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EFFECT OF SIDE CHAIN LENGTH ON THE STABILITY AND STRUCTURAL PROPERTIES OF 3-(2',5'-DIALKOXYPHENYL)THIOPHENES: A THEORETICAL STUDY

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ABSTRACT. We report on the effect of the alkoxy chain length on the thermodynamic properties of neutral and the corresponding radical cations of 3-(2',5'-dibutyloxyphenyl)thiophene (DBOPT), 3-(2',5'-diheptyloxyphenyl)thiophene (DHOPT), and 3-(2',5'-dioctyloxyphenyl)thiophene (DOOPT) and their dimers studied by Hartree-Fock (HF) and Density Functional Theory (DFT) methods. The DFT calculations suggest that dimers of the dialkoxyphenylthiophenes with longer side chains are thermodynamically more stable by about 61.39 kJ/mol than the ones with shorter side chains at the radical cation state. The results correlate well with the experimental observations made during the electrochemical synthesis of these polymers from their monomers.

KEY WORDS: Density functional theory, Hartree-Fock, Dialkoxyphenylthiophenes

INTRODUCTION

Electronically conducting polymers, like polyaniline, polythiophene, poly(*p*-phenylene vinylene) and polypyrrole, have attracted a lot of interest because of the large number of possible applications of these materials in various electronic devices such as solar cells, electrochromic displays (ECD), light emitting diodes (LED), field effect transistors (FET) and chemical sensors [1-6].

Quantum chemical studies on the electronic structures of conducting polymers have contributed a lot to the understanding of the structure-property relationships of known polymers and to the prediction of new ones prior to chemical synthesis [7-14].

We reported earlier the experimental studies on the electrochemical synthesis and photoelectrochemical properties of polymers derived from 3-(2',5'-dibutyloxyphenyl)thiophene (DBOPT), 3-(2',5'-diheptyloxyphenyl)thiophene (DHOPT) and 3-(2',5'-dioctyloxyphenyl)-thiophene (DOOPT) [15]. We observed that the strength of adherence of the polymers to bare glassy carbon and indium tin oxide (ITO) electrodes follows the order of increasing side chains of the alkoxy groups: PDBOPT < PDHOPT < PDOOPT. Attempt to polymerize DBOPT, the compound with the shortest alkoxy side chain, was not successful because it adhered slightly on bare glassy carbon and poorly on ITO-glass. The detachment from the electrodes was assumed to be due to the high reactivity of the species generated upon monomer oxidation, which diffused away from the electrodes in to the solution by forming oligomers [15-16].

In this paper, we report the results of our calculations on the change in thermodynamic properties corresponding to the oxidation process and geometrical changes of neutral and radical cations of DBOPT, DHOPT, and DOOPT monomers (Figure 1) and their dimers using Hartree-Fock (HF) and Density Functional Theory (DFT) methods to understand the difference in stabilities and properties observed experimentally by these materials [15-16].

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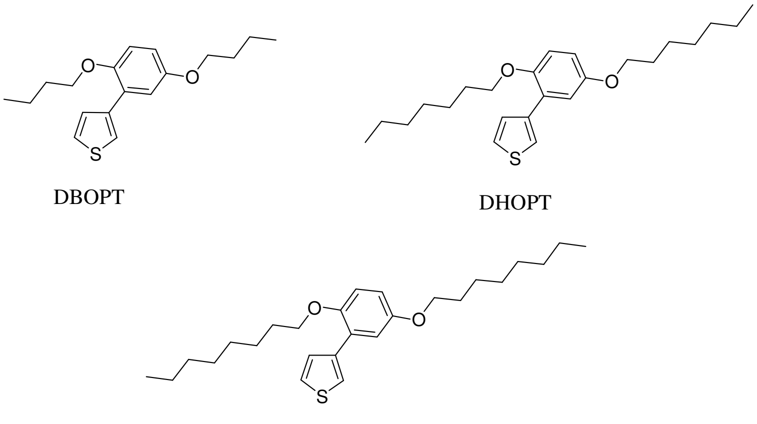


DBOPT DHOPT

DOOPT

Figure 1. Structure of the three dialkoxyphenylthiophenes.

