

Theoretical Calculations of Refractive Index of Synthesized One and Two Substituted Derivatives of Functionalized Bithiophene Compounds

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In order to study the variation of electronic properties, a set of bithiophene derivatives was developed. The effect of substitution on the aromatic properties of some cyclic bithiophene derivative compounds was investigated using theoretical calculations. Calculations were performed at B3LYP/6-31+G (d,p) level, and calculated properties included energy, dipole moment, total charge on sulfur atom, energy gap, hardness and dipole polarizability. Experimental polarizability values were comparable with the theoretical values. Theoretical refractive indices were obtained using average polarizability in Lorentz-Lorentz equation. The results of comparison between theoretical and experimental refractive indices demonstrated that the scaling factors for refractive index and polarizability were 0.99-1.14 and 0.98-1.28, respectively.

Keywords: Bithiophene, Polarizability, Refractive index, Lorentz-Lorentz equation

INTRODUCTION

The 2,2'-bithiophene, as an oligomer, is the smallest structural block of polythiophene [1-3]. In the recent optical research, thiophene oligomer has been used extensively. Since oligothiophenes have particular electronic and optical features, alkyl-thiophene basically has been applied in electrochemical system of polyalkylthiophenes [2]. Due to the complex structure of polythiophene polymer, the calculations may be confusing. For ease of use, oligomers might be considered in several high-level computations, and then the results are generalized to polythiophene [1,3]. These polymers are used for batteries, light diodes and field effect transmissions [2].

Since 2,2'-bithiophene is a heterocyclic compound containing sulfur with delocalized π electrons, total (electrophilic or nucleophilic) substitution, can affect different aromaticity aspects like electronic properties, dipole polarizability, refractive index, and so on. Surely, increased number of substitutions is another factor in the

mentioned aromaticity changes. In 2011, Oftadeh *et al.* conducted a study based on DFT theory to probe the electronic properties and dipole polarizability of thiophene and thiophenol derivatives [4]. The alignment between theoretical and experimental polarizability showed that the selection of B3LYP/6-31+G(d,p) has been adequate to calculate the dipole polarizability value for such compounds, because the discrepancy was only less than 0.07%.

Since polythiophene is a significant part of conjugated organic polymers [3] and due to the conjugated system of bithiophene, many different studies have already been carried out on derivatives of bithiophene. Synthesis of imidazo[1,2-a]pyridine, benzimidazole, and pyridine derivatives, obtained in different stages, are the symmetrical and unsymmetrical novel bithiophene-substituted heterocycles bearing carbonitriles [5]. Synthesis of a novel electron donor unit 3,3'-dialkynyl-2,2'-bithiophene (BTRY) instead of 3,3'-dialkyl-2,2'-bithiophene (BTR) and its incorporation into conjugated polymer backbones show high degree of conjugation and 1.6 eV band gap, therefore, its incorporation into organic thin-film transistors leads to

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notable hole mobility in top-gated transistors. BTRY-based polymers design exhibits good power conversion efficiencies, suitable light absorption and high optoelectronic property [6]. In addition, the relationship between the effect of different side chains on the liquid crystalline properties, alignment ability and charge carrier mobility of nine different α - ω -phenyl-encaped bithiophene compounds have been studied. The effects of increasing chain length and introducing an asymmetric carbon center close to the conjugated segment on the liquid crystalline phase have also been studied. Therefore, using linear hydrocarbon chain as solubilizing tails improves the electronic performance [7]. The structural and electronic properties of π conjugated compounds were also evaluated based on bithiophene using quantum chemistry through density functional theory (DFT) at the B3LYP/6 31G(d,p) level to examine the absorption spectra, HOMO-LUMO level and energy gap. The reported electronic, optical, photovoltaic properties were needed for predicting the BHJ solar cell device efficiency [8]. A theoretical study has been done in order to access the stabilizing effects due to closeness of two chalcogen atoms (O, S, Se, Te) of the conformation of the model 2,2'-bitheterocycles (furan, thiophene, selenophene, tellurophene). The geometries of the ground state were in good agreement with experimental results. In addition to the dipole moments, the torsional barriers were calculated through planner and orthogonal transition states [9]. Time-dependent DFT (TD-DFT) calculations and molecular dynamics (MD) simulations with three different solvation models (the continuum dielectric, the discrete approach, and combined discrete/continuum) were applied to get the lowest dipole-allowed excitation energies of 5-dimethylamino-5'-nitro-2,2'-bithiophene (Me2N-2T-NO2) in seven solvents with dielectric constant range of 2.33-111.00. The combined discrete/continuum solvent model was proper for the study and led to similarity with experimental results [10]. Thiophene/phenylene co-oligomers (TPCOs): 5,5'-bis(4-biphenyl)-2,2'-bithiophene (BP2T) and its methoxy derivative 5,5'-bis(4'-methoxybiphenyl-4-yl)-2,2'-bithiophene (BP2T-OMe) were used in crystal growth methods performed in a liquid phase, and finally it was possible to define the anisotropic refractive indices [11]. Synthesized conjugated systems of dicyanovinyl electron-acceptor units linked to a

