Regular Article

Optical Properties of Some Oligothiophene Derivatives: DFT Study

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Polythiophenes are of considerable interest as synthetic metals. The optical properties of polythiophenes can be easily affected by alkyl chain or other side groups to the thiophene ring. The effect of polymerization degree on the energy gap was studied in the case of polythiophene as a conjugated polymer at B3LYP/6-31+G(3d,3p) level of theory. Up to n = 16 could be confident that this degree of polymerization represents the bulk of polymer. The effect of the substitution of different groups in functionalized-bithiophene and -terthiophene on the polarizability was studied. The correlation study was performed between descriptors representing the molecular structure and refractive index for the set of 9 oligothiophenes. Three descriptor models including energy gap, polarizability and heat of formation were developed to estimate the refractive index with $R^2 = 0.81$ and $S = 0.068$ by multi-linear regression analysis. The obtained model was used to predict the refractive indices of other six oligothiophenes. The model may be improved to predict the refractive index of the other oligothiophene derivatives.

INTRODUCTION

The conducting polymers or synthetic metals have many advantages such as lower weight, more applications, resistance to corrosion and chemical attack and lower cost in addition to the electrical properties [1]. The optical and nonlinear optical properties of polymers, particularly π-conjugated polymers, are of growing interest in view of their expected application in photonics, integrated optics, optical communication and optoelectronics [2]. Among conjugated polymers, polythiophenes are of considerable interest as materials for nonlinear optics because of their large optical third-order response, chemical stability and processability [3]. The optical properties of polythiophenes can be easily tailored by adding an alkyl chain or other side groups to the thiophene ring [4].

Successful synthesis of poly(3-alkylthiophene), through introducing an alkyl group into the β-position of thiophene

ring, was followed by an impressive development in polythiophene derivatives [5,6]. Head-to-tail (HT) regiospecificity of poly(3-alkylthiophene) is notable in electrical, optical, magnetic and mechanical properties [7-10]. Polythiophene derivatives with electron donating and electron withdrawing groups have been synthesized [11-14]. Presence of electron donating substituent groups such as alkyl or alkoxy groups can raise the energy level of the highest occupied molecular orbital (HOMO) due to narrow band gap of the polythiophene derivatives from the electronic effect viewpoint [15]; while introduction of substituent groups which reduce the coplanarity of polythiophene backbone increases the band gap of polythiophene derivatives from the steric effect viewpoint [16]. So balancing both electronic and steric effects is a very basic step in choosing appropriate substituent functional groups.

One of the important optical properties of the polymers directly related to other optical, electrical and magnetic properties is refractive index, so prediction of this property

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is of great importance in designing new optical polymeric materials and studying physical and chemical properties of polymers by optical techniques [17]. A long tradition of successful procedure for predicting the properties of polymers is additive (group contribution) methods [18]. Group contribution calculations for prediction of refractive index of polymers are based on the molar refraction as the additive function and different models of refractive index such as Lorentz-Lorenz and Gladstone-Dale [19].

$$\frac{n^2-1}{n^2+2}\frac{M}{\rho} = \frac{n^2-1}{n^2+2}V = R_{LL} = \sum R_{LL,i} \qquad (1)$$

$$\frac{M}{\rho}(n-1) = (n-1)V = R_{GD} = \sum R_{GD,i} \qquad (2)$$

where n, M, ρ, V, R_{LL} and R_{GD} are refractive index, molecular mass, density, molar volume, and group contributions based on Lorentz-Lorenz and Gladstone-Dale, respectively. Despite its usefulness, the group contribution approach has some inherent limitations [18]. Agrawal and Jenekhe [20] demonstrated that the refractive index of π-conjugated polymers can be predicted by existing group contribution methods which have deviation from experimental values as high as 22%. Yang and Jenekhe [21] used new R_{LL} data of 24 functional groups that are commonly found in conjugated polymers and they calculated the refractive indices of 33 conjugated polymers (with an average error of 0.9%) [21].

