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PM3 Study Of Conformational Analysis And Electronic Properties Of Functionalized Oligohexylfurans

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ABSTRACT

A semi empirical analysis of functionalized 3-hexylfurans[3XHF, where X= Br, NH_2, SH, CN, COOH, $CONC(CH_3)_2$ and $N(CH_3)_2$] having functional group attached to the hexyl substituent up to four monomeric units in head-tail-head-tail regioselectivity was carried out. The energy band gap obtained at PM3 level showed that oligomers with 3HAHF present lowest energy band gap not in consonant with that of 3DAHP and 3DAHT[12,13]. All the structures increase in twisting at equilibrium geometries as the polymer chains grow except 3HF that remains nearly constant which means that in condensed phase the functional group interactions present modification of the polymer structure. The 3AHF, 3DAHF and 3THF have electronic donating effect through the intervening hexyl carbon atoms by reducing HOMO-LUMO band gap as compared to 3HF while 3CHF, 3DTHFand 3BHF affect otherwise. The energy band gap changed with the functional group attached to hexyl substituents, which affect the molecular properties related to the electronic conductivity.

KEYWORDS

Functionalized hexylfurans;
Energy band gap;
Semi empirical(PM3).

INTRODUCTION

Conjugated organic polymers have been subject of intense experimental and theoretical studied since 1977 when this class of material was fully tested[1]. In the recent years systematic efforts have been aimed at investigating the molecular and electronic structures of polymers, polyfurans inclusive and its derivatives for building photonic devices[2,3]. Polyfuran has been used in copolymerizing conducting polymers as gas sensors, wires, mircoactuators, antielectrostatic coating, solid electrolytic capacitors, polymeric batteries, electronic devices and functional membranes[4-6]. The nature, length of alkyl side chains and bulkiness of side chains have been found to have great effect on performance and field-effect mobility of the polymers. The hexyl group at position 3 on the heterocyclic polymers has found to have better and long-term performance[7]. Theoretically, conformational analysis of un-substituted and mono-substitution of furans at various semi empirical methods as well as heats of formation and energy band gaps using ab initio(G2:MP2) and density functional theory(DFT)have been carried out[8-10]. In this work, the functionalized hexylfurans (3XHF) oligomers of n monomeric units(n=1,2,3 and 4) were studied in Head-Tail-Head-Tail using semi empirical method at PM3 level of calculations. The functional groups chosen are electron donating(NH_2, SH and $N(CH_3)_2$), electron withdrawing(CN and COOH) and the intermediate between the two classes(Br and CONC$(CH_3)_2$) to study the effect of functional groups on electronic properties of hexylfuran energy band gaps are discussed as a function of the number of monomeric units and functionalized hexyl substituents.

COMPUTATIONAL DETAILS

Conformational analysis was carried out on the molecules sketched in figure 1. Initial geometries were fully optimized using semi empirical method at PM3 level[11]. The vibrational frequency calculations were carried out to characterize the stationary points and symmetry constraints were not imposed. The functionalized hexylfurans(3XHF) considered are 3-bromohexylfuran(3BHF), 3-(2(4,4-dimethylthyloxazolin-2-yl)-heptylfuran(3DTHF), 3-Heptanic acid furan(3HAF), 3-thiohexylfuran(3THF), 3-cyanohexylfuran(3CHF), 3-aminofuran(3AHF), 3-(N,N-dimethyl)-aminohexylfuran (3DAHF) and 3-hexylfuran (3HF). All calculations were performed using Spartan essential 2.0.1[12].

TABLE 1: Selected bond lengths(Å) and bond angles(^{0}C) for optimized structure of functionalized poly(3-hexylfurans) oligomers at PM3