triphenylamine by thiophene (T), thienylenevinylene (TV) and bithiophene (BT) were used to study the electronic properties of the molecules by UV-Vis absorption spectroscopy, the cyclic voltammetry and theoretical calculations [12]. Spectral properties of derivatives of 2,2'-bithiophene (1-BT) with carbonyl substituent: -COCF₃ (trifluoroacetyl, 2-BTCF), -COCH₂CN (oxopropanenitrile, 3-BTCN), -COCH₃(acetyl, 4-BTCE) and complex 5'-((9H-fluoren-9-ylidene)methyl)-3-methyl, 5-methyl carboxylate (5-BTFL) were studied in order to measure the absorption, fluorescence spectra and fluorescence lifetimes in different polarity of solvents and compared with those in polystyrene, PS, polymethyl methacrylate, PMMA, polyvinyl chloride, and PVC. The polymer matrices affect the fluorescence and lifetimes of derivatives of 2,2'-bithiophene [13].

In continuation of our previous studies [4], we calculate refractive index in Lorentz-Lorentz equation for some derivatives of bithiophene compounds (Fig. 1) to show that experimental polarizability values are comparable with the theoretical values. The number and effects of resonance structures or induction of electrophilic or nucleophilic substitutions including methyl, phenyl, propyn, formyl and carboxylic acid on the aromaticity properties such as energy, HOMO-LUMO energy gap, dipole moment, and dipole polarizability are studied. The DFT calculations are used to probe the electronic properties of 1-10 compounds (Fig. 1). We develop a set of bithiophene derivatives to study the variation of electronic properties.

COMPUTATIONAL METHOD

Theory

The chemical stability measurement of a molecule against practical changes in its electronic structure is called hardness η [14], which is defined by the following equation:

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_v = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right) = \frac{(I - A)}{2}$$

where E is the electronic energy, N is the number of electrons, v is the potential due to the nuclei, and μ is the chemical potential. The ionization, I, and electron affinity, A, are HOMO and LUMO respectively as follows [15]:

