molecule. See Ref. [5] for a review. Compared to other advanced computational methods, the calculation procedure of the Hückel method is relatively simple, which has led the process to known as "behind the envelope" [6]. The weakness of this method is rough approximations for the calculation. However, this method can be used to calculate the molecular orbital of various conjugated molecules and relatively easily understandable by undergraduate students [7,8].

Biphenylene molecule (C12H8) is a planar polycyclic hydrocarbon molecule consisting of 2 aromatic benzene rings held together by a pair of antiaromatic bonds known as cyclobutadiene [9,10] to form a 6-4-6 system, as shown in Figure 1a. Biphenylene has been widely studied both experimentally and theoretically [9,11–14] and can be used as a basis for studying molecular physics with characteristic properties. From the structurally theoretical point of view, while benzene is an aromatic molecule, the existence of a cyclobutadiene ring in between two benzene rings has emerged the anti-aromaticity of this molecule [10]. However, the results of current-density calculations by application of a unit magnetic field perpendicular to the molecular plane has shown a strong paratropic (anti-aromatic) circulation within the four-membered ring (represented by a clockwise circulation) and a somewhat weaker diatropic (aromatic) circulation along the six-membered rings (represented by a counterclockwise circulation) [15]. This result is in agreement with a naive application of a local version of Hückel 4n+2 rule for aromaticity and 4n rule for anti-aromaticity [16].

Biphenylene and its derivatives offer many applications such as thin films polymer with anomalously high electrical conductivity [17], and the precursor for 2D porous graphene dehydrogenation or biphenylene carbon with intrinsic nonzero gap value and delocalized frontier orbitals that indicate a structure with high electronic mobility [18]. A recent study by Takano et al. [19] shows that biphenylene motif can be used in functional materials, namely, it can act as a spacer in a variety of functional

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molecules and serves as a backbone for catalysts and ligands. Recently, Pagano et al. [20] reported that actinide substitution into one of the benzene rings of the biphenylene produces a new, more stable electronic structure whose usefulness led to energy storage applications. It is to be noted that the local aromaticity of the annelated biphenylene derivatives is very dependent on the modes of annelation, and can vary from highly anti-aromatic to nonaromatic [15].

Among the derivatives of biphenylene, benzo{3,4}cyclobuta{1,2-c}thiophene (Figure 1 (b)) in which one of the benzene rings is replaced by the thiophene ring is very interesting. This change produces significant changes in the electronic properties, and based on DFT computational study, Hashimoto and Tahara [21] has predicted that the presence of sulfur (S) atom in the benzo{3,4} cyclobuta{1,2-c}thiophene responsible for the most stable molecule in terms of its degree of aromatization. In this work, the purely Hückel method will be used to determine the energy levels and molecular orbitals of biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene by using the HuLis software. The results will be further analyzed to obtain various parameters, such as molecular orbital shape, gap energy, resonance energy, bond order, bond length, and electron density. The change in aromaticity will be analyzed in terms of HOMA (harmonic oscillator measure of aromaticity) value [22], as the structural criterion for local aromaticity and nonaromaticity of benzene and thiophene rings.

2. Materials and methods

Solution for the energy level and molecular orbital within the Hückel theory is based on Schrödinger equation for π electron system,

$$\hat{H}\,\varphi = E\,\varphi \qquad (1)$$

Using the linear combination of atomic orbital (LCAO) model [5], the molecular orbitals (φ_n) of π electron system are expressed as a linear combination of the atomic orbitals defined in equation (2),

$$\varphi_n = \sum_{i=1}^{N} c_{ni} p_i \qquad (2)$$

with c_{ni}'s are the linear combination coefficients to the i atom and p_i is the $2p_z$ atomic orbital in the i atom, and i index (i = 1, 2, …4.) run for all carbon atom that build the molecule.

Within Hückel's approximation, the matrix element of the system's Hamiltonian can be written as [5],

$$H_{ij} = \langle p_i|\hat{H}|p_j\rangle = \begin{cases} \alpha, & i = j \\ \beta, & i - j = \pm 1 \end{cases} \qquad (3)$$

with α and β are the Coulomb integral and resonance integral of the π electron system, respectively. Besides, the overlap matrix is diagonal, as expressed by

$$S_{ij} = \langle p_i|p_j\rangle = \delta_{ij} \qquad (4)$$

In this work, we use computational calculations to determine molecular orbitals by using the HuLis software, as shown in Figure 2. HuLis is a Java/html5-based software for Hückel molecular orbital analysis. This software is freely available for molecular orbital analysis and can be found at http://www.hulis.free.fr [23–26]. As shown in Figure 2, the software consists of 3 panels, namely Hückel tools (blue-left), central panel (center), and Lewis tools (orange-right) [27]. The central panel gives a facility to draw the molecule's carbon skeleton with atomic numbering, parameters related to α and β values, and charges. Besides that, a selection of orbital molecule's energy also gives a display for orbital molecules. To input the molecular structure, as depicted in the central panel, besides choosing the appropriate atom, one has to give attention to the coordination number.