Applying QSPR approach can eliminate some of the limitations of group contribution methods [17]. A correlation between 7 descriptors and refractive indices of 35 π-conjugated polymers with R = 0.93 was obtained by Gao *et al.* [22]. Garcia-Domenechand deJulian-Ortiz [23] used graph theoretical indices for prediction of refractive indices of some polymers with R = 0.98.

In previous work, we studied electronic and optical properties of thiophene derivatives [24]. In comparison with small molecules, prediction of these properties for polymers are often difficult [25], therefore in this work we study the effect of substitution groups and polymerization degree on the electronic and optical properties of some oligothiophenes, also a correlation model is developed for prediction of the refractive indices of oligothiophenes.

COMPUTATIONAL METHOD

Geometries of the functionalized oligothiophene derivatives were optimized at B3LYP/6-31+G(3d,3p) level and polarizabilities were calculated using Gaussian 09 [26]. Electric dipole polarizability [27,28], which is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, F, and represents a second-order variation in the energy, *viz.*:

$$\alpha = -(\frac{\partial^2 E}{\partial F_a \partial F_b}) \qquad a, b = x, y, z \qquad (3)$$

If some of applied molecules are planar and some are not, it will be useful to report polarizability quantities that are invariant to the choice of coordinate system. One of them is the mean polarizability given by the trace invariant

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3) \qquad (4)$$

where $\alpha_1 = \alpha_{xx} \le \alpha_2 \le \alpha_3$ are the eigenvalues of the polarizability tensor. The calculated characters are the components α_{ii} (i = x, y, z) and average of the dipole polarizability (a.u.) [24]. An adequate basis set and a good level of exchange-correlation are requirement factors for high accuracy in the theoretical determination of dipole polarizabilities. The B3LYP/6-31+G(3d,3p) has shown a good performance for polarizability calculations of conjugated molecules such as anthracene and phenanthrene [29], acenaphthene and acenaphthylene [30]. In current study, all molecules are conjugated systems. Also, the best theoretical estimation for the dipole polarizability of benzothiophene molecule has been obtained by this method [31]. Thus we applied this level of theory for all calculations. Statistical evaluation of the data and multilinear regression analysis has been performed by Excel2010 and Sigmaplot packages [32].

RESULTS AND DISCUSSION

Energy Gap and Degree of Polymerization
For finding the relation between degree of polymerization and energy gap in polythiophene, the

structures of the repeating units (α-nT, n = 1-16) were optimized. Calculation was carried out until an almost constant value of energy gap was gained. Up to n = 16 could be confident that this degree of polymerization (n = 16) is representation of the whole polymer. The relation between degree of polymerization (DP) and energy gap (E_g) has been presented in Fig. 1.

The Effect of Substitution Groups

To investigate the effect of substitution groups on the electronic and optical properties, five derivatives of polythiophene including poly(3-nitrothiophene), poly(3-methoxythiophene), poly(3-cyanothiophene), poly(3-fluoromethylthiophene) and poly(methylthiophene-3-carboxylate) were chosen [33]. Because of the high molecular weight of polymers, calculation of electronic and optical properties of entire molecule is not an easy task; so repeating units of selected polymers (dimer and trimer) were optimized at B3LYP/6-31+G (3d, 3p) level, Fig. 2. The evaluated properties from the output file are energy gap
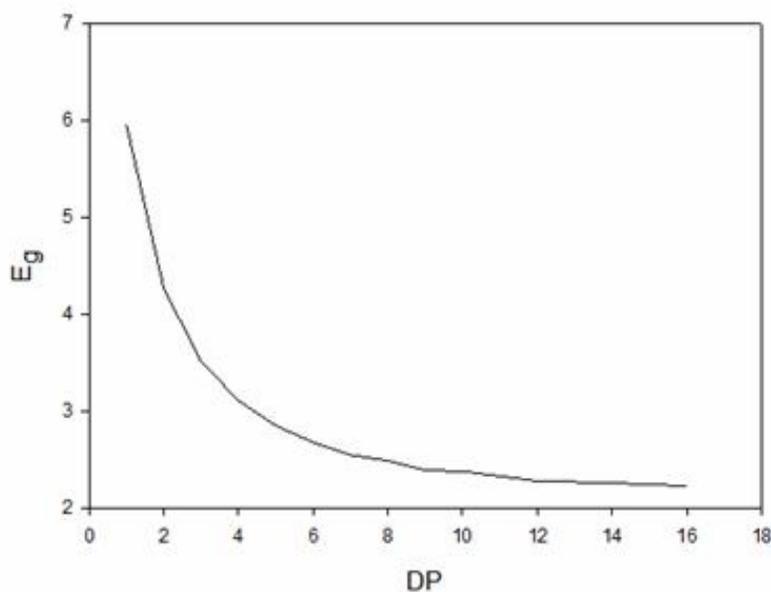
Fig. 1. Relation between the degree of polymerization and energy gap.
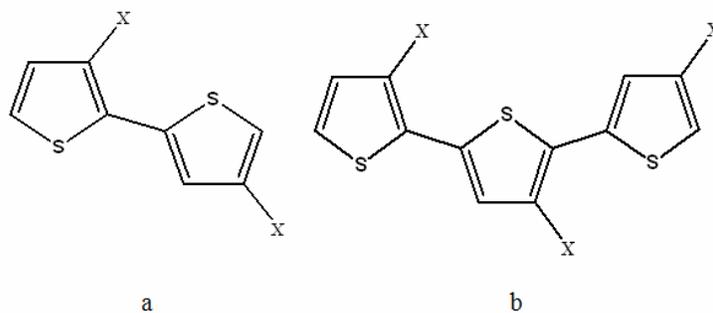
Fig. 2. HT regioisomer in a) bithiophene and b) terthiophene derivatives.