COMPUTATIONAL METHODS

The initial geometries of the neutral and radical cations of the monomers and dimers were optimized by Becke's three-parameter hybrid functional for exchange, combined with the correlation functional due to Lee, Yang, and Parr (DFT/B3LYP) [17-18] and Hartree-Fock methods [19] at STO-3G, 3-21G* and 6-31G* [19] levels which were shown to produce reliable results for organo-sulfur molecular systems [20-21]. The optimized structures of the radical cations were obtained by removing an electron from the optimized geometries of the neutral forms and performing further optimizations.

Based on the optimized geometries, the thermodynamic properties and band gaps of all the compounds were calculated by HF methods using the STO-3G basis set and by the B3LYP method using STO-3G, 3-21G* and 6-31G* basis sets [22-23]. The 3-21G* and 6-31G* basis sets give extra d-orbital for sulfur and oxygen atoms and improve the calculations [19]. The changes in the thermodynamic properties were calculated by subtracting the thermodynamic properties of the neutral species from the radical cations [22]. All calculations were performed using the Gaussian 03W program package at 298.15 K [24].

RESULTS AND DISCUSSION

The calculated bond lengths for the optimized structures of the monomers and dimers are shown in Tables 1-4. The numbering system followed for the dialkoxyphenylthiophenes is shown in Figure 2.

For the three monomers, the C_4C_5 bond length decreases upon removal of an electron. This bond was a double bond in the neutral state and retained its double bond character after removal of an electron since the change is small. On the other hand the length of the C_2C_3 bond increased after oxidation, which indicates a single bond character in the radical cation. The C_3C_4 bond was a single bond in the neutral state and after oxidation its length still increased. This shows that the C_3C_4 bond also retained its single bond character. These results clearly showed that the π-bond that is more susceptible for the oxidation process is the one on the C_2C_3 double bond.

Table 1. Optimized bond lengths (Å) of neutral and radical cations of the monomer and dimer of DBOPT obtained at B3LYP/6-31G* level.

Parameter	DBOPT		Dimer of DBOPT	
	Neutral	Radical cation	Neutral	Radical cation
C_4C_5	1.36354	1.36163	1.36334	1.38364
C_3C_4	1.43969	1.44867	1.43530	1.40595
C_2C_3	1.37579	1.39269	1.38551	1.43191
S_1C_2	1.73155	1.70759	1.75648	1.77898
S_1C_5	1.73743	1.74869	1.73287	1.71274
$C_2C_{2'}$	-	-	1.45904	1.43594
$C_{2'}C_{3'}$	-	-	1.37394	1.38995
$C_{3'}C_{4'}$	-	-	1.43428	1.41468
$C_{4'}C_{5'}$	-	-	1.37645	1.42004
$S_{1'}C_{5'}$	-	-	1.72803	1.70093
$S_{1'}C_{2'}$	-	-	1.75673	1.78576
$C_3C_{1'}$	1.48148	1.42349	1.48505	1.46753
$C_{1'}C_{2'}$	1.41889	1.46849	1.41718	1.44416
$C_{2'}O$	1.37081	1.27311	1.37051	1.35078
$C_{2'}C_{3'}$	1.39398	1.46332	1.39403	1.39774
$C_{3'}C_{4'}$	1.40099	1.35995	1.40110	1.39216
$C_{4'}C_{5'}$	1.39384	1.42368	1.39432	1.42102
$C_{5'}O$	1.36937	1.30639	1.36936	1.32944
$C_{5'}C_{6'}$	1.40090	1.40895	1.40125	1.39562
$C_{6'}C_{1'}$	1.39593	1.38574	1.39439	1.39884
$C_{4'}C_{1'''}$	-	-	1.48117	1.44138
$C_{2'''}O$	-	-	1.37037	1.32239
$C_{5'''}O$	-	-	1.36997	1.32981

Table 2. Optimized bond lengths (Å) of neutral and radical cations of the monomer and dimer of DHOPT obtained at B3LYP/6-31G* level.

