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ON THE STRUCTURAL EFFECTS OF THE HEAD-TO-TAIL COUPLED OLIGO(3-ALKYLTHIOPHENES) ON THEIR OPTICAL PROPERTIES

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In the memory of our colleague and friend Dr. Š. Pollák (*1945 – ✞2002)

Abstract. *The dependence of electronic spectra of unsubstituted and alkyl substituted α-bithiophenes on the mutual ring orientation was investigated by ZINDO/S method. The calculated λ_{max} values exhibit the uniform shape of the torsional dependence for all the systems under study (minima occur for perpendicular geometries and maxima are indicated for planar structures). However, the head-to-head couplings cause a sterically driven twist of thiophene rings resulting in a loss of conjugation. The dependence of the ZINDO/S calculated λ_{max} values as a function of the inverse number of thiophene units was evaluated and it has the linear character. Using the simple linear model we obtained the polymer limits of electron spectra for unsubstituted (500 nm) and methyl (539 nm), hexyl (433 nm), dodecyl (521 nm) head-to-tail substituted polythiophenes. The trends of our theoretical results agree with experimental data.*

Key words: *regiochemical coupling, alkylthiophenes, oligothiophenes, molecular engineering, optical spectra*

Introduction

Thiophene-based materials have received enormous attention due to their unusual electrical and optical properties [1,2] which are related to intramolecular delocalisation of π electrons. This dependence on the overlap extent between out-of-plane p orbitals (usually denoted as p_z) of the carbon atoms forming the inter-ring bonds and is therefore governed by the internal rotation around this bond. The degree of planarity directly determines the effective conjugation lengths.

Early preparations of polythiophene derivatives employed both electrochemical and chemical methods [3]. The thiophene rings coupled in the 2 and 5 positions allow the conjugation of the π orbitals along the polymer chain that leads to an electrical conductivity. The synthesis and development of chemically stable, soluble poly(3-alkylthiophenes) (PATs) was first reported by Elsenbaumer and co-workers [4]. PATs can readily be solution-processed into films that is desirable from the technological point of view.

The influence of the torsion angle along the chains on the electronic and geometric structures of the conjugated aromatic rings is very important [5,6]. Rotational defects are the most abundant types of irregularities which interrupt and weaken the extent of π conjugation in a polymer chain. A substitution pattern of polythiophene derivatives controls the degree of π conjugation between adjacent rings and hence the electrical and optical properties of the polymers [7,8]. The structure of the unsubstituted 2,2'-bithiophene (T2) is well-known in the vapour phase [9] (*anti-gauche* conformation with a torsional angle of 146°) and in the crystal [10] (*anti* planar conformation). NMR spectroscopy experiments show that both the *syn* and *anti* conformations co-exist at room temperature [11] with energy difference of ca 0.2 kcal/mol. For larger oligomers, the crystal structure data show an *all-anti* conformation [12-15], whereas in chloroform an *anti-gauche* conformation is found [15,16]. The characterisation of the torsional barrier in polythiophenes is far from satisfactory. It is assumed that both the delocalisation energy and the attractive intermolecular interactions favour a co-planar structure whereas, depending on the substitution pattern, the repulsive steric interactions can favour any conformation between 0 and 180° [17-19]. The dependence of photoluminiscence on the inter-ring angles in 2,2'-bithiophene derivatives has been proven experimentally [20]. High external pressure or temperature may be used as a tool to vary the magnitudes of these angles [21].

Potential functions representing the internal conversion between two reference isomers along a torsional variable θ may be expressed as [22]

$$E(\theta) = B_0 + \sum B_m \cos(m\theta) \tag{1}$$

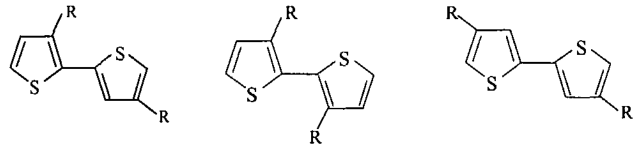
which is a simplified form of a truncated Fourier expansion [5,6]

$$E(\theta) = \sum V_m/2[1 + \cos(m\theta - \gamma_m)] \tag{2}$$

where E_m is the torsional energy barrier of the m-Fourier term for the rotation around the bond, γ_m is the phase angle of this term (usually considered equal to 0) and θ is the torsion angle [23]. Three lowest terms are sufficient for a reliable fit of double-well and double-barrier potential functions. Triple-barrier potentials have been reproduced by additional 4-fold [22] or 6-fold terms [5,6]. It is supposed [5,6] that the π conjugative interactions between the rings (which tend to keep the molecule planar) only contribute to the 2-fold term in the Fourier expansion, whereas the nonbonding interactions (between the groups attached to the different rings) contribute to all terms. The aim of this study is a deeper insight into the angular dependence of electron absorption spectra on the conformation and on the increasing number of the aromatic rings of unsubstituted (Tn) and methyl (Tn-CH_3), hexyl (Tn-C_6H_{13}) and dodecyl (Tn-$C_{12}H_{25}$) substituted α-oligothiophenes. This information may be useful for the estimation and understanding of the optical properties what is necessary for suggestion of suitable candidates for possible technological application.