Number of units (n)	3- Hexylfurans derivatives							
n =1	3BHF	3AHF	3THF	3CHF	3HAHF	3DTHF	3DAHF	3HF
Bond length								
O_1-C_1	1.378	1.379	1.378	1.378	1.378	1.378	1.378	1.378
O_1-C_2	1.377	1.377	1.377	1.377	1.377	1.377	1.377	1.377
Bond angle								
$C_1O_1C_2$	103.94	106.91	106.94	106.94	106.93	106.94	106.93	106.95
n =2								
Bond length								
O_1-C_1	1.373	1.373	1.373	1.373	1.373	1.373	1.373	1.373
O_1-C_2	1.391	1.390	1.390	1.390	1.390	1.391	1.394	1.394
C_2-C_3	1.439	1.438	1.439	1.439	1.438	1.439	1.441	1.441
O_2-C_3	1.391	1.390	1.390	1.390	1.390	1.392	1.392	1.392
O_2-C_4	1.373	1.374	1.374	1.374	1.374	1.373	1.374	1.374
Bond angle								
$C_1O_1C_2$	106.71	106.59	106.61	106.61	106.60	106.71	106.73	106.74
$C_3O_2C_4$	106.59	106.46	106.48	106.48	106.46	106.59	106.58	106.58
n =3								
Bond length								
O_1-C_1	1.372	1.373	1.372	1.372	1.372	1.372	1.373	1.373
O_1-C_2	1.391	1.392	1.391	1.390	1.391	1.391	1.390	1.394
C_2-C_3	1.440	1.439	1.440	1.439	1.439	1.440	1.439	1.440
O_2-C_3	1.387	1.385	1.387	1.387	1.387	1.387	1.387	1.386
O_2-C_4	1.387	1.388	1.387	1.387	1.386	1.387	1.387	1.390
C_4-C_5	1.439	1.440	1.439	1.440	1.439	1.439	1.440	1.440
O_3-C_5	1.391	1.391	1.391	1.391	1.390	1.391	1.391	1.391
O_3-C_6	1.373	1.372	1.373	1.372	1.372	1.373	1.372	1.373
Bond angle								
$C_1O_1C_2$	106.73	106.75	106.72	106.54	106.77	106.71	106.51	106.72
$C_3O_2C_4$	106.32	106.32	106.32	106.33	106.35	106.31	106.30	106.48
$C_5O_2C_6$	106.52	106.63	106.52	10974	106.55	106.53	106.70	106.56

RESULTS AND DISCUSSION

Geometries

The bond lengths and bond angles are listed in TABLES 1 and 2. The interring C-C bond lengths are quite similar(1.438Å to 1.442Å) for all the functionalized hexylfurans (3XHF). This is similar to that of hexylpyrroles(3XHP)[13] but shorter than that of hexylthiophenes(3XHT) analogues calculated at the same PM3 level[14]. The interring distances calculated for 3XHF dimers are slightly shorter than that of unsubstituted pyrrole dimers calculated at Hartree Fock (HF) using different basis sets[15]. The interring bonds are not change even as the polymer chains become larger. There is slight lengthening of O_1-C_2 and shortening of O_1-C_1 as 3XHF becomes larger, which indicates an increment in delocalization of π-electrons, hence increase in conductivity character[16]. The functional groups on the hexyl have little or no effect on bond lengths and bond angles, but reducing the dihedral angles as compared to that of 3HF (TABLE 3). All the structures are increase in twisting at equilibrium geometries as the polymer chains grow except 3HF that remains fairly constant (TABLE 3). It means that in condensed phase the functional group interacts and presents modification of the polymer structure. The O-C bond lengths are shorter and C-O-C bond angles are larger than that of thiophenes and pyrroles analogues[13].

HOMO-LUMO energy band gap

Spectroscopic data for organicπ-systems are usually determined either in solution or in solid state (crystal or thin film). However, since our calculations are for isolated molecules in the gas phase, we have attempted to correlate functional groups on the hexyl substituent to the energy band gap of the furans and attempt to compare them to corresponding functionalized hexylpyrroles[13] and hexylthio

TABLE 2 : Selected bond lengths(Å) and bond angles(^0C) for optimized structure of functionalized poly(3-hexylfurans) oligomers at PM3

Number of units (n)	3- Hexylfurans derivatives							
n =4	3BHF	3AHF	3THF	3CHF	3HAHF	3DTHF	3DAHF	3HF
Bond length								
O_1-C_1	1.373	1.373	1.373	1.372	1.372	1.372	1.372	1.373
O_1-C_2	1.391	1.391	1.391	1.394	1.394	1.394	1.391	1.393
C_2-C_3	1.439	1.439	1.439	1.441	1.441	1.441	1.440	1.441
O_2-C_3	1.385	1.384	1.384	1.386	1.385	1.386	1.386	1.387
O_2-C_4	1.390	1.392	1.392	1.390	1.392	1.390	1.387	1.388
C_4-C_5	1.442	1.441	1.441	1.442	1.441	1.442	1.439	1.440
O_3-C_5	1.386	1.385	1.385	1.386	1.386	1.386	1.387	1.384
O_3-C_6	1.388	1.388	1.388	1.388	1.388	1.387	1.385	1.388
C_6-C_7	1.442	1.438	1.438	1.441	1.439	1.441	1.438	1.440
O_4-C_7	1.391	1.391	1.391	1.391	1.391	1.392	1.389	1.390
O_4-C_8	1.373	1.373	1.373	1.373	1.374	1.372	1.375	1.374
Bond angle								
$C_1O_1C_2$	106.60	106.59	106.60	106.74	106.74	106.73	106.70	106.66
$C3O_2C_4$	106.20	106.33	106.33	106.30	106.50	106.33	106.51	106.25
$C_5O_3C_6$	106.31	106.33	106.31	106.39	106.30	106.33	106.07	106.58
$C_7O_4C_8$	106.57	109.65	106.55	106.61	106.55	106.60	106.36	106.46