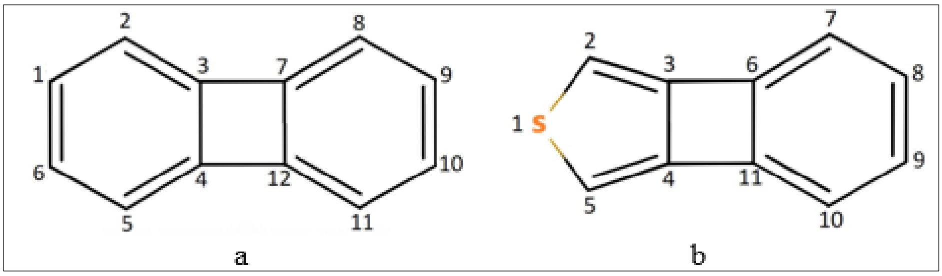


Figure 1. The molecular structure of (a) biphenylene and (b)benzo{3,4}cyclobuta{1,2-c}thiophene

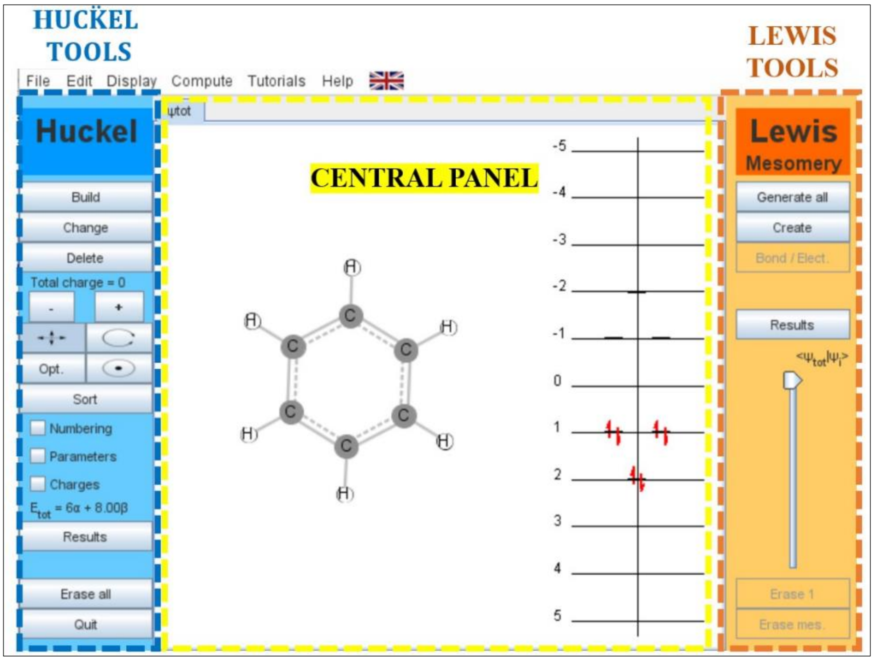


Figure 2. The view of HuLis software

Biphenylene is a molecule consisting of 12 C atoms while its derivative benzo{3,4}cyclobuta{1,2-c}thiophene consisting of 10 C atoms and 1 S atom. The molecular structures of the biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene are shown in Figure 1a and Figure 1b, respectively. From the molecular structure, the HuLis software will generate the Hamiltonian of the system as shown in Figure 3a for biphenylene and Figure 3b for benzo{3,4}cyclobuta{1,2-c}thiophene.

$$\begin{vmatrix}
\alpha & \beta & 0 & 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
\beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \beta & \alpha & \beta & 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\
0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
\beta & 0 & 0 & 0 & \beta & \alpha & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \beta & 0 & 0 & 0 & \alpha & \beta & 0 & 0 & 0 & \beta \\
0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta \\
0 & 0 & 0 & \beta & 0 & 0 & \beta & 0 & 0 & 0 & \beta & \alpha
\end{vmatrix}
\qquad
\begin{vmatrix}
\alpha & \beta & 0 & 0 & 0.69\beta & 0 & 0 & 0 & 0 & 0 & 0 \\
\beta & \alpha & \beta & 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 \\
0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\
0 & 0 & \beta & \alpha & 0.69\beta & 0 & 0 & 0 & 0 & 0 & 0 \\
0.69\beta & 0 & 0 & 0.69\beta & \alpha + 1.1\beta & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \beta & 0 & 0 & 0 & \alpha & \beta & 0 & 0 & 0 & \beta \\
0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta \\
0 & 0 & \beta & 0 & 0 & \beta & 0 & 0 & 0 & \beta & \alpha
\end{vmatrix}$$

a b

Figure 3. Hamiltonian matrix element of (a) biphenylene and (b) for benzo{3,4}cyclobuta{1,2-c}thiophene within the Hückel approximation