and components of polarizability, α_{ii} (I = x, y, z). The average of polarizability are calculated as the following equation [27,28]:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{5}$$

where α_{xx}, α_{yy} and α_{zz} are the diagonal elements of the polarizability tensor. The results have been listed in Tables 1 and 2. Based on the values reported in Tables 1 and 2, with addition of the repeating units polarizability increases and energy gap decreases, it might be due to growth in size

Table 1. Calculated Energy Gap (in eV), Component (XX, YY, ZZ) and Average of Polarizability (in a.u.) at B3LYP/ 6-31+G (3d, 3p) for Bithiophene Derivatives

No.	X	E_g	α_{xx}	α_{yy}	α_{zz}	α_{ave}
1	NO_2	3.755	256.579	178.499	91.404	175.494
2	OCH_3	3.945	252.028	174.008	95.960	173.990
3	CN	4.136	241.545	179.117	87.772	169.478
4	CH_2F	4.734	211.512	154.494	107.883	157.963
5	CO_2CH_3	4.163	290.755	204.735	116.788	204.092

Table 2. Calculated Energy Gap (eV), Component (XX, YY, ZZ) and Average of Polarizability (in a.u.) at B3LYP/ 6-31+G (3d, 3p) for Terthiophene Derivatives

No.	X	E_g	α_{xx}	α_{yy}	α_{zz}	α_{ave}
6	NO_2	3.401	431.253	278.139	148.264	285.885
7	OCH_3	3.156	469.502	276.971	138.013	294.828
8	CN	3.455	416.404	293.037	125.128	278.189
9	CH_2F	4.190	361.090	217.374	175.674	251.379
10	CO_2CH_3	4.136	415.407	280.321	233.973	309.900

and conjugation length of the molecules. In terthiophene derivatives, trimethoxyterthiophene has minimum energy gap which might be due to balance between steric and electronic effects, furthermore it has an almost maximum polarizability.

Energy Diagram of Frontier Orbitals

Electrons in the highest occupied molecular orbitals are most free to participate in the reaction so that instead of thinking about the total electron density in a molecule, localization of the HOMO should be thought. According to Fig. 3, in thiophene derivatives, cyano thiophene has the most widespread distribution of the HOMO. Just in this derivative of thiophene, there exists electron distribution around S atom in HOMO. Except for fuluromethyl bithiophene, electron distribution of the HOMO around S atom increases for all bithiophene derivatives. Among terthiophene derivatives, the most widespread distribution

of the HOMO electrons is observed for trimethoxy terthiophene, and electron distribution of the HOMO around S atom decreases only in fuluro methyl derivative. A site where the lowest unoccupied orbital is localized, is a good electrophilic site. According to Fig. 4, in thiophene, bithiophene and their derivatives, LUMO is mainly localized on carbons of thiophene and of bithiophene rings. Over substitution, the electrophilic site becomes more expanded and also lies on the substitution. The distribution around S atom increases only in the case of NO_2 derivative. In terthiophene and its derivatives LUMO is localized on carbons of thiophene rings. The substitution leads to more expansion of the electrophilic site and lies on the elements of substitutions. LUMO distribution around S atom increases in NO_2 and CH_2 derivatives.