TABLE 3 : Dihedral angles(in degree) of functionalized poly(3-hexylfurans) oligomers(n =2,3and 4)at PM3

Furans	n =2,	n =3		n= 4		
	$O_1C_2C_3O_2$	$O_1C_2C_3O_2$	$O_2C_4C_5O_3$	$O_1C_2C_3O_2$	$O_2C_4C_5O_3$	$O_3C_6C_7O_4$
3BHF	-11.77	-13.05	3.86	-18.80	145.55	-160.27
3AHF	6.51	-2.73	16.89	-52.66	143.23	-161.79
3THF	7.49	-12.60	3.60	-51.68	145.52	-159.90
3CHF	7.52	-12.16	3.65	-53.89	141.69	-160.34
3HAHF	6.59	-9.27	4.61	-51.39	142.18	-161.21
3DTHF	-12.30	-14.66	3.32	-54.06	142.54	-124.72
3DAHF	6.53	-15.35	3.62	-19.54	144.76	-161.52
3HF	170.43	171.69	172.39	155.94	168.19	-176.37

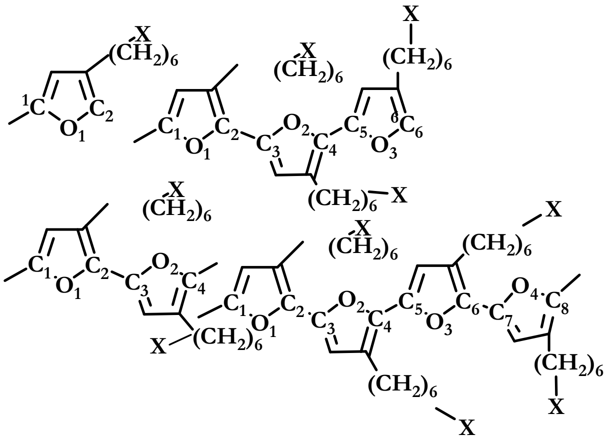

Figure 1 : Head-Tail-Head-Tail(HT-HT) structure of functionalized poly(3-hexylthiophenes) oligomers of n monomeric units(n=1,2, 3 and 4)

Where, X = Br, NH_2, SH, CN, COOH, $CONC(CH_3)_2$ and $N(CH_3)_2$

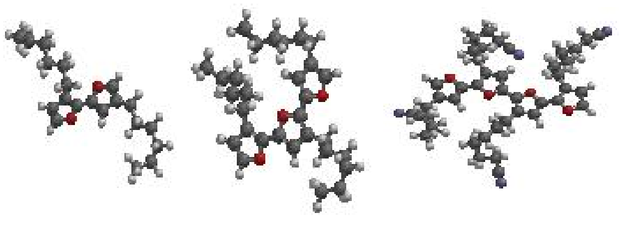

Figure 2 : The optimized structures of dimer, trimer and tetramer of 3-cyanohexylfuran(3CHF) at PM3

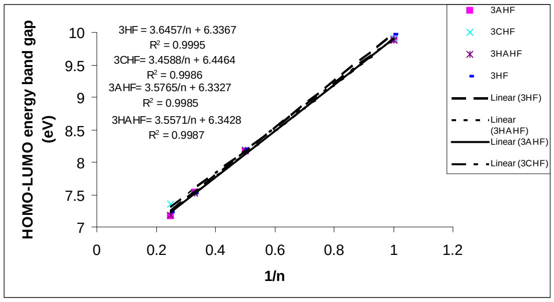

Figure 3 : Correlation of energy band gap (Eg) and reciprocal of the number of furans (1/n) , n being the number of monomeric units

TABLE 4. HOMO-LUMO energy band difference (energy band gap(Eg)) in eV at PM3 level of semi empirical calculations

Furans	3HF	3BHF	3AHF	3THF	3CHF	3HAHF	3DTHF	3DAHF
Monomer	9.97	9.17	9.89	9.61	9.91	9.88	9.86	9.65
Dimer	8.20	8.22	8.17	8.18	8.18	8.18	8.22	8.23
Trimer	7.53	7.53	7.54	7.54	7.53	7.52	7.55	7.52
Tetramer	7.23	7.41	7.17	7.21	7.36	7.19	7.37	7.19
H*	6.34	6.85	6.33	6.50	6.45	6.34	6.50	6.47