From Figure 3b one can see that the presence of S atoms in the thiophene ring of benzo{3,4} cyclobuta{1,2-c}thiophene molecule will change the α and β values of the Hamiltonian [28]. We note that these values change is related to different core energies compared to C and the change in the effective electronegativity of the remaining nonbonded *p* orbitals at the center.

The gap energy (E_{gap}) is calculated from the difference in energy levels between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies which are formulated in equation (5) [5].

$$E_{gap} = E_{HOMO} - E_{LUMO} \tag{5}$$

In addition, the resonance energy or delocalization energy is calculated from the difference between the energy of the actual structure (*E*) and the energy of the separate structure (*E'*) which is formulated in equation (6) [5].

$$E_R = E' - E \tag{6}$$

The bond order between atoms is related to the strength (or degree of electron sharing) between adjacent atoms. The bond order between atoms *i* and *j* (ρ_{ij}) is calculated using equation (7) [5].

$$\rho_{ij} = \sum_{n}^{N} v_n c_{ni} c_{nj} \tag{7}$$

Here, n is the orbital number of the molecule, N is the number of filled molecular orbitals, v_n is the number of π electron populations in the *n* molecular orbital that is filled, and c_{nj} is the linear combination coefficients to the *i* atom.

The bond order has a relationship with the bond length. The greater the bond order, the stronger the bond, and the shorter the bond length. The relationship between bond order and bond length (l_{ij}) follows the empirical formula of Mochalkhin et al. [13] shown in equation (8).

$$l_{ij} = 1.54 - 0.21\rho_{ij} \tag{8}$$

The charge distribution (π electron population) is determined according to equation (9) [5].

$$\rho_i = 2\sum_{n} c_{ni}^2 \tag{9}$$

Following the empirical formula of Krygowski [29] we calculate HOMA (Harmonic-Oscillator Measure of Aromaticity) as the structure indicator for local aromaticity and nonaromaticity of π-electron molecules based on values of bond length. Smaller HOMA indicates lower aromatic character [30]. The HOMA value of the benzene ring were calculated using equation (10).

$$\mathrm{HOMA} = 1 - \frac{\alpha_{CC}}{6}\sum_{i}^{6}\left(R_{opt,cc} - R_{cc,i}\right)^2 \tag{10}$$

while the HOMA value of thiophene ring was calculated using equation (11)

$$\mathrm{HOMA} = 1 - \frac{\left\{\alpha_{CC}\sum_i^3\left(R_{opt,cc} - R_{cc,i}\right)^2 + \alpha_{CS}\sum_i^2\left(R_{opt,cs} - R_{cs,i}\right)^2\right\}}{5} \tag{11}$$

with CC and CS denote as a carbon-carbon and carbon-sulfur, respectively. Optimal bond lengths R_{opt} and constants α were derived from equation (12) and (13), respectively

$$R_{opt,cc} = \left(R_{s,j} + wR_{d,j}\right) / \left(1 + w\right) \tag{12}$$

$$\alpha_j = 2\left[\left(R_{s,j} - R_{opt,j}\right)^2 + \left(R_{d,j} - R_{opt,j}\right)^2\right]^{-1} \tag{13}$$

Here, j is bond type, R_s and R_d correspond to the value of reference lengths for single or double bonds, respectively, and w is the ratio of force constants for single and double bonds (w=2). $R_{s,j}$ and $R_{d,j}$ correspond to the C–C and C=C bonds of 1,3 butadiena and C–S and C=S bonds of dimethyl sulfide and methanethial

3. Results and discussions

The energy levels of biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene molecules are represented in Figure 4a and Figure 4b, respectively. Both of biphenylene and benzo{3,4}cyclobuta {1,2-c}thiophene molecule, the bonding orbitals are fully occupied by the electrons with opposite spins so that their ground state is a singlet.