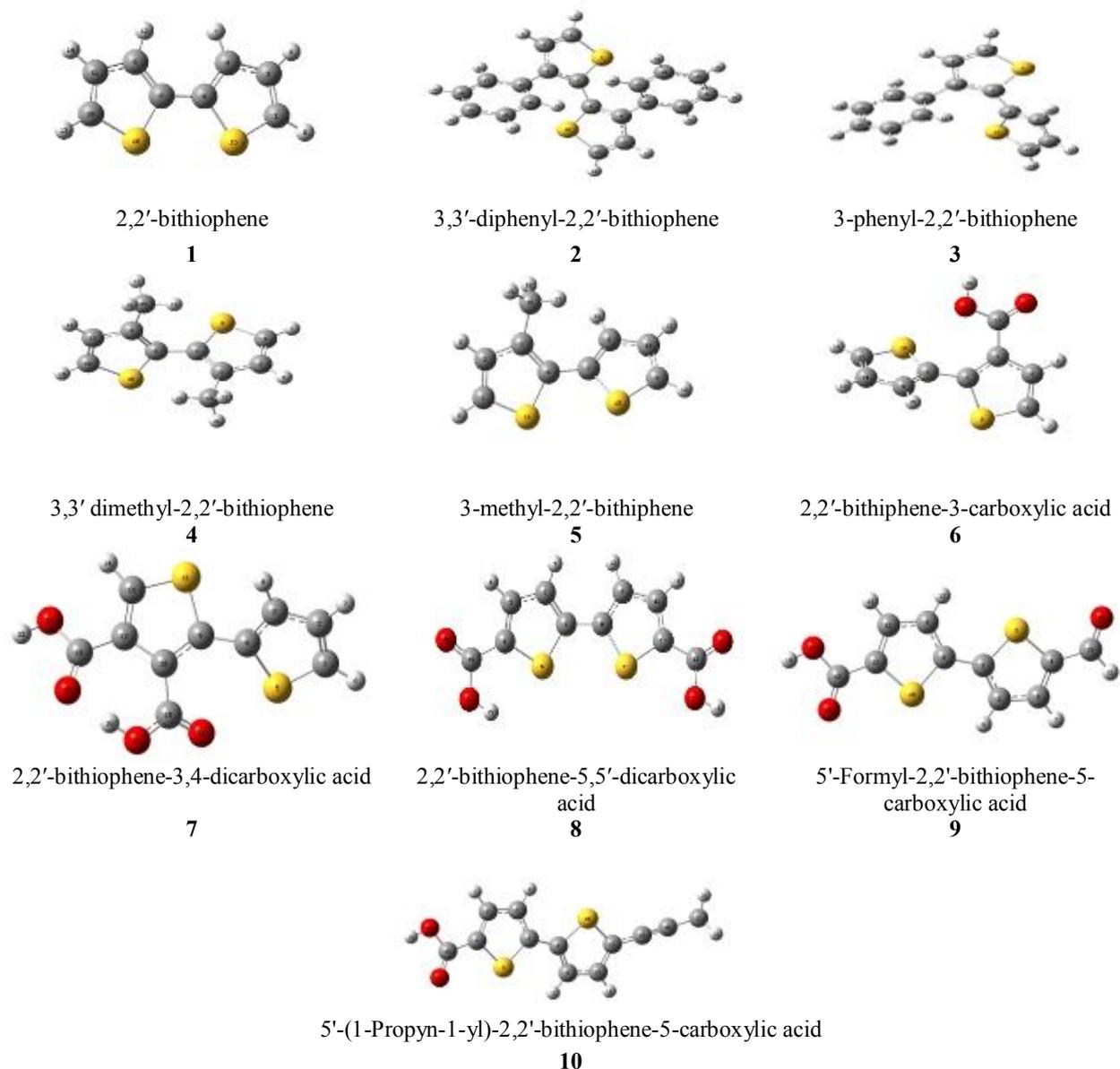


Fig. 1. Chemical structures of entitled molecules.

$$-\varepsilon_{HOMO} = I$$

$$-\varepsilon_{LUMO} = A$$

According to the “Principle of Maximum Hardness”, there is a direct and proportional relationship between hardness and stability, so the greater of the hardness, the

greater of the strength, and the molecule changes to a compressed form. The results of quantum mechanical molecular energy computations indicate that it also applies to the relationship between stability and energy gap [15].

Another main property is dipole polarizability, α , affecting dipole moment, μ , subsequently. The electromagnetic field as an external field can cause electron

clouds of molecules to change into linear form and then vary dipole moment eventually [16] which is described as follows:

$$\mu_e(E) = \mu_e(E=0) + \alpha E + (1/2!) \beta E^2 + (1/3!) \gamma E^3 + \dots$$

where μ_e ($E = 0$) is the permanent dipole moment in the absence of an electric field, α is a second rank tensor, and β and γ are the first and second of an infinite series of dipole hyperpolarizabilities [16]. Mean values of polarizability is defined by α_{ii} ($i = x, y, z$) component of the diagonalized α tensor as [16,17]:

$$\alpha_{\text{ave}} = \langle \alpha \rangle = \frac{1}{3} (\alpha_{ii} + \alpha_{jj} + \alpha_{kk})$$

A molecule which is easily polarized has low energy gap, so it represents an appropriate relationship between refractive index and energy gap with polarizability [18]. The significance of enthalpy is to characterize the thermodynamic stability of the molecules. The high positive values of heat of formation possess higher refractive index and decrease the stability; as a result, the electron clouds of molecules encounter the light response conveniently [18].

