

Structural and electronic properties of chloromethylfuran oligomers: Semiempirical and DFT study

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ABSTRACT

Structural and electronic properties of oligomers of chloromethylfurans (CMFs), $OC_4H_4-CH_nCl_3$, with $n = 0, 1, 2, 3$ and 4 have been studied using ZINDO/AM1 and B3LYP/6-31G* split basis set. Preliminary study using AM1 and *ab initio* (HF) 6-31G* with medium basis set was carried out on di-, tri- and tetramer CMFs in order to investigate the stability of configuration of the polymer chains. There is noticeable effect of substituents on the geometries of CMFs as compared to polyfuran and polymethylfuran. The modeled CMFs have improved characteristics as conducting polymers compared to polyfurans and polymethylfurans. The energy band gaps, electronic spectroscopy and electronic dipole moment vectors of the compounds are presented. Generally CMFs present lower energy band gaps, longer wavelength and higher electric dipole moments and are therefore more suitable as monomer for conducting polymer especially trichloromethylfuran.

Key words: Chloromethylfurans, electronic properties, ZINDO and DFT.

INTRODUCTION

Conjugated conducting polymers have been a subject of intense experimental and theoretical studies since 1977 when this class of material was fully tested¹. They are called "synthetic metals" because of the electric, electronic, magnetic and optical properties inherent in metals or semiconductors which they possess, while they also retain the mechanical properties of conventional polymers. In intrinsic conducting polymers, the conductivity is assigned to the delocalization of δ -bonded electrons over the polymeric backbone, exhibiting unusual electronic characteristics, such as low energy optical transitions, low ionization potentials and high electron affinities². Electron delocalization is a consequence of the presence of conjugated double bonds in the polymer backbone.

In 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^{3,4}. Polyfuran films are found to exhibit electrical and optical properties similar to those of polythiophene and polypyrrole, though the electrical conductivity in a doped state is a little lower than the latter two polymers. The resistivity of polyfuran is found to be very sensitive to humidity and its application as a sensor of humidity is proposed⁵. Polyfurans have been used in co-polymerizing conducting polymers as gas sensors, wires, microactuators, antielectrostatic coating, solid electrolytic capacitors, polymeric batteries, electronic devices and functional membranes⁴.

The aim of this present study is to theoretically study the structural and electronic properties of oligomers including dimer, trimer and tetramer of chloromethyl furans (CMFs) for the preparation of corresponding conducting polymers

with improved electrical and mechanical properties. The oligomers consisted of furan and methylfuran monomers as reference compounds for all comparative studies. The structures and the numbering scheme used for CMF monomers and their oligomers in this study are arranged in head-tail and head-tail fashion in the oligomer chain as illustrated in Fig. 1.

Methods of calculation

Quantum chemical calculations were performed at ZINDO based on optimized geometry from AM1 and B3LYP level of theory with 6-31G* basis set¹¹. All the parameters were allowed to relax and all the calculations converged to an optimized geometry. The RHF method failed to predict reasonable values for the thermochemical stabilities of the representative CMFs. Based on these preliminary studies B3LYP/6-31G* method was employed as implemented in Spartan program¹².

Geometries of Chloromethylfurans

The connecting bond length between an adjacent pair monomer ring of an extended chain, R_i-R_j is affected by substituent groups (Table 1). Chlorine substitutions in the CMF oligomers increase the R_i-R_j with respect to the furan and methylfuran oligomers. This is due to the polarity of chlorine substitutions in the oligomer chains. Also, the geometrical data (Table 1) show that the R_i-R_j bond decreases when the number of monomers increase in an oligomer chain. The dihedral angle defining torsion between an adjacent pair ring plane of an extended chain, $D_{R_i-R_j}$ values for furan, methylfuran and $Fu-CCl_3$ oligomers show that they are more planar than other CMFs. As expected of conducting polymers the distortions decrease with increase in the length of a polymer chain. Since, the planarity of polymers chain is a necessary factor for electrical conducting of polymers^{2,8,13}. The chloromethylfurans would be less conductive as compared to corresponding chloromethylpyrroles due to higher $D_{R_i-R_j}$ values¹⁴, however we predict the $Fu-CCl_3$ oligomers to have preferred structure for producing conducting polymer as compared to other furan and its derivatives as considered in this

study (Fig. 2). The values of bond lengths obtained from ZINDO/AM1 are shorter than that of B3LYP/6-31G* whereas dihedral angles from ZINDO/AM1 are larger than the corresponding DFT/6-31G*.