Refractive Index Correlation

Structures of oligothiophenes listed in Fig. 6 were
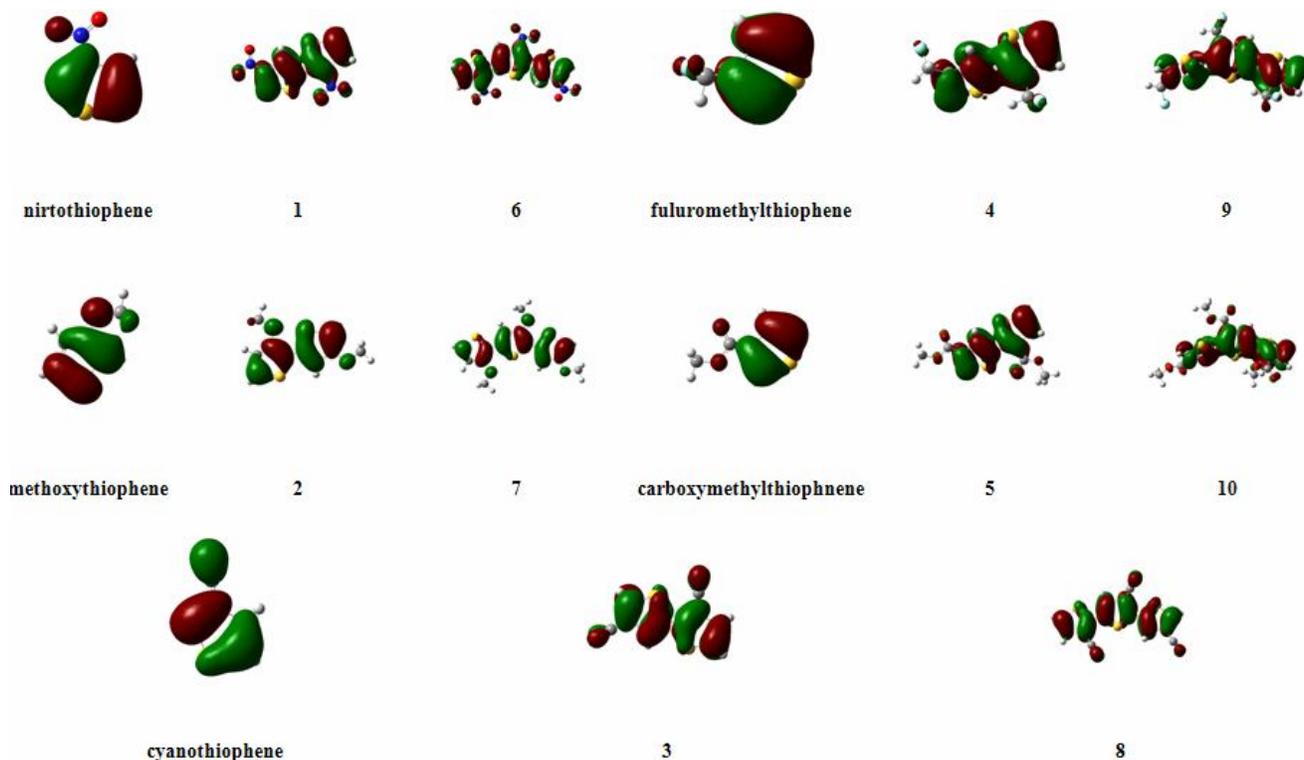
Fig. 3. HOMO density map for the bi- and terthiophene molecules No. 1-10 compared with corresponding thiophene derivatives.
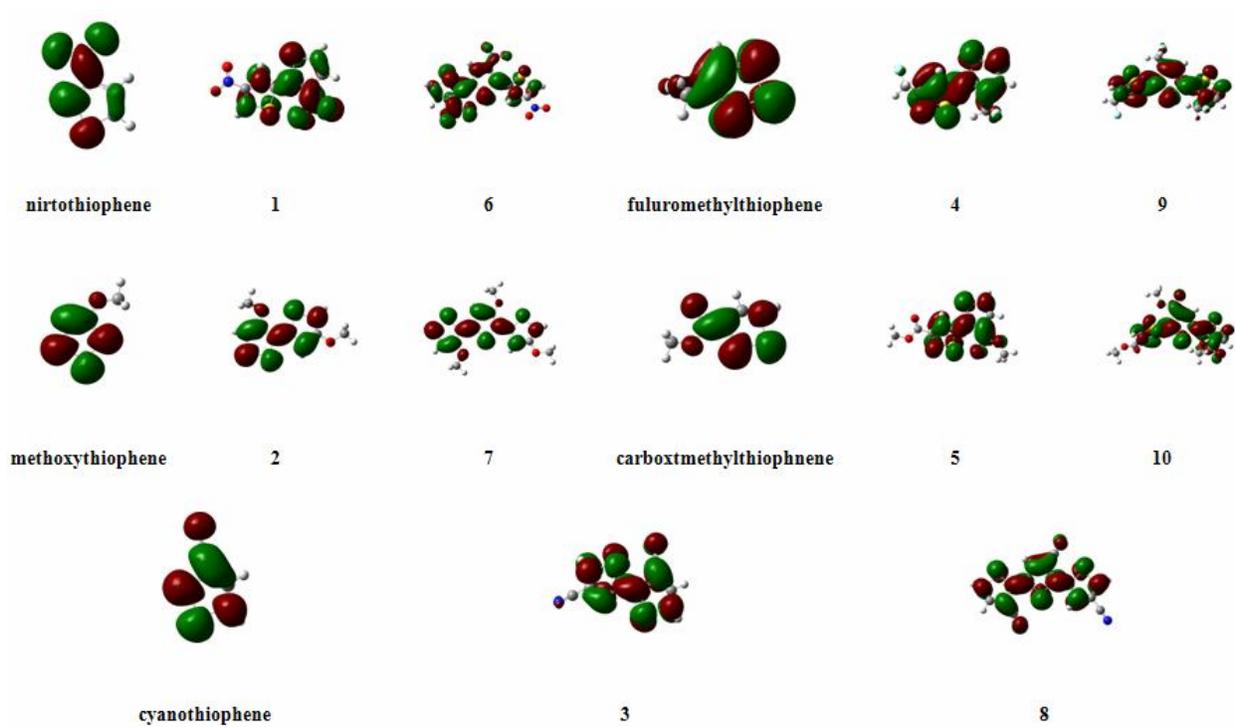