Method

After full optimization of the molecules using Gaussian 09 at the B3LYP/6-31+G** level by ensuring positive data of frequencies, the electronic, structural parameter, dipole polarizability values and dipole moment were derived. The experimental values of polarizability and refractive index are accessible. The Lorentz-Lorentz equation is defined as follows [16,19]:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi N_0 \langle \alpha \rangle \frac{\rho}{M_w}$$

where N_0 is Avogadro constant, M_w is molecular weight (g mol^{-1}), ρ is density (g cm^{-3}), and $\langle \alpha \rangle$ is average dipole polarizability (in esu). The polarizability tensor of the molecules is symmetric (C_s symmetry for 2,2'-bithiophene and the rest of molecules have C_1 symmetry) and has six independent components. Thus, the 3×3 matrix representation of the polarizability was set up leading to

three eigenvalues $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$ [4] and then the average was obtained using Eq. (5). The refractive index was calculated by Eq. (6) and compared with the experimental results.

RESULTS AND DISCUSSION

(4)

Electronic Properties

According to Table 1, the lowest total energy belongs to molecule 2 with -1567.0 Hartree among the entitled molecules because of resonance energy of delocalized π electron. The results also demonstrate that in a compound with diphenyl and alkyl substitution, the energy decreases about -231 (Hartree) and -39 (Hartree) per phenyl and methyl substitutions, respectively. Then, any kind of substitution decreases energy. The results of the enthalpy demonstrate that the compound 2 is more stable than other compounds. The lowest stability belongs to 2,2'-bithiophene, 1. As a result, any substitution causes 2,2'-bithiophene to be stabilized. The order of thermodynamic stability is $2 > 8 \cong 7 > 10 > 9 > 3 > 6 > 4 > 5 > 1$. Both electron accepting and asymmetric characters of the substitution for 7 are simultaneously two effective factors leading to increase in dipole moment compared to 8 (symmetric with two electron accepting factors) and 6 (asymmetric with one electron accepting factor). The molecule 10 with substitution propyn group has the highest dipole moment (3.806 Debye), and molecule 2 has the lowest dipole moment (0.484 Debye) because of delocalized π electrons. Electron donating of substitutions in 2, 3, 4, 5 and 9 molecules leads to decrease the dipole moments. So, the order of dipole moment is $7 > 10 > 8 > 6 > 9 > 5 > 4 > 1 > 3 > 2$.

The hyper conjugation effects on two bithiophene rings lead to positive total charge on sulfur atom in the molecule 4. In bithiophene molecule, the nature of electronegativity of sulfur atom is the main reason for negative charge on sulfur atom. In a compound with two regioregular phenyl-disubstituted bithiophene, 2, the charge on sulfur atom is more positive (+0.231), since phenyl substitution delocalizes π electrons, and also a strong nucleophilic substitution leads to electrons involvement and then the mode of electrophilic emerges between the two cycles. The charge on sulfur atom in 4 shows reduction compared to

Table 1. List of Calculated Heat of Formation (kcal mol⁻¹), Total Energy (Hartree), Dipole Moment (Debye), Mulliken Charge on Sulfur Atoms Q (esu), HOMO, LUMO, Energy Gap (eV) and Hardness η (eV) Values at the B3LYP/6-31+G (d,p) level

No.	$\Delta H_f/10^5$	E	μ	Q(S1)	Q(S2)	E_{HOMO}	E_{LUMO}	Egap	η
1	-6.9	-1104.8	1.045	-0.091	-0.091	-0.2106	-0.0598	4.10	2.05
2	-9.8	-1567.0	0.484	0.231	0.231	-0.2169	-0.0537	4.44	2.22
3	-8.4	-1335.9	0.499	0.242	0.081	-0.2162	-0.0532	4.43	2.22
4	-7.4	-1183.5	1.147	0.147	0.147	-0.2267	-0.0334	5.25	2.62
5	-7.2	-1144.2	1.357	0.065	0.008	-0.2151	-0.0447	4.55	2.27
6	-8.2	-1293.4	2.348	0.170	0.113	-0.2352	-0.0711	4.45	2.22
7	-9.2	-1482.0	5.923	0.183	0.017	-0.2339	-0.0863	4.01	2.01
8	-9.2	-1482.0	3.267	-0.064	0.094	-0.2481	-0.1097	3.76	1.88
9	-8.8	-1406.7	1.906	-0.027	-0.019	-0.2425	-0.1119	3.55	1.78
10	-8.8	-1409.0	3.806	-0.018	-0.118	-0.2159	-0.0901	3.42	1.71