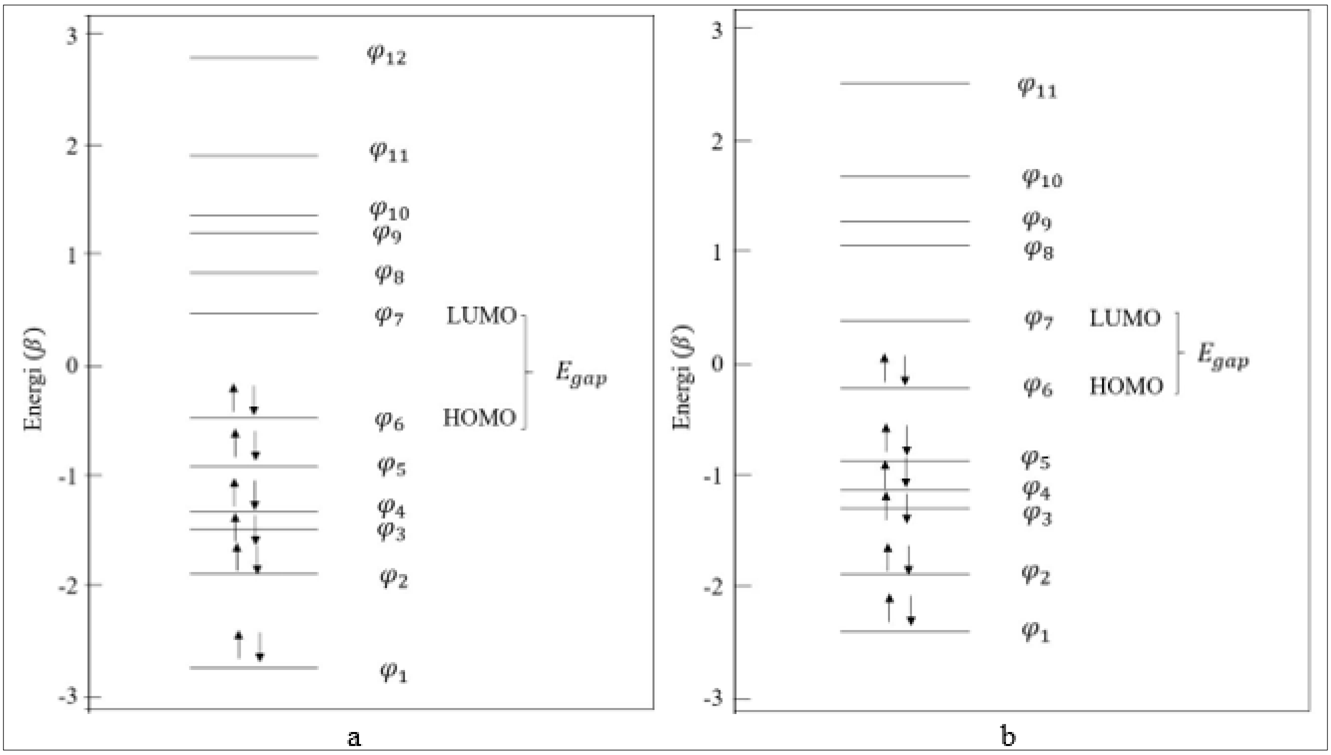
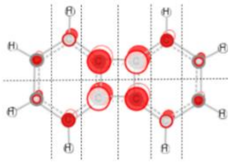
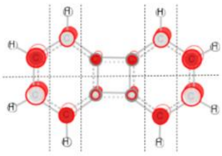
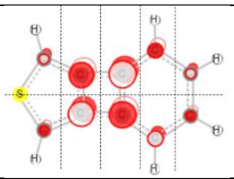
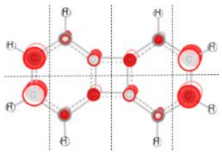
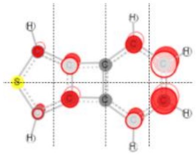
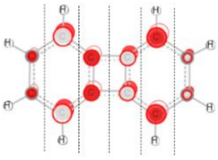
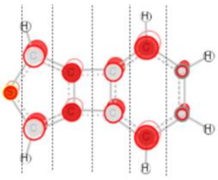
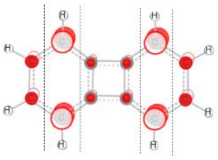
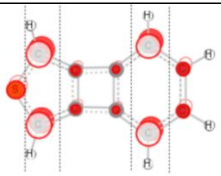
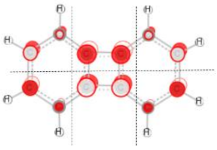
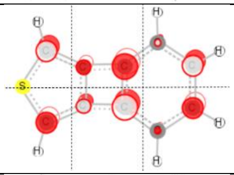
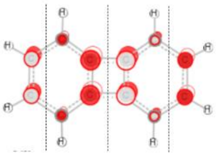
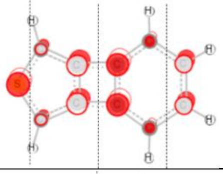
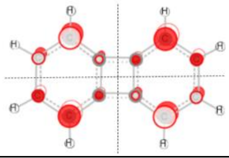
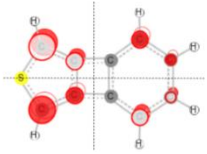
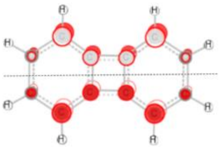
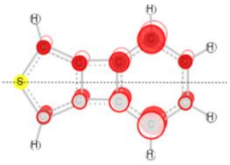
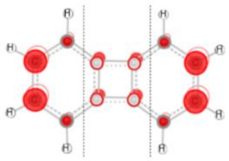
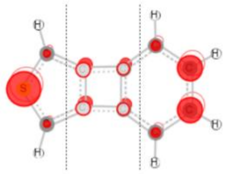
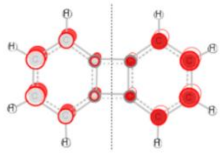
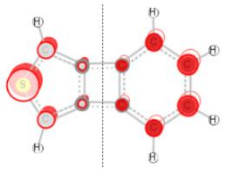
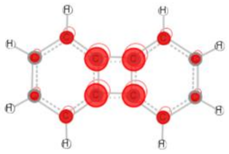
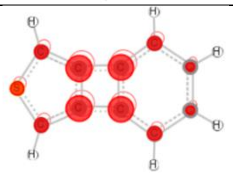