Parameter	DHOPT		Dimer of DHOPT	
	Neutral	Radical cation	Neutral	Radical cation
C_4C_5	1.36349	1.35478	1.36398	1.35478
C_3C_4	1.43964	1.44897	1.43054	1.44897
C_2C_3	1.37574	1.39653	1.38321	1.39653
S_1C_2	1.73177	1.70042	1.76341	1.70042
S_1C_5	1.73735	1.74984	1.73216	1.74984
$C_2C_{2'}$	-	-	1.44376	1.41094
$C_{2'}C_{3'}$	-	-	1.36972	1.38424
$C_{3'}C_{4'}$	-	-	1.41537	1.39854
$C_{4'}C_{5'}$	-	-	1.36523	1.39842
$S_{1'}C_{5'}$	-	-	1.70941	1.68515
$S_{1'}C_{2'}$	-	-	1.73278	1.75390
$C_3C_{1'}$	1.48151	1.43853	1.46512	1.44529
$C_{2'}O$	1.37088	1.32100	1.36326	1.33671
$C_{5'}O$	1.36946	1.33659	1.36578	1.34879
$C_{4'}C_{1'''}$	-	-	1.45216	1.43894
$C_{2'''}O$	-	-	1.37356	1.32631
$C_{5'''}O$	-	-	1.36979	1.33001

Table 3. Optimized bond lengths (Å) of neutral and radical cations of the monomer and dimer of DOOPT obtained at B3LYP/6-31G* level.

Parameter	DOOPT		Dimer of DOOPT	
	Neutral	Radical cation	Neutral	Radical cation
C_4C_5	1.36348	1.36101	1.36421	1.35333
C_3C_4	1.43967	1.44155	1.43943	1.44563
C_2C_3	1.37572	1.39215	1.38321	1.39655
S_1C_2	1.73179	1.70976	1.76348	1.71762
S_1C_5	1.73738	1.74201	1.74256	1.75478
$C_2C_{2'}$	-	-	1.45367	1.42111
$C_{2'}C_{3'}$	-	-	1.36375	1.38666
$C_{3'}C_{4'}$	-	-	1.44564	1.47211
$C_{4'}C_{5'}$	-	-	1.36627	1.39774
$S_{1'}C_{5'}$	-	-	1.71653	1.67542
$S_{1'}C_{2'}$	-	-	1.74288	1.76321
$C_3C_{1'}$	1.48149	1.46082	1.47652	1.45326
$C_{2'}O$	1.37097	1.31981	1.36344	1.33241
$C_{5'}O$	1.36957	1.32446	1.36436	1.34121
$C_{4'}C_{1'''}$	-	-	1.45342	1.43564
$C_{2'''}O$	-	-	1.38322	1.34654
$C_{5'''}O$	-	-	1.36174	1.34265

Table 4. Bond lengths (Å) of the three monomers as calculated by B3LYP/6-31G* level.

Parameter	DBOPT		DHOPT		DOOPT	
	Neutral	Radical cation	Neutral	Radical cation	Neutral	Radical cation
C_4C_5	1.36354	1.36163	1.36349	1.35478	1.36348	1.36101
C_3C_4	1.43969	1.44867	1.43964	1.44897	1.43967	1.44155
C_2C_3	1.37579	1.39269	1.37574	1.39653	1.37572	1.39215
S_1C_2	1.73155	1.70759	1.73177	1.70042	1.73179	1.70976
S_1C_5	1.73743	1.74869	1.73735	1.74984	1.73738	1.74201
$C_3C_{1'}$	1.48148	1.42349	1.48151	1.43853	1.48149	1.46082
$C_{2'}O$	1.37081	1.27311	1.37088	1.32100	1.37092	1.31981
$C_{5'}O$	1.36937	1.30639	1.36946	1.33659	1.36957	1.32446

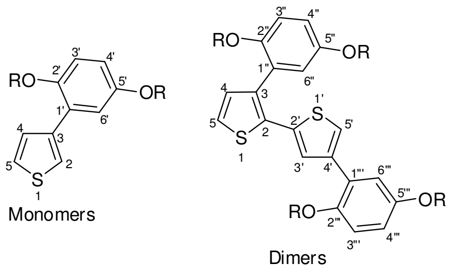


Figure 2. Atom labeling in the monomers and dimers of the three dialkoxy-phenylthiophenes.