H* is the energy band gap for the infinity polymers calculated considering a linear behavior Eg with 1/n being number of monomeric units

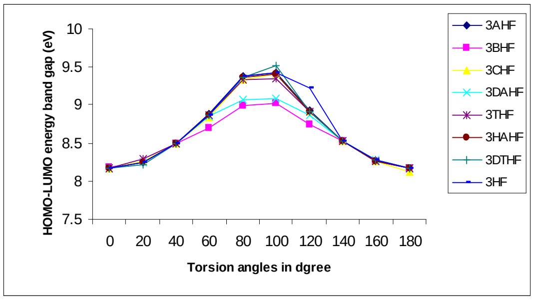

Figure 4 : Evolution of the energy difference between the HOMO and the LUMO as a function of the torsion angle between rings

phenes[14]. TABLE 4 summarizes the energy band gap of intrinsic functionalized hexylfurans(3XHF) monomers, dimers, trimers and tetramers at PM3. It is interesting to note the decrease in energy band gap as the oligomer chain becomes larger. The infinity energy band gaps for 3XHF predicted in figure 3 were lowered than that of thiophene(≈1.27eV) and pyrrole(≈0.59eV) analogues[13,14]. The quality of the correlation used is exemplified for the HT-HT derivatives as shown in figures 1 and 2. Analysing the values HOMO-LUMO differences(TABLE 4) show that the energy band gaps obtained for 3XHF could be arranged in decreasing order as 3AHF>3HAHF≈ 3DAHF>3THF>3HF>3CHF>3DTHF>3BHF from the tetramers energy band gaps. Therefore 3AHF, 3DAHF and 3THF have electronic donating effect through the intervening hexyl carbon atoms by reducing HOMO-LUMO band gap as compared to 3HF while 3CHF, 3DTHFand 3BHF affect otherwise. However, COOH though an electron withdrawing group present a lower energy band gap comparable to that of $N(CH_3)_2$ in this study. In 3XHF, 3AHF has the lowest energy band gap in contrary to 3-(N,N-dimethyl)-aminohexylthiophene (3DAHT)[14] and 3-(N,N-dimethyl)-aminohexylpyrrole (3DAHP)[13].

Figure 4 shows the evolution of the energy difference (ΔE) between the HOMO and the LUMO of 3AHF, 3BHF, 3CHF, 3DAHF, 3THF, 3HAHF, 3HF and 3DTHF dimers as functions of torsion angles. As expected, the increment in interring torsion angles reduces the π-electrons delocalization and consequently increases the energy gap(ΔE) between the HOMO and the LUMO[17]. The increment in ΔE becomes faster at the larger torsion angles until it reaches optimum at 90^0(Figure 4). This is important for the effect of the torsion angles in different torsion range, which means that the effect is less at lower torsion angles than at higher ones. All curves of 3XHF overlapped especially at lower torsion angles, the electronic donating effect of 3BHF and 3DAHF is pronounced than others at higher torsion angles(60^0 to 90^0). This is quite different from the semi empirical(PM3) results for thiophene analogues in which N,N-dimethylhexylthiophene(3DAHT) has the stronger electronic donating effect[14]. Although, bromohexyl substituent has highest electronic donating effect in both 3XHF and 3XHP[13] when the polymer is torsioned, it was more pronounced in 3XHP. This is an indication that the nature of heteroatom on the rings and twisting or torsioning of polymer has effect on the functional groups modification in relation to electronic and molecular properties of the polymer.

Finally, the results obtained in the present study showed that the inclusion of functional groups to alkyl side chain in furan derivatives allow selective control of the molecular structure and energy band gaps that are sufficient to control macroscopic properties.

Torsion potential of dimers

The torsion potential curves for 3BHF, 3AHF, 3THF, 3CHF, 3HAHF, 3DTHF, 3HF and 3DAHF associate with the rotation of the dimers in different directions are displayed in figure 5. Analysis of figure 5 shows that potential curves for 3XHF dimers are not flat with increase in barrier height energies towards perpendicular conformations(except 3CHF). Therefore, the segments would be slightly twisted in their free states and increase in twisting as the molecular packing increases in conformity with the dihedral angles of the moststable conformations as shown in TABLE 3.