Figure 4. Energy level diagram for molecules (a) biphenylene and (b) benzo{3,4}cyclobuta{1,2-c}thiophene

Molecular orbitals of the biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene molecules are shown in Table 1 along with characteristic nodal lines. The white colour shows a positive charge while the red colour is a negative charge. From this table, one can see that the lowest energy level corresponding to the delocalization of π electrons along with two benzene rings and cyclobutadiene ring for biphenylene molecule while for benzo{3,4}cyclobuta{1,2-c}thiophene molecules along with benzene, thiophene, and cyclobutadiene ring. With increasing the energy, the number of nodal lines is also becoming more, signifying the reduction of π electron delocalization, in good agreement with a previous study [15].

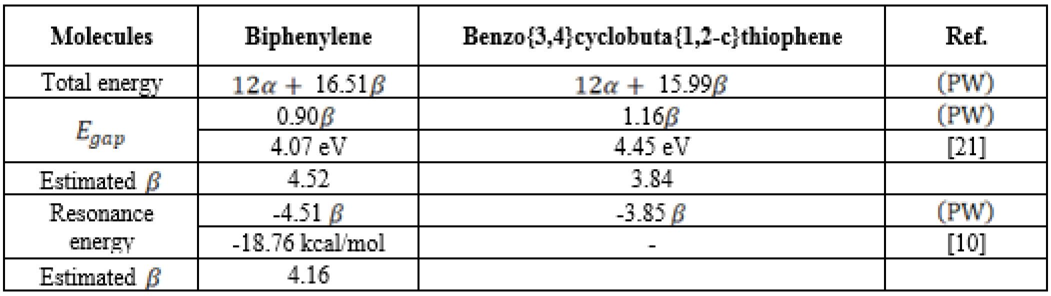
Table 1. Molecular orbitals of biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene. Dotted lines indicate the characteristic nodal lines

MO	Biphenylene	Benzo{3,4}cyclobuta{1,2-c}thiophene
φ_{12}		
φ_{11}		
φ_{10}		
φ_{9}		
φ_{8}		
φ_{7}		
φ_{6}		
φ_{5}		
φ_{4}		

φ_3		
φ_2		
φ_1		

The total energy, gap energy (E_{gap}) and resonance energy of biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene obtained from this calculation and previous studies [10,21] are summarized in Table 2. The HOMO energy in the biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene molecules is at the ε_6 energy level while LUMO energy is at the ε_7 energy level. Since the aromatic molecule has high stability with relatively large gap energy, the decrease of energy gap might indicate the increase of non-aromaticity of the molecule [21]. In terms of β parameter, the larger energy gap of benzo{3,4}cyclobuta{1,2-c}thiophene compared to biphenylene obtained in this work is in good agreement with a previous calculation study based on DFT method. This result indicates that biphenylene is more non-aromatic than benzo{3,4}cyclobuta{1,2-c}thiophene [21].