Fig. 4. LUMO density map for the bi- and terthiophene molecules No. 1-10 compared with corresponding thiophene derivatives.
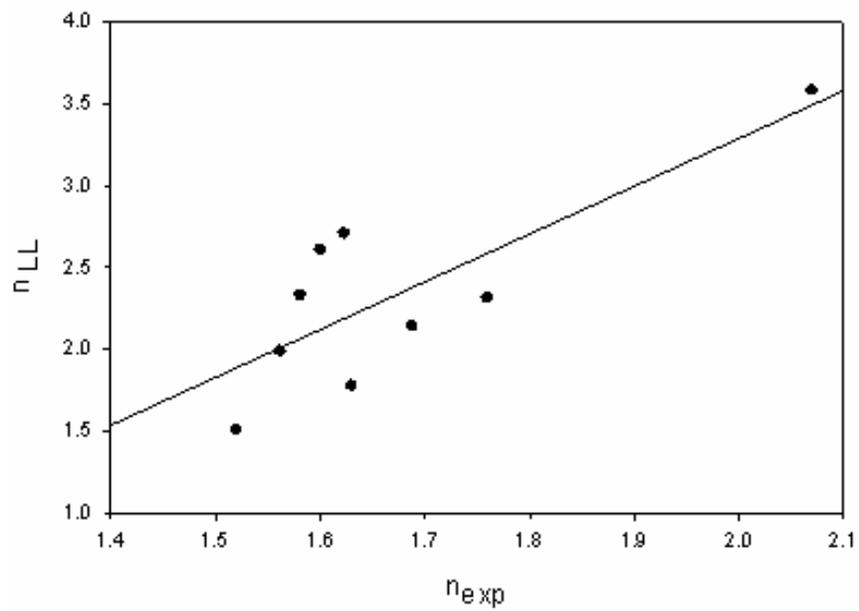
Fig. 5. Correlation diagram based on the Lorentz-Lorenz formula for the molecules11-19 with $R^2 = 0.64$.