Electronic characteristics of oligomers

It is known that energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), or

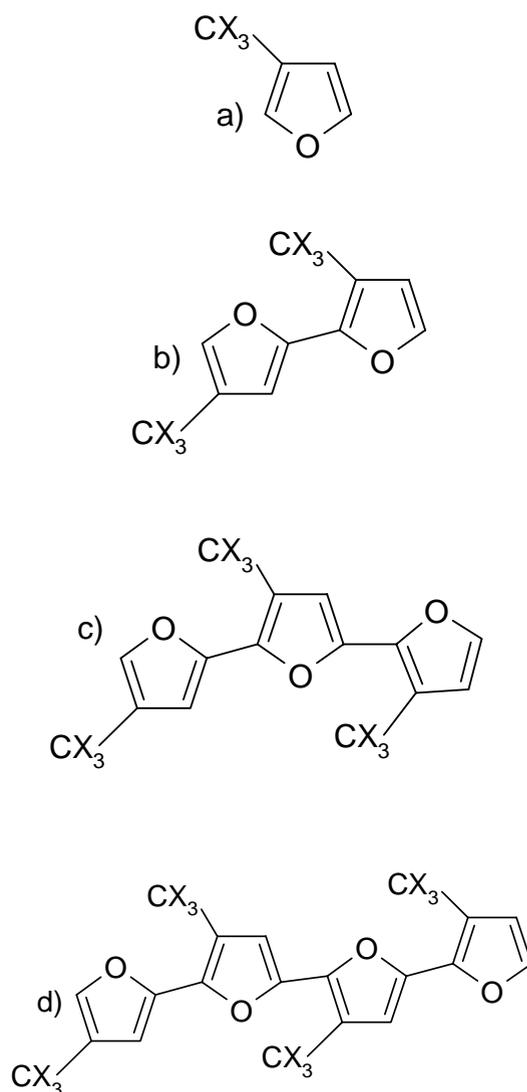


Fig. 1: Structure and numbering scheme used for the CMFs monomers and their oligomers where CX_3 stands for $-CH_3$, $-CH_2Cl$, $-CHCl_2$, $-CCl_3$

simply HOMO-LUMO gap (HLG), is a key parameter which determines the molecular admittance because it is a measure of the electron density

hardness^{15,16}. The HLG values of CMF oligomers, defined in Fig. 2, are calculated at B3LYP/6-31G* level of theory. As shown in Figure 2, the HLG values

Table 1: Selected bond lengths (Å) and dihedral angles (degree) of CMF oligomers obtained at B3LYP/6-31G* and ZINDO/AM1 (bold) methods

Oligomer	R ₁ -R ₂	R ₂ -R ₃	R ₃ -R ₄	D _{R1-R2}	D _{R2-R3}	D _{R3-R4}
Di-Fu	1.4480; 1.4440			0		
Di-FuCH ₃	1.4482; 1.4440			0.6 ;4.6		
Di-FuCH ₂ X	1.4483; 1.4440			23.4; 28.2		
Di-FuCHX ₂	1.4486 1.4442			24.5; 30.4		
Di-FuCX ₃	1.4438; 1.4402			-0.4; 0.8		
Tri-Fu	1.4446; 1.4439	1.4449; 1.4439		-0.6 ;0.4	2.0; -2.4	
Tri-FuCH ₃	1.4455; 1.4435	1.4458; 1.4446		0.4; 10.4	-0.5; 9.8	
Tri-FuCH ₂ X	1.4462; 1.4476	1.4465; 1.4448		21.9; 26.6	24.5; 31.2	
Tri-FuCHX ₂	1.4478; 1.4446	1.4478; 1.4444		22.4; 16.8	25.2; 30.4	
Tri-FuCX ₃	1.4472; 1.4446	1.4471; 1.4446		1.4; 0.2	-0.3; 6.8	
Tetra-Fu	1.4451; 1.4442	1.4422; 1.4439	1.4453; 1.4439	0.0; -6.4	-0.6 ;2.6	0.6; 5.8
Tetra-FuCH ₃	1.4452; 1.4444	1.4426; 1.4438	1.4455; 1.4439	0.0; -10.2	-1.4; 0.8	-0.6; 2.6
Tetra-FuCH ₂ X	1.4422; 1.4442	1.4441; 1.4440	1.4483; 1.4440	39.1; 52.4	23.4; 36.4	33.7; 28.2
Tetra-FuCHX ₂	1.4472; 1.4439	1.4462; 1.4442	1.4484; 1.4441	26.0; 41.4	20.4; 14.2	25.0; 35.8
Tetra-FuCX ₃	1.4471; 1.4446	1.4442; 1.4444	1.4463; 1.4442	-0.4; -5.6	2.6; 8.2	0.8; 10.4