Table 2. The total energy, gap energy, resonance energy of the biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene from present work (PW) and previous studies [10,21] along with estimated β values from each energy parameter



Molecules	Biphenylene	Benzo{3,4}cyclobuta{1,2-c}thiophene	Ref.
Total energy	$12\alpha + 16.51\beta$	$12\alpha + 15.99\beta$	(PW)
E_{gap}	0.90β	1.16β	(PW)
	4.07 eV	4.45 eV	[21]
Estimated β	4.52	3.84	
Resonance energy	$-4.51\ \beta$	$-3.85\ \beta$	(PW)
	-18.76 kcal/mol	-	[10]
Estimated β	4.16		

Figure 5a and Figure 5b show the bond order of the biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene, respectively, which is calculated using equation (7). According to Ref. [31] the bond order is proportional to the dissociation energy, which is a measure of the chemical bond strength and molecule stability. The bond order of benzene ring in biphenylene molecules is greater than the corresponding bond order in benzo{3,4}cyclobuta{1,2-c}thiophene . On the other hand, in the middle of anti-aromatic connecting region, the bond order of the biphenylene (atomic number 3-7) is smaller than that of benzo{3,4}cyclobuta{1,2-c}thiophene (atomic number 2-6). The bond order comparison for biphenylene molecule and those reported in Ref. [13] (Figure 6) shows a satisfactory agreement and the regularity of the resulted values. As far as we know, there is no available bond order of benzo{3,4}cyclobuta{1,2-c}thiophene from the previous study.

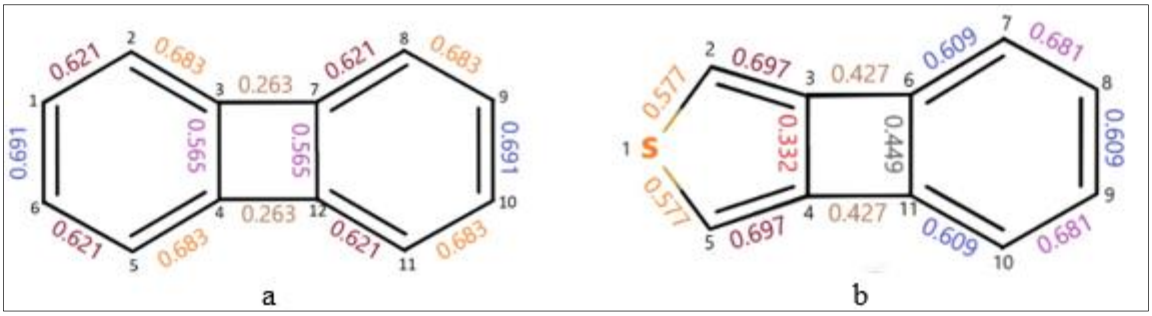


Figure 5. The bond order of (a) biphenylene and
(b) benzo{3,4}cyclobuta{1,2-c}thiophene.
For each figure, the same number is indicated by the same color

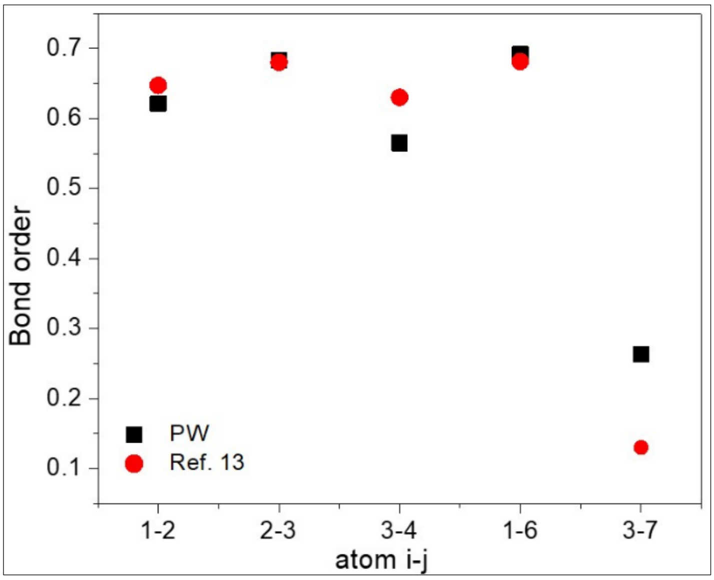


Figure 6. The selected bond order of biphenylene
compared to a previous study [13]

The calculated bond length of biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene from equation (8) are shown in Figure 7a and Figure 7b, respectively. The results of bond length calculation are also compared with different methods of previous studies, namely theoretical calculation [13], computational with DFT method [21,14], computational rotation and oscillation photographs of crystals [11], experimental neutron scattering [32] for biphenylene, and computational with DFT method [21] for benzo{3,4}cyclobuta{1,2-c}thiophene. It can be seen that bond length alternation is shown for the two molecules. Besides that, the bond length for the benzene ring in the biphenylene molecule is smaller than that of benzo{3,4}cyclobuta{1,2-c}thiophene. The results of comparison as shown in Figure 8a show that the bond lengths of biphenylene molecule (Figure 8a) have good regularity with those reported in Refs. [13,14,32]. A pronounced difference with the Ref. [21] for C–S bond length is shown for the benzo{3,4}cyclobuta{1,2-c}thiophene (Figure 8b).