optimized and correlation between experimental refractive indices [34] and calculated values of refractive indices was obtained using Lorentz-Lorenz formula with $R^2 = 0.6406$,

$$\frac{n^2-1}{n^2+2} = \frac{N_A <\alpha>}{3\varepsilon_0 V} \qquad (6)$$

where n, $<\alpha>$, ε_0 and N_A are refractive index, average polarizability, dielectric constant and Avogadro number, respectively. The correlation diagram has been presented in Fig. 5. For a prediction study, a pre selection of descriptors was carried out [17,35,36]. Four descriptors including

energy gap, average polarizabilty, heat of formation and partial negative surface area (PNSA) were selected and evaluated out of the Gaussian output file (Table 3). PNSA is sum of the solvent- accessible surface areas of all negatively charged atoms [37].

$$PNSA = \sum_{a^-} SA_{a^-} \qquad (7)$$

For finding the best model between refractive index and molecular descriptors, the correlation coefficient and standard error for four models were considered (Table 4).

Correlation between independent variables declines
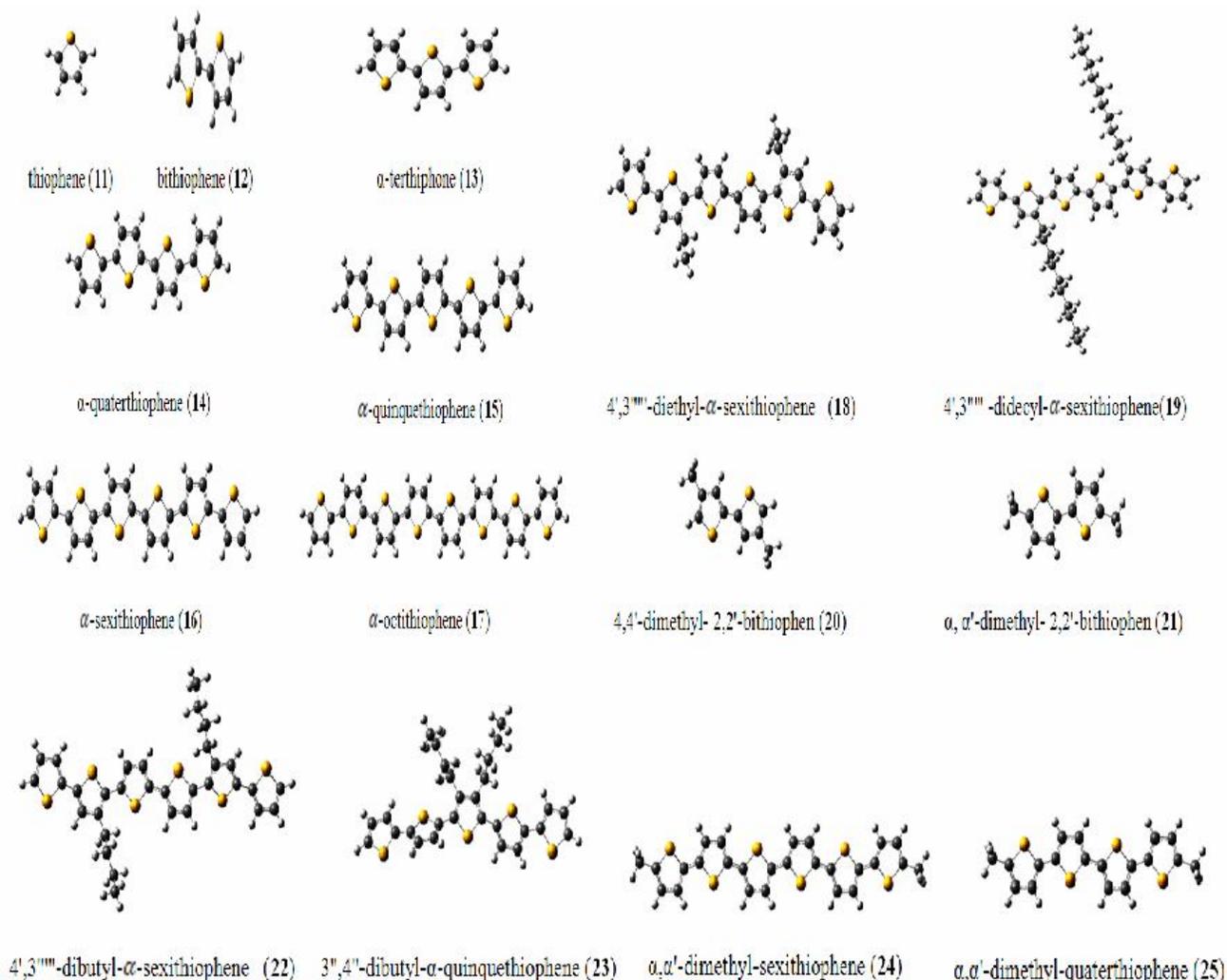
Fig. 6. Optimized structures of oligothiophenes.