Table 2. List of Density (g cm⁻³), Molecular Weight (g mol⁻¹) and Calculated Average of the Dipole Polarizability (in a.u. and esu) Values at the B3LYP/6-31+G (d,p) Level

No.	ρ	M	α_{xx}	α_{yy}	α_{zz}	α_{ave} (a.u)	α_{ave} (esu)
1	1.24	166.26	132.46	71.87	199.42	134.59	1.96
2	1.20	318.45	345.52	263.94	216.57	275.35	4.01
3	1.21	242.35	239.11	228.11	141.15	202.79	2.95
4	1.16	194.31	191.66	144.44	121.55	152.55	2.22
5	1.20	180.28	198.23	143.99	91.20	144.47	2.10
6	1.43	209.98	199.89	151.54	101.28	150.90	2.19
7	1.60	254.28	257.83	170.45	98.55	175.61	2.55
8	1.60	254.28	318.76	165.70	90.34	191.60	2.79
9	1.50	238.28	328.06	164.66	84.83	192.52	2.80
10	1.40	248.32	419.11	169.91	97.78	228.93	3.33

that for 2. Here, not only electrophilic or nucleophilic effect is important, but also the resonance effect is the main cause. For molecules 6 and 7 the electrophilic factor is just effective, while for 8 one sulfur is negative (-0.0647) and another is positive (+0.0943) and for 9 and 10 both sulfurs are negative.

The variations in HOMO-LUMO energy gap indicate that all compounds have non-conductivity (dielectric) feature, or all compounds act as an isolator materials, and subsequently, hardness values are high. Molecule 4 has the highest energy gap and hardness. It shows that this molecule cannot be easily targeted for chemical attack and should be chemically inert; thus, structurally, 4 is the most stable (the least chemical reactivity) [20]. The order of stability of molecules is arranged as follows: $10 < 9 < 8 < 7 < 1 < 3 < 2 < 6 < 5 < 4$.

Figure 3 represents the HOMO and LUMO electronic distribution. The HOMO and LUMO of the molecules can be interpreted from donor and acceptor substituted groups point of view. The active sites for the nucleophilic reaction are shown in Fig. 3. Some of the substituted groups more decrease and the others groups less decrease the distribution around the S-atom. We have found that in molecules 1-5 containing electron donor substitutions, more electric charge has been localized on bithiophene rings. This was a reason for the nucleophilic attack on bithiophene ring, the most susceptible site. Therefore, such molecules can be applied in NLO materials. However, in other bithiophene derivatives, electron-acceptor groups pull all charges of the ring towards themselves and the ring loses its activity to contribute in nucleophilic reaction. Propyn and carboxylic acid groups cause to decrease the reactivity of the bithiophen via electronic donating toward the S-atom in the reactions. It was found that in molecule 2 is an electron donor, based on the localization of the HOMO and that the nucleophilic attack will take place toward the bithiophene ring.

Refractive Index

Molecular weight, density and calculated average of the dipole polarizability values have been evaluated and listed in Table 2. The results show that the different numbers and various groups (phenylmethyl, carboxylic acid, propylene and formyl) increase the mean polarizability leading to more reactivity than 2,2'-bithiophene. It shows that the

polarizability of the molecules 2 and 10 is the highest due to the resonance of unpaired π electrons of the substituted groups. Theoretical refractive indices were evaluated using average polarizability in Lorentz-Lorentz equation, as listed in Table 3. The plot of experimental versus calculated refractive index has been shown in Fig. 2. Theoretical refractive index was well correlated to the experimental values ($R^2 = 0.7084$). A comparison of the polarizabilities can be made between the theoretical and experimental data. According to Table 3, with a high accuracy (the average percentage error of 3.98%), the results demonstrate that the experimental polarizability is 0.87-1.01 times more than the theoretical values (scaling factor is 0.87-1.01).