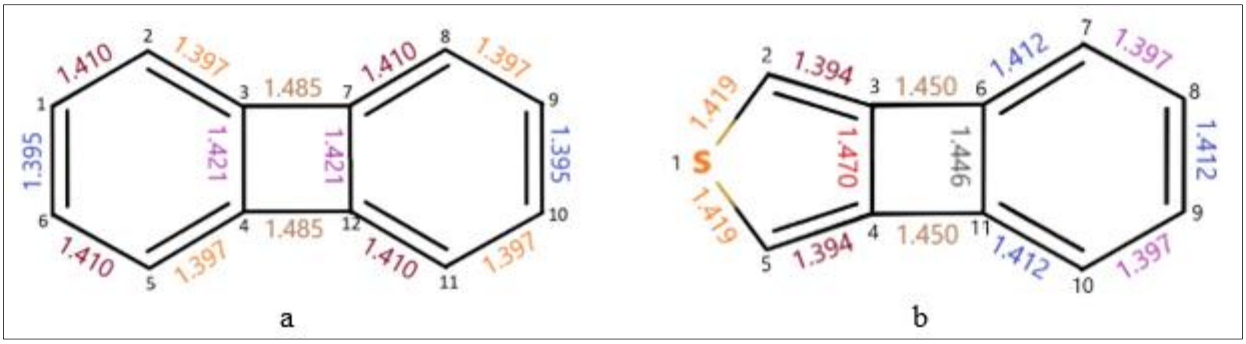


Figure 7. The bond length of (a) biphenylene and (b) benzo{3,4}cyclobuta{1,2-c}thiophene. For each figure, the same number is indicated by the same colour

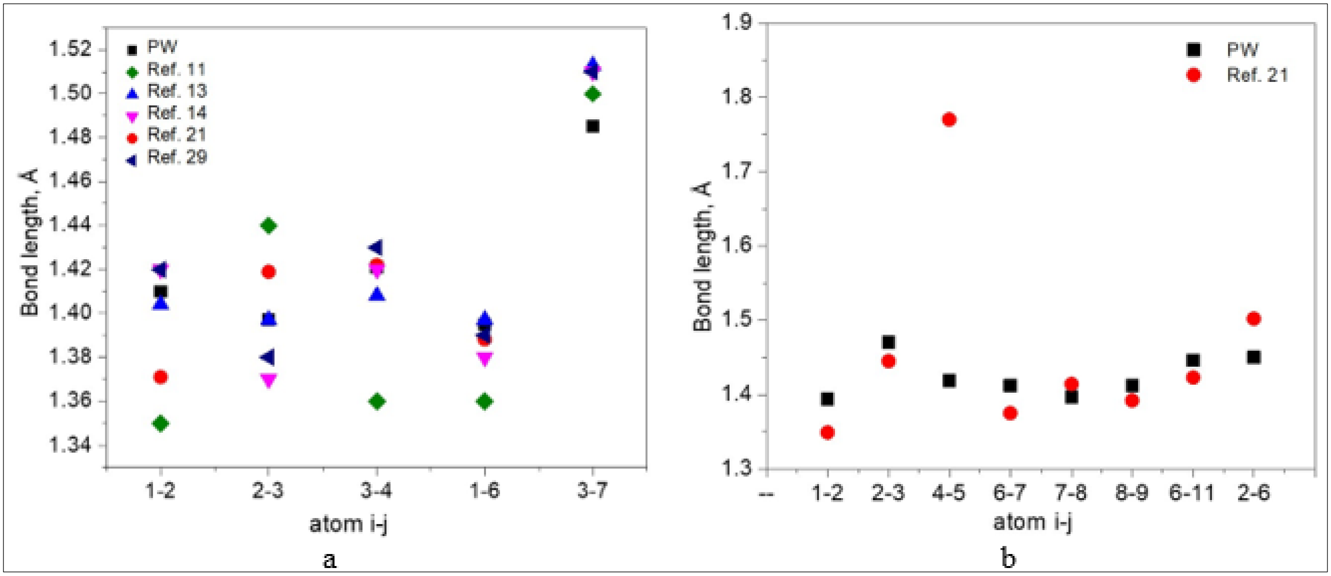


Figure 8. The selected bond length of a) biphenylene and (b) benzo{3,4}cyclobuta{1,2-c}thiophene, compared with the results from previous studies

Table 3 shows the charge distribution or π electron population determined using equation (9) for each atom of the biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene molecules. The π electron charge distribution in the biphenylene molecule is evenly distributed, which indicates that the biphenylene molecule has a resonant structure in the presence of ring currents [15,21]. On the other hand, for benzo{3,4}cyclobuta{1,2-c}thiophene, the π electron charge distribution is slightly uneven, particularly at the position of S atom of thiophene ring. The relatively large charge at this position might correspond to the atomic number (*Z*) of the S atom which is greater than the C atom (*Z* for the atom S = 16 and C = 6).