The S_1C_2 bond length decreased upon the removal of an electron but the S_1C_5 bond length increased, which shows that the S_1C_2 bond exhibits double bond character in the radical cations. The inter-ring bond length decreased, which indicates the formation of a double bond after the removal of the electron. In the case of the phenyl rings, the $C_{1'}C_{2'}$, $C_{2'}C_{3'}$, $C_{4'}C_{5'}$, $C_{5'}C_{6'}$ bonds became longer, and $C_{2'}O$, $C_{5'}O$ bond lengths decreased which indicates a double bond character.

For all the three dimers, the bond lengths of the C_4C_5, C_2C_3, S_1C_2, $S_{1'}C_{2'}$, $C_{2'}C_{3'}$ and $C_{4'}C_{5'}$ bonds increased while the bond lengths of the S_1C_5, C_3C_4, $C_2C_{2'}$, $C_{3'}C_{4'}$, and $S_{1'}C_{5'}$ bonds decreased. These calculations suggest an increase of single bond character for the former and an increase of double bond character for the latter bonds up on oxidation. All the inter-ring bonds attained double bond character and the results indicate that the electron was removed from the $C_{4'}C_{5'}$ double bond since its length increased. For the monomers, an electron was removed from the C_2C_3 π-bond since its length increased, and the C_4C_5 bond retained its double bond character in the radical cation.

These changes in the structural parameters were observed for all the three dialkoxyphenyl-substituted thiophenes, except for slight changes in bond lengths, in both the neutral and radical cations, with increasing the chain length of the alkoxy substituents. The C–C bond lengths of the thiophene ring were decreased with increasing the alkoxy chain lengths, while the C–S bond lengths were increased. The inter-ring and C–O bond lengths were also increased with increasing the chain lengths of the alkoxy substituents as shown in Table 4.

The C–C and C–O bond lengths of the monomers and their dimers show a small difference in both the neutral and radical cations with increasing chain length of the alkoxy substituents. The $C_{2'}$-O bond in the neutral DBOPT has a length of 1.37081 Å. The corresponding bond lengths of DHOPT and DOOPT are 1.37088 Å and 1.37092 Å, respectively. For both the monomers and dimers, C–O bond lengths became shorter up on the removal of an electron, indicating a partial double bond character and delocalization of the radical and the cation.

For the dimers of DBOPT and DHOPT, the dihedral angles between the two thiophene rings (S_1-C_2-$C_{2'}$-$S_{1'}$) have been varied in 10^o steps and the single point energy was calculated to compare the effect of the chain length on the dihedral angle of the stable conformer. From the single point energy versus dihedral angle plot shown in Figure 3, it is observed that the two dimers have different dihedral angles at their stable conformations. The dimer of DBOPT, with the shorter alkoxy chain length, is stable at a dihedral angle of 120^o whereas the dimer of DHOPT is stable at 130^o. This result shows that the alkoxy chain length has an effect on the rotation of the adjacent rings along the thiophene-thiophene inter-ring bond.

The dihedral angles between the thiophene and phenyl rings for the dimers (C_2-C_3-$C_{1''}$-$C_{6''}$) were also calculated and plotted in Figure 4. From the figure it is observed that the chain length of the alkoxy substituent affected the thiophene-phenyl inter ring dihedral angle. The dimer of DBOPT has five minima, whereas the dimers of DHOPT and DOOPT have four minima, which shows five conformers for the former and four for the latter two. The dimer of DBOPT has a global minimum at 250^o whereas both the dimers of DHOPT and DOOPT have a global minimum at 230^o. From the plot, it is observed that longer side chains restrict the number of possible conformations at the energy minimum.

The Mulliken charges calculated for the three monomers and their dimers are tabulated in Tables 5 and 6. From the Mulliken charges of the monomers, it was observed that the cations can delocalize on all the carbons since their charges became more positive up on oxidation. The phenyl and the alkoxy substituents made the carbon atoms, at which they are attached, more positive than the other carbon atoms. This indicates that the alkoxy and phenyl substituents have electron withdrawing properties. The lengths of the alkoxy substituents have negligible effect on the charges of the carbon and sulfur atoms.