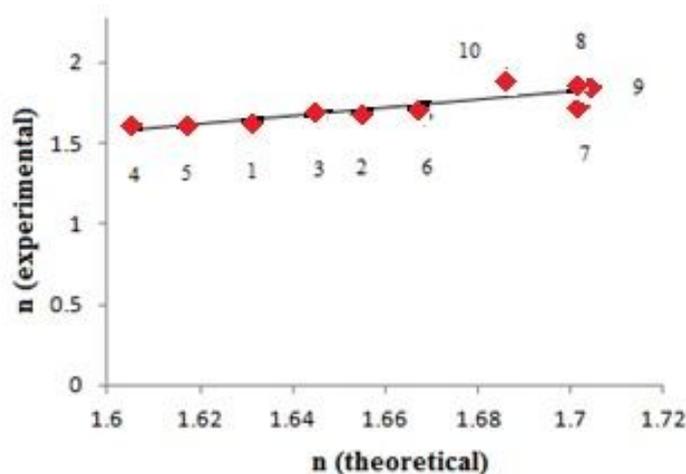
In the previous study [4], at B3LYP/6-31+G(3d,3p) level of theory, the refractive index and polarizability were calculated for some of thiophene derivatives with NH_2 , Ph, CH_3 , C_2H_5 and H substitutions and the corresponding refractive indexes are 0.1055, 0.0903, 0.1053, 0.0902 and 0.1094, respectively. Also, the studied substitutions on the thiophenol were Ph, CH_3 and H and their refractive indexes are 1.6323, 1.5842 and 1.5880, respectively, using DTM-1 refractometer at 60/50 Hz at 20 °C. They were compared with theoretical data using the Lorentz-Lorentz equation α_{cal} with an error of 30% for thiophene derivatives and less than 0.07% for thiophenol derivatives due to sulfur as heteroatom in the ring of thiophene derivatives. The good agreement between experimental and theoretical polarizability in thiophenol and its derivatives indicates the correct choice of the method and base set for calculating the polarizability values. As shown in Table 3, this is also true for the entitled compounds. It means the lowest error value of 0.49 for molecule 5 and the highest error of 13.93 for molecule 10, and the overall error average of 3.98%, which confirm the selected method and base set. In accordance with the diagram in Fig. 3, molecule 4 exhibits the highest hardness due to two methyl as electrodonating. Thus, it shows the highest structural stability among the compounds.

CONCLUSIONS

The molecule with electron-acceptor group (propyn group) has the highest dipole moment because of better charge distribution and increased radial distribution. The highest energy gap belongs to 3,3'-dimethyl-2,2'-

Table 3. Calculated and Experimental Refractive Index, n , Dipole Polarizability (esu), α , and Scaling Factors for n and α Values at the B3LYP/6-31+G (d,p) Level

No.	n_{exp}	α_{exp}	n_{cal}	α_{cal}	Δn	%Error	Scaling n	Scaling α
1	1.63	1.88	1.65	1.96	-0.02	1.71	1.02	1.04
2	1.65	3.83	1.68	4.01	-0.03	2.05	1.02	1.05
3	1.64	2.86	1.66	2.95	-0.02	1.45	1.01	1.03
4	1.60	2.27	1.58	2.22	0.01	1.12	0.99	0.98
5	1.61	2.07	1.62	2.10	-0.01	0.49	1.00	1.01
6	1.66	2.16	1.68	2.19	-0.01	0.77	1.01	1.02
7	1.70	2.44	1.74	2.55	-0.04	2.40	1.02	1.05
8	1.70	2.44	1.83	2.79	-0.13	7.87	1.08	1.14
9	1.70	2.43	1.84	2.80	-0.13	8.09	1.08	1.15
10	1.68	2.61	1.92	3.33	-0.23	13.93	1.14	1.28

**Fig. 2.** The correlated plot of experimental *versus* the calculated refractive index of the entitled molecules.

bithiophene. All compounds have non-conductivity feature. The lowest energy is related to di-phenyl substitution because of resonance energy of delocalized π electrons; moreover, the values of heat of formation demonstrate that

the highest thermodynamic stability belongs to 3,3'-diphenyl 2,2'-bithiophene. The comparison between theoretical and experimental refractive indices (polarizability) data demonstrated that the theoretical