Table 3. Charge distribution (π electron population) of biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene molecules

π electron population for atom-	**Molecule**	
	Biphenylene	Benzo{3,4}cyclobuta{1,2-c}thiophene
1	1.00	0.99
2	1.00	1.10
3	1.00	1.10
4	1.00	0.99
5	1.00	1.73

6	1.00	1.01
7	1.00	1.02
8	1.00	1.02
9	1.00	1.02
10	1.00	1.02
11	1.00	1.01
12	1.00	

The parameter value for HOMA calculation consisting R_s, R_d, R_{opt}, and α_j calculated using equation (12-13) are summarized in Table 4, while Figure 9 show the HOMA values for the two investigated molecules. We note that the HOMA value of benzene ring in the biphenylene molecule is similar to those reported in Ref. [21], and smaller than pure benzene of 0.890. However, the HOMA value of benzene ring in biphenylene molecule is higher than that of benzo{3,4}cyclobuta{1,2-c}thiophene, which is in contradicts with the previous report by Hashimoto and Tahara [21] and the aromaticity picture of the molecules related to their gap energy. The negative HOMA value of thiophene ring in benzo{3,4}cyclobuta{1,2-c}thiophene molecule indices has no physical meaning because the HOMA value is not accurate for molecules containing heteroatoms [33].

Table 4. Parameter values for HOMA calculation.

j **(type of bond)**	R_s	R_d	R_{opt}	α_j
carbon-carbon bond	1.446	1.352	1.384	408.553
carbon-sulfur bond	1.411	1.387	1.395	6484.525

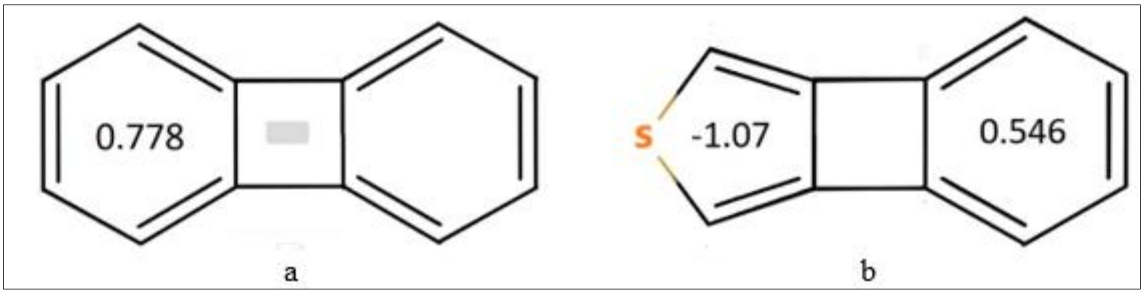


Figure 9. The HOMA values of (a) biphenylene and
(b) benzo{3,4}cyclobuta{1,2-c}thiophene

4. Conclusions

Based on the calculation using the Hückel method, both biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene molecule, the bonding orbitals are fully occupied by the electrons with opposite spins, so that their ground state is a singlet. The energy gap for the biphenylene and benzo{3,4}cyclobuta{1,2-c}thiophene molecules are 0.90β and 1.16β while the resonance energy is -4.51β and -3.85β. The larger energy gap of benzo{3,4}cyclobuta{1,2-c}thiophene compared to those of biphenylene is in good agreement with a previous calculation study [21] based on DFT method and might indicate the biphenylene is more non-aromatic than benzo{3,4}cyclobuta{1,2-c}thiophene. The bond order and bond length for the biphenylene are in good agreement with some of previous studies, while the bond length of C-S in benzo{3,4}cyclobuta{1,2-c}thiophene differs from the result of a previous study [21]. The distribution of the π electron charge in the biphenylene molecule is evenly distributed, which indicates that the biphenylene molecule has a resonant structure in the presence of ring currents, whereas for the benzo{3,4}cyclobuta{1,2-c}thiophene the π charge distribution is uneven and the largest charge distribution is centered on the S atom of the thiophene ring. Aromaticity prediction through HOMA parameter gives the results that HOMA value for benzene ring in biphenylene is higher than the corresponding value of benzo{3,4}cyclobuta{1,2-c}thiophene. The negative HOMA value of thiophene in benzo{3,4}cyclobuta{1,2-c}thiophene molecule has no physical meaning due to its low accuracy HOMA value for molecules containing heteroatoms. This study shows the limited validity for the Hückel calculation to predict the molecule's aromaticity based on the HOMA parameter.

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