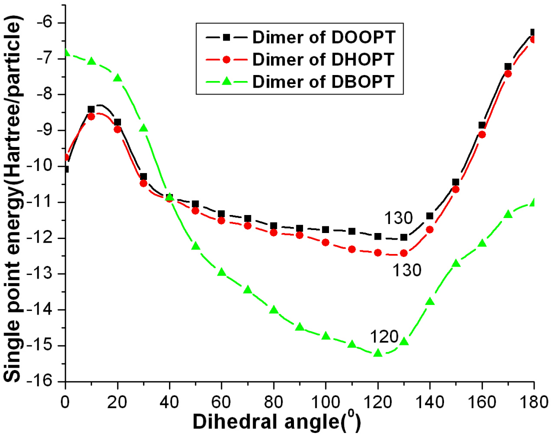


Figure 3. Single point energy *versus* S-C-C-S inter-ring dihedral angle of dimers of DBOPT, DHOPT and DOOPT obtained at B3LYP/6-31G* level. (-2481 hartree is subtracted from the actual value).

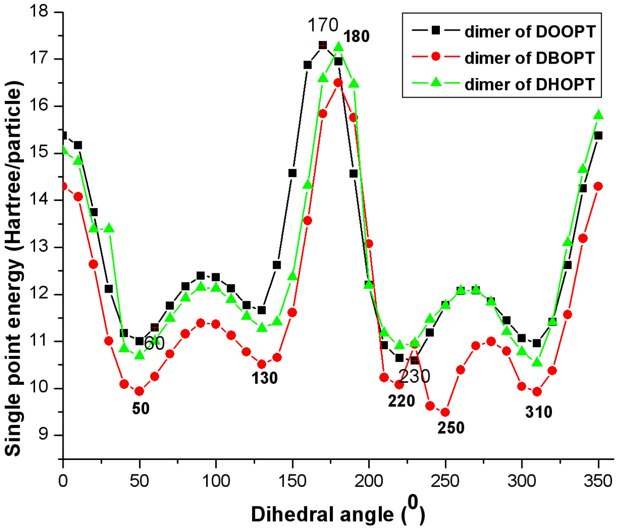


Figure 4. Single point energy *versus* thiophene-phenyl inter-ring dihedral angle of dimers of DBOPT, DHOPT and DOOPT obtained at B3LYP/6-31G* level. (-580 hartree is subtracted from the actual value).

Table 5. Mulliken charges for the monomers of DBOPT, DHOPT, and DOOPT calculated by DFT/ B3LYP/6-31G* level.

Atom number	DBOPT		DHOPT		DOOPT	
	Neutral	Radical cation	Neutral	Radical cation	Neutral	Radical cation
C$_5$	-0.361	-0.322	-0.361	-0.322	-0.361	-0.322
C$_4$	-0.084	-0.054	-0.084	-0.054	-0.084	-0.054
C$_3$	0.099	0.096	0.099	0.096	0.099	0.096
C$_2$	-0.389	-0.379	-0.389	-0.379	-0.389	-0.379
S$_1$	0.245	0.403	0.245	0.403	0.245	0.403
C$_{1'}$	-0.055	-0.034	0.055	-0.034	0.055	-0.034
C$_{2'}$	0.337	0.394	0.337	0.394	0.337	0.394
C$_{3'}$	-0.208	-0.179	-0.208	-0.179	-0.208	-0.179
C$_{4'}$	-0.204	-0.168	-0.204	-0.168	-0.204	-0.168
C$_{5'}$	0.390	0.451	0.390	0.451	0.390	0.451
C$_{6'}$	-0.254	-0.208	-0.254	-0.208	-0.254	-0.208

Table 6. Mulliken charges for the dimers calculated by DFT/ B3LYP/6-31G* level.