R: bond length between an adjacent pair monomers ring of an extended chain. DR_i-R_j; dihedral angle between an adjacent pair monomers ring of an extended chain

Table 2: The total dipole moments (in Debye, m) of the CMF monomers and their oligomers obtained with B3LYP/6-31G* method

	Furan	FuCH ₃	FuCH ₂ Cl	FuCHCl ₂	FuCCl ₃
Monomer	0.46	0.69	1.72	2.04	3.35
Dimer	0.00	0.12	0.76	1.98	2.32
Trimer	0.61	0.74	1.85	2.56	3.65
Tetramer	0.00	0.17	1.33	3.42	4.33

Table 3: The wave lengths (λ) and oscillation strength (O.S) calculated for CMF monomers and their oligomers at ZINDO/S-CI

Oligomer	λ nm	O. S	Oligomer	λ nm	O. S	
Fu	154.77	1.107	Di-FuCCl ₃	187.77	0.531	
		226.08	0.254		302.83	0.626
FuCH ₃	161.08	0.962	Tri-Fu	176.52	0.539	
		232.25	0.212		268.66	0.128
FuCH ₂ Cl	161.21	0.889		347.16	0.814	
		230.20	0.228	Tri-FuCH ₃	178.37	0.708
FuCHCl ₂	153.50	0.345		271.08	0.131	
		159.62	0.250		351.68	0.786
		163.81	0.589	Tri-FuCH ₂ Cl	179.44	0.545
		231.24	0.223		273.04	0.136
FuCCl ₃	153.58	0.359		354.06	0.770	
		164.89	0.833	Tri-FuCHCl ₂	186.77	0.146
		232.22	0.225		247.87	0.359
Di-Fu	165.41	0.265		284.67	0.176	
		169.82	1.134		371.42	0.648
		300.59	0.635	Tri-FuCCl ₃	278.14	0.151
Di-FuCH ₃	169.76	0.272		362.66	0.637	
		176.03	1.136	Tetra-Fu	165.90	0.258
		306.91	0.608		249.70	0.425
Di-FuCH ₂ Cl	223.45	0.392		374.82	1.075	
		293.29	0.492	Tetra-FuCH ₃	302.71	0.102
		303.33	0.204		322.33	0.839
		329.83	0.180	Tetra-FuCH ₂ Cl	410.05	0.553
Di-FuCHCl ₂	168.89	0.365	Tetra-FuCHCl ₂	517.89	0.590	
		187.00	0.570	Tetra-FuCCl ₃	596.45	0.603
		305.37	0.602			

of the furan and methylfuran monomers are lower than that of monochloro-, dichloro- and trichloromethylfuran monomers; however the HLG values decrease slowly with the increase in number of chlorine atoms. Therefore, it is predicted that the oligomers consisting of Fu-CCl₃ monomer will have the highest conductivity. This is proved by comparing the trend of the HLG values of the CMF oligomers which have same number of monomers. As seen from Fig. 2, the HLG values for the Fu-CCl₃ tetramers are considerably lower than that of the other CMF tetramers.