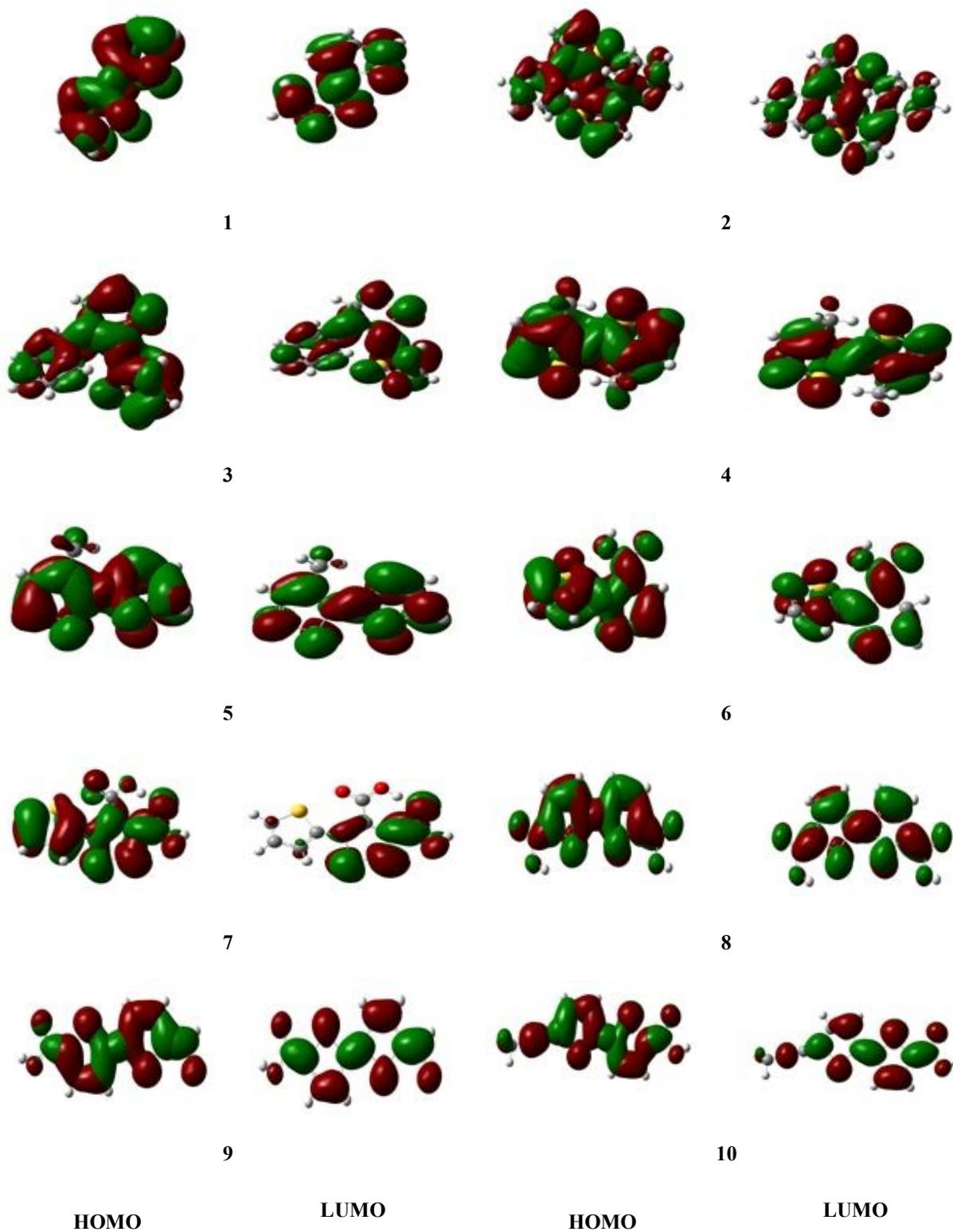


Fig. 3. HOMO and LUMO electronic distribution of the entitled compounds.

polarizabilities and refractive indices are 0.99-1.28 and 0.98-1.14 times of the experimental values, respectively. The alignment between theoretical and experimental polarizability shows that the selection of the method has been adequate for calculation of the dipole polarizability values for such compounds.

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