Atom number	Dimer of DBOPT		Dimer of DHOPT	
	Charge		Charge	
	Neutral	Radical cation	Neutral	Radical cation
C$_5$	-0.357	-0.351	-0.357	-0.353
C$_4$	-0.101	-0.086	-0.101	-0.089
C$_3$	0.092	0.102	0.089	0.104
C$_2$	-0.225	-0.210	-0.223	-0.213
S$_1$	0.250	0.326	0.248	0.326
C$_{2'}$	-0.175	-0.135	-0.172	-0.139
C$_{3'}$	-0.125	-0.130	-0.125	-0.128
C$_{4'}$	0.108	0.113	0.109	0.112
C$_{5'}$	-0.391	-0.326	-0.390	-0.326
S$_{1'}$	0.270	0.383	0.272	0.379

The changes in charges, before and after oxidation, on carbon atoms at position 4, and 5, in both the monomers and dimers, are different. For example, for the dimer of DBOPT, the charge on C$_5$ is -0.357 in the neutral form and -0.351 in the radical cation (a difference of 0.06), while the charge of the carbon atom at position 4 of the dimer of DBOPT is -0.101 in its neutral form and -0.086 in its radical cation (a difference of 0.015). Similarly, the charge on carbon atom 3 was 0.092 before oxidation and 0.102 after oxidation, which has a difference of 0.01, whereas for carbon atom 2 the charge before oxidation was -0.225 and after oxidation it was -0.210, with a difference of 0.015. These results suggest that the positive charge resided on carbons 4 and 5. When carbon 3 is compared with carbon 4, the change is very small suggesting that as the electron is removed, the cation will reside on carbon atom 2 and the odd electron stays at carbon atom 3. These observations agree with the calculated optimized bond lengths.

The band gaps for the monomers and the dimers were calculated using B3LYP/6-31G* level of calculation and are listed in Table 7. From the table it is observed that the compound with shorter alkoxy substituent has relatively wider band gap than the other two in their neutral and radical cation states. On the other hand, DHOPT and DOOPT have comparable band gaps in both the neutral and radical cations of the monomers and the dimers. It was observed that up on dimerization and removal of an electron, the band gaps for both the monomers and dimers decreased.

Table 7. Band gaps of the monomers and dimers calculated by DFT/B3LYP/6-31G*.

Compounds	Neutral form			Radical cation		
	HOMO	LUMO	E (eV)	HOMO	LUMO	E (eV)
DBOPT	-5.2105	-0.4563	4.7542	-9.5473	-6.9575	2.5898
Dimer-DBOPT	-4.9907	-0.78392	4.2068	-7.6741	-6.0466	1.6275
DHOPT	-5.1840	-0.4499	4.7341	-9.5139	-6.9211	2.5928
Dimer-DHOPT	-4.9733	-0.7937	4.1796	-7.6497	-6.0117	1.6380
DOOPT	-5.1735	-0.4397	4.7338	-9.5089	-6.9162	2.5927
Dimer-DOOPT	-4.9432	-0.7637	4.1795	-7.6496	-6.0103	1.6393

The thermodynamic properties calculated for the monomers and their dimers are summarized in Table 8. The three dialkoxyphenylthiophenes show very small difference in the change in thermodynamic properties calculated by HF/STO-3G level of theory. But in the DFT/B3LYP/STO-3G, DFT/ B3LYP/3-21G* and DFT/ B3LYP/6-31G* levels of calculation larger difference in thermodynamic properties were obtained between the three monomers and their dimers.

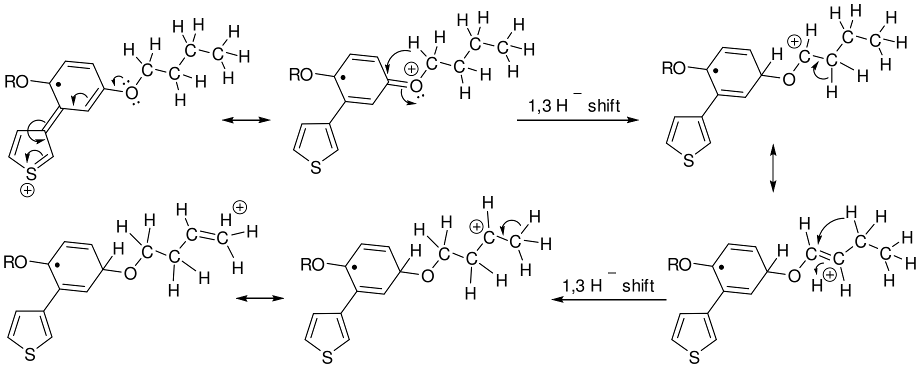
Table 8. Thermodynamic properties related to the oxidation process of monomers and dimers.