Table 3. Calculated Descriptors for the Molecules with the Experimental Refractive Index Compared to the Predicted Data Based on Eq. (6)

No.	E_g	α_{ave}	ΔH	PNSA	n_{exp}	n_{Pred}
	(Hartree)		(Hartree)	(Bohr^2)		
11	0.2190	60.77	-552.95	516.89	1.52	1.56
12	0.1570	134.29	-1104.72	1065.07	1.63	1.55
13	0.1290	227.18	-1656.49	1468.39	1.56	1.54
14	0.1142	338.32	-2208.26	2130.15	1.58	1.57
15	0.1050	464.42	-2760.03	2275.02	1.60	1.64
16	0.0986	603.78	-3311.81	2807.56	1.62	1.75
17	0.0917	900.39	-4415.35	3743.41	2.07	2.01
18	0.1077	611.91	-3468.96	3453.66	1.76	1.66
19	0.1070	750.18	-4097.51	5427.32	1.68	1.70

Table 4. Statistical Parameter for Various Combinations of Descriptors

Model	Descriptor	R^2	Std. Error	p-Value	F Statistic
1	α, E_{gave}	0.6499	0.0844	0.0087	12.99
2	E_g, α_{ave}, ΔH	0.8178	0.0683	0.0008	31.43
3	E_g, α_{ave}, PNSA	0.7623	0.0753	0.0021	22.44
4	E_g, α_{ave}, PNSA, ΔH	0.8204	0.0679	0.0008	31.98

efficiency of QSPR model, so the correlation of selected variables was tested by constitution of correlation matrix for each model (Table 5). Correlation coefficient more than 0.9 means it has a fewer correlation with dependent variable and it should be eliminated from the model. Among four descriptors, PNSA has the most correlation with the others. Thus the model No. 2 with 3 descriptors is the best

correlation equation:

$$n_{MLR} = 2.104 - 1.747E_g + 0.003\alpha_{ave} + 0.001\Delta H \qquad (8)$$

where the units of the quantities of E_g, α_{ave}, and ΔH are in Hartree, au, and Hartree, respectively. Figure 7 shows the correlation diagram based on the Eq. (8) for the molecules