Dipole moments of the oligomers

The orientation of the electric dipole moment vector (μ) of the oligomers with respect to the direction of the polymer chain determines electrochemical characteristics of the polymer on the electrode surface. In addition to their orientations, size of the electric dipole moment vector of the monomers and their interactions with the solvent and support electrolyte are the key factors in their selection for electropolymerization. Furthermore, the structure of the electrical double layer at the surface of electrodes which determines the kinetics of the diffusion-controlled electrode reactions depends on the dipole moment of the solute molecules^{14,17}. Thus, the calculated values of the electric dipole moment vectors for CMF monomers and their corresponding oligomers have

been listed in Table 2. The data presented in this table show that the number of halogen atom precisely chlorine determines the values of electric dipole moment vector. The comparative size of the dipole moment vectors for all of monomers and their oligomers with the same size follows: Fu-CH₂Cl < Fu-CHCl₂ < Fu-CCl₃

According to this trend, the oligomers consisting of Fu-CCl₃ oligomers are expected to be more soluble in polar solvents because of the larger electric dipole moments. Also, it is observed (Table 2) that the electron donor characters of the -CH₃ substituent decreases the dipole moment vector of the methylfuran oligomers, if the furan oligomers are taken as references as it was observed for fluoromethylpyrrole¹⁴.

UV-visible of the Oligomers

The electronic spectra involving transition of valence electrons that occur in the UV-vis absorption was studied theoretically, in order to investigate the effect of chlorine substituent on oligomethylfurans. Table 3 shows some selected absorption λ_{\max} and their oscillator strength for the oligomethylfurans. The oscillator strength values (O.S) showing the probability of the transition (corresponding to a fraction of negative charges (electrons) which accomplish the transition in question (oscillate). The λ_{\max} values for furan and

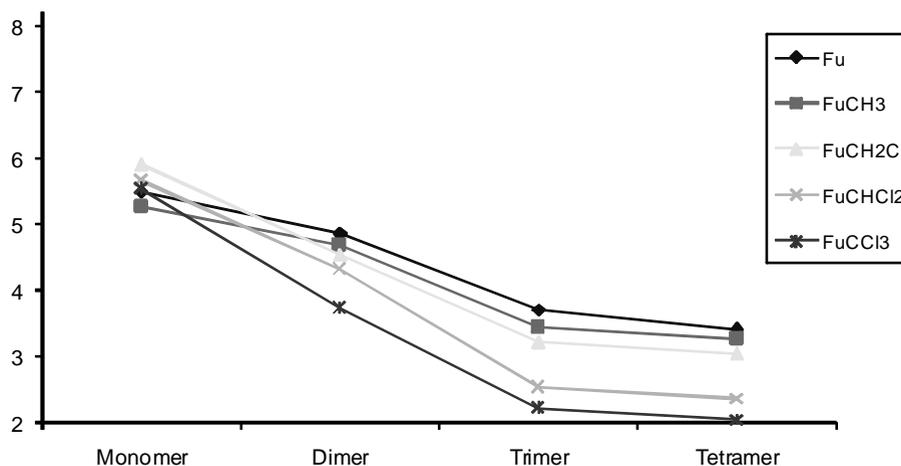


Fig. 2: The HLG values obtained for all CFM oligomersB3LYP/6-31G*

methylfuran monomers are 156.77 and 161.08nm respectively which show the electron donating effect of methyl group by shifting to longer wavelength, however this effect reduces as the number of chlorine atoms increases with increase in the chain length of the oligomers. The λ_{\max} values for chloro-, dichloro- and trichloromethylfuran monomers are 161.21, 163.81 and 164.89nm respectively, which show that the number of chlorine atoms on methylfuran affect the electronic properties of the polymer. It is noticed that with increasing chain length of the oligomers the λ_{\max} shift to a longer wavelength due to enlargement of p-conjugation in the systems. For example, the calculated λ_{\max} are 161.21, 293.29, 354.06 and 410.05nm, going from monomer, dimer, trimer to tetramer for chloromethylfuran (Table 3).

CONCLUSION

The results of this study show that the CMF oligomers can be regarded as the possible candidates for the synthesis of corresponding conducting polyfuran derivatives with improved properties as compared to the polymers of methylfuran and furan. In this series of CMF oligomers, the Py-CCl₃ oligomers have the higher capability as building blocks for conducting polymers because these oligomers have higher planarity, lower HLG values and higher dipole moment vectors, which are all in favor of electropolymerization. It is also found that the increase in the number of monomers of a CMF oligomer chain provides a better condition for modifying CMF polymers.

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