Method	Property	DBOPT	DHOPT	DOOPT	Dimer of DBOPT	Dimer of DHOPT	Dimer of DOOPT
HF/ STO-3G	ΔG^0 (kJ/mol)	420.94	418.99	418.53	381.33	379.37	378.60
	ΔH^0 (kJ/mol)	421.36	419.60	419.40	381.45	380.29	380.07
	ΔS^0 (J/mol.K)	1.401	2.054	2.920	0.372	3.075	4.920
DFT/ STO-3G	ΔG^0 (kJ/mol)	437.33	426.57	425.06	386.25	367.52	365.49
	ΔH^0 (kJ/mol)	438.63	428.35	427.05	388.16	366.65	363.93
	ΔS^0 (J/mol.K)	4.370	5.987	6.678	6.414	-2.971	-5.23
DFT/ 3-21G*	ΔG^0 (kJ/mol)	645.65	632.75	628.47	603.95	582.54	578.38
	ΔH^0 (kJ/mol)	647.63	636.37	631.99	606.96	586.60	581.561
	ΔS^0 (J/mol.K)	6.652	12.154	11.83	10.09	13.602	10.67
DFT/ 6-31G*	ΔG^0 (kJ/mol)	661.99	635.00	631.31	613.21	563.141	551.82
	ΔH^0 (kJ/mol)	667.36	639.013	634.74	617.661	566.843	555.423
	ΔS^0 (J/mol.K)	17.987	13.456	11.504	14.93	12.418	12.084

DOOPT showed a smaller change in Gibbs free energy than DHOPT and DBOPT. The dimers also show similar behavior like the monomers as shown in Table 8. For example, the dimer of DOOPT has a smaller change in Gibbs free energy (a difference of 61.39 kJ/mol, Table 8, B3LTP/6-31G*) than the dimer of DBOPT. From all the levels of calculations, compounds with longer alkoxy substituents on the phenyl ring have lesser value of change in Gibbs free energy. These lesser values of Gibbs free energy change for DOOPT suggest that the oxidized state is lees reactive to form dimers or oligomers that quickly diffuse away from the electrode surface into the solution. On the contrary, those with relatively higher values of Gibbs free energy change are more reactive in their oxidized state and the tendency to form dimers and oligomers that diffuse away from the electrode surface into the solution is high and forming stable polymer film at the electrode surface becomes difficult. This was observed during the electrosynthesis of electroactive conductive polymers from the corresponding monomers as reported earlier [15].

The incorporation of alkoxy side chains help the dialkoxyphenylthiophene radical cations to disperse the positive charge through the hyperconjugative effect. The dispersal of the positive charge increases the stability of the radical cations, which is favored by the smaller change in

Gibbs free energy. The dialkoxyphenylthiophenes with the longer alkoxy substituents have more possibilities for the delocalization of the cation through the hyperconjugative effect. The hyperconjugation in the radical cation derived from DBOPT is shown in Scheme 1.



Scheme 1. Hyperconjugation in the radical cation of DBOPT.

CONCLUSIONS

In this paper, the thermodynamic and structural properties of monomers and dimers of three dialkoxyphenylthiophenes have been described. The optimized bond lengths and charges on the atoms showed the delocalization of the radical cation through the double bonds. The cation also stabilizes itself through hyperconjugation in the longer alkoxy-substituted phenylthiophenes. The thermodynamic properties also showed that radical cation of DOOPT, with the longest alkoxy side chain on the phenylthiophene, is more stable than the other two with respect to both dimerization and oxidation. Of the three compounds, DOOPT is most stable at the radical cationic state and can best be used for electrodeposition of its polymer on glassy carbon as was observed experimentally [15-16].

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