Table 5. Pearson Correlation Matrix for the Selected Descriptors

	E_g	α_{ave}	ΔH	PNSA
E_g	1			
α_{ave}	-0.806	1		
ΔH	0.815	-0.993	1	
PNSA	-0.715	0.902	-0.924	1
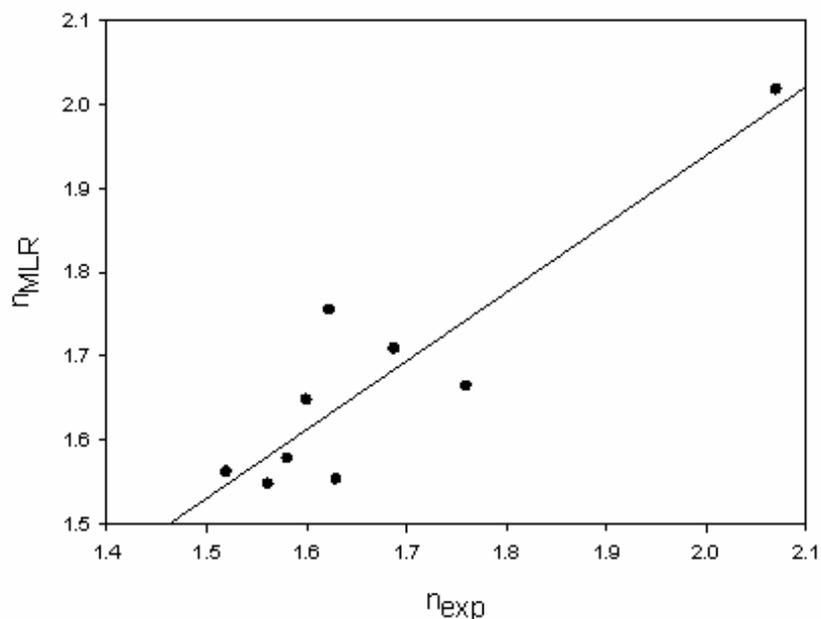
Fig. 7. Correlation diagram based on Eq. (6) for the molecules 11-19 with $R^2 = 0.8178$.

Table 6. Calculated Descriptors and Predicted Refractive Indices for the Molecules 20-25

No.	E_g (Hartree)	α_{ave} (a.u.)	ΔH (Hartree)	n_{pred}
20	0.1588	162.55	-1183.30	1.60
21	0.1492	166.43	-1183.30	1.62
22	0.1083	658.17	-3626.11	1.73
23	0.1210	516.08	-3074.33	1.60
24	0.0974	653.34	-3390.39	1.88
25	0.1114	381.78	-2286.85	1.68

11-19 by MLR ($R^2 = 0.81$). By using the best model, **model 2** or Eq. (8), the refractive indices of 6 oligothiophenes, No. 20-25, were predicted and collected in Table 6.

By comparing the results with bithiophen and terthiophene, it shows electron donating groups including OCH_3 and NO_2 lead to decrease the energy gap, and electron withdrawing groups including CH_2F, CN and CO_2CH_3 relatively increase the energy gap. This may be due to the inductive (electronic) effect of the groups on the thiophene ring. Polarizability and refractive index of all derivatives are increased with respect to the base of the molecules, bithiophene and terthiophene, due to this effect of the substitution groups. This effect is more for electron withdrawing groups because of the less resonance (or steric effect) in thiophene ring. The OCH_3 and CH_2F groups have the most and the least effect on this property, respectively. The refractive indices of the oligothiophene molecules, No. 20-25, are more than those of the bithiophene and terthiophene molecules. This is more clear for polythiophenes, No. 22-25, and the molecules can be empirically used as conductive polymers.

CONCLUSIONS

It is observed that substitution of different groups in

bithiophene and terthiophene causes the increase in polarizability. Substitution groups made value of energy gap decreasing except for CH_2F and CO_2CH_3 groups. In general, methoxy substitutional group has the best effect on electronic and optical properties of terthiophene. Refractive indices of 9 oligothiophenes correlated with 3 descriptors by MLR ($R^2 = 0.81$). Refractive indices of 6 other oligothiophenes were predicted by using the QSPR model. Among 6 oligothiophenes predicted their refractive indices, α,α'-dimethyl-sexithiophene (No. 24) has the maximum refractive index, minimum energy gap and almost maximum polarizability. Also the foregoing oligothiophene has high thermodynamic stability, so it can be used for synthesis of new polymer.

ACKNOWLEDGMENTS

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