The energy barrier height is compared to the equilibrium energy of 3XHF dimers in the free state. The energy barriers towards co-planar conformation are in the range of 0.45-1.98 Kcal/mol for 3BHF and 3DTHF and they are about 2.0Kcal/mol for the 0^0 conformation and less than 1.0Kca/mol towards 180^0 conformation respectively. The energy barriers towards perpendicular conformation for 3BHF and 3DTHF are 1.50 and 0.54Kcal/mol respectively.

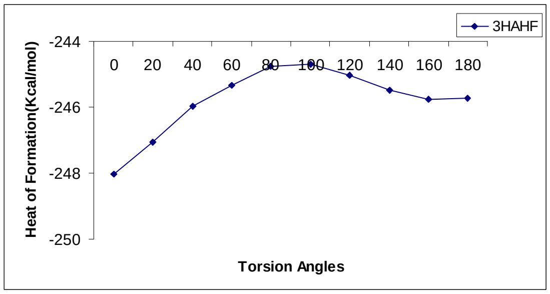

Figure 5(a)

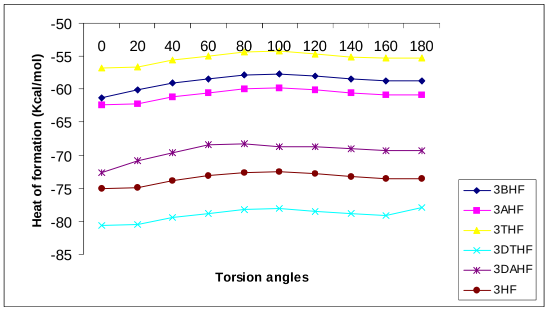

Figure 5(b)

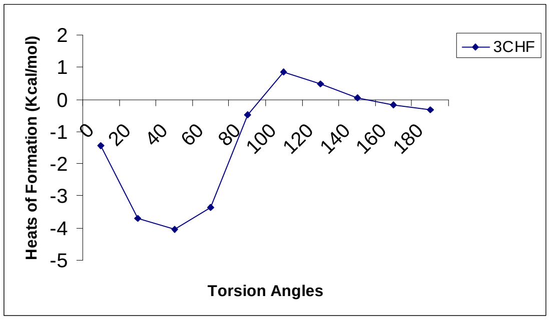

Figure 5(c)

Figure 5 : Torsion potential curves of the functionalized hexylfurans obtained with PM3 calculations

In the case of 3THF, 3CHF, DAHF and 3HAHF, the energy barriers towards 0^0 conformation is approximately 3.0 Kcal/mol and that of towards 180^0 conformation are 1.40, 0.67, 0.45 and 0.70 Kcal/mol respectively. The energy barriers towards perpendicular conformation for 3THF, 3CHF, 3DAHF and 3HAHF are 0.37, 1.18, 1.39 and 0.32Kcal/mol respectively. The barrier height towards 0^0 and 180^0conformations for 3AHF are 4.01 and 2.58 Kcal/mol respectively and that towards perpendicular conformation is 1.57Kcal/mol. In 3HF, the barrier height towards 0^0 and perpendicular conformations is about 1.0Kcal/mol, and that towards 180^0 conformation is 0.02Kcal/mol. Therefore, there is increase in energy barrier of the functionalized polymers (3XHF) as compared to hexyl polymer (3HF), this indicates that addition of functional groups can be used to selectively control the electronic and molecular properties of the hexylpolymer. However, all the polymers would be very flexible in the polymer chains and probably adopt perpendicular and 180^0 conformations expect 3AHF where the polymers chains are closely packed enough. The change of the torsion curves of 3CHF is very similar with that from 3-Bromohexylthiophene(3CHP, and 3CHT)[13,14]. From the potential curves, the hexyl carbon-carbon atoms may not be the major factor that determines the cofacial packing distance, but also the interactions of functional group attached to the hexyl substituent as predicted in our previous works.

CONCLUSION

The structure and energy band gap are calculated for series of 3XHF oligomer using semi empirical methodology based on PM3 approaches. The 3XHF has lowest energy band gap than 3XHT and 3XHP studied at the level of semi empirical method(PM3). All the structures are increase in twisting at equilibrium geometries as the polymer chains grow except 3HF that remains constant. It means that in condensed phase the functional group interactions present modification of the polymer structure. 3AHF, 3DAHF and 3THF have electronic donating effect through the intervening hexyl carbon atoms by reducing HOMO-LUMO band gap as compared to 3HF while 3CHF, 3DTHFand 3BHF affect otherwise. In general, our results show that the energy band gap does change with the functional group attached to hexyl substituent and that the nature of the heteroatom in the rings chain affect the conjugation, and hence the molecular properties related to the electronic conductivity.

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