Geometry Definitions and Calculation Methods

3-alkylthiophene is not a symmetrical molecule. There are three relative orientations when two thiophene rings are coupled in the 2- and 5- positions (see Figure 1). The first of these is 2,5' or head-to-tail coupling (HT), the second one is 2,2' or head-to-head coupling (HH), and the third one is 5,5' or tail-to-tail coupling (TT).



HT **HH** **TT**

R	Compound
H	T2
CH_3	T2–CH_3
C_6H_{13}	T2–C_6H_{13}
$C_{12}H_{25}$	T2–$C_{12}H_{25}$

Figure 1. The possible conformations of 3,3'-dialkylbithiophenes under study.

The ground-state geometry of selected molecules (see Figure 1) is optimised (at the Hartree-Fock level) using the standard semiempirical AM1 (Austin Model 1) method [23, 24] of the MOPAC 7.0 package [25] (energy cut-off of 10^{-5} kcal/mol, final RMS energy gradient under 0.01 kcal mol^{-1} L^{-1}). On the basis of the optimised geometries, the electronic spectra were calculated by standard semiempirical ZINDO/S method for single excitations from 10 highest occupied to 10 lowest unoccupied molecular orbitals at single level of theory using σ-σ and π-π overlap weighting factors of 1.3 and 0.6, respectively [26,27].

Results

Torsional dependences. To investigate the conformational energetics, ten bithiophene derivatives were modelled in the gas phase by AM1 methods. The torsional dependence of the total energy of the systems under study (Figure 1) indicates that the number of minima and maxima qualitatively corresponds to (scaled) cos(5Θ) function and no higher-order terms are necessary. Lower terms ($m < 5$) are responsible for scaling whereas the higher ones ($m > 5$) fit the numerical errors only. This conclusion is based on the results of fitting of the energy data according to eq. (1) with $m = 1 \rightarrow 5$, where the minimal standard deviations have been observed for T2, TT and HT conformations (see Tab. 1). The unfavourable HH couplings cause a sterically driven twist of thiophene rings resulting in a loss of conjugation. This is illustrated in Figure 2. On the other hand, TT couplings can easily access a low energy planar conformation, leading to highly conjugated polymers.

In the next step, we have investigated the dependence of the λ_{max} on the torsional angle Θ. This exhibits an uniform shape of the torsional dependence for all the systems under study (see Figure 3). In all cases, the minimum occurs for perpendicular geometries and the maxima are indicated for planar structures. The origin of the minimum might be explained from the natural reduction of the electronic delocalisation caused

Table 1. Calculated parameters, statistical characteristics and extrema positions of the total E energy torsional dependencies, $E = B_0 + B_1\cos\Theta + B_2\cos2\Theta + B_3\cos3\Theta + B_4\cos4\Theta + B_5\cos5\Theta$. (Parameters values in au. Standard deviation of parameters in parentheses).

	T2	T2-CH_3			T2-C_6H_{13}			T2-$C_{12}H_{25}$		
		HH	HT	TT	HH	HT	TT	HH	HT	TT
B_0	-1755.913(4)	-2312.5(6)	-2321.24(3)	-2322.140(4)	-5136.2(7)	-5138.50(3)	-5140.079(5)	-8508(2)	-8521.02(4)	-8523.024(5)
B_1	0.172(6)	14(1)	0.47(5)	0.185(5)	2(1)	1.02(5)	0.172(7)	21(4)	1.8(6)	0.172(7)
B_2	-0.125(6)	10.7(8)	0.12(4)	-0.095(5)	3(1)	0.92(5)	-0.100(8)	15(3)	1.41(6)	-0.083(8)
B_3	0.013(6)	6.8(5)	0.30(5)	0.008(6)	0.6(7)	0.49(5)	0.012(8)	9(2)	1.10(6)	0.024(8)
B_4	0.096(6)	2.6(2)	0.12(4)	0.099(5)	0.9(4)	0.58(5)	0.099(7)	4(1)	0.79(6)	0.105(7)
B_5	0.018(6)	0.94(7)	0.19(5)	0.019(5)	-0.3(1)	0.09(5)	0.016(7)	1.0(4)	0.35(6)	0.023(8)
Correlation coefficient R	0.997	0.999	0.980	0.997	0.996	0.993	0.998	0.986	0.995	0.995
Minima positions	41°, 154°	81°, 180°	45°, 180°	40°, 150°	70°, 129°	60°, 139°	40°, 150°	80°, 170°	60°, 160°	40°, 140°
Maxima positions	0°, 90°, 180°	0°, 135°	0°, 85°	0°, 85°, 180°	0°, 100°,180°	0°, 85°, 180°	0°, 85°, 180°	0°, 131°,180°	0°, 85°, 180°	0°, 85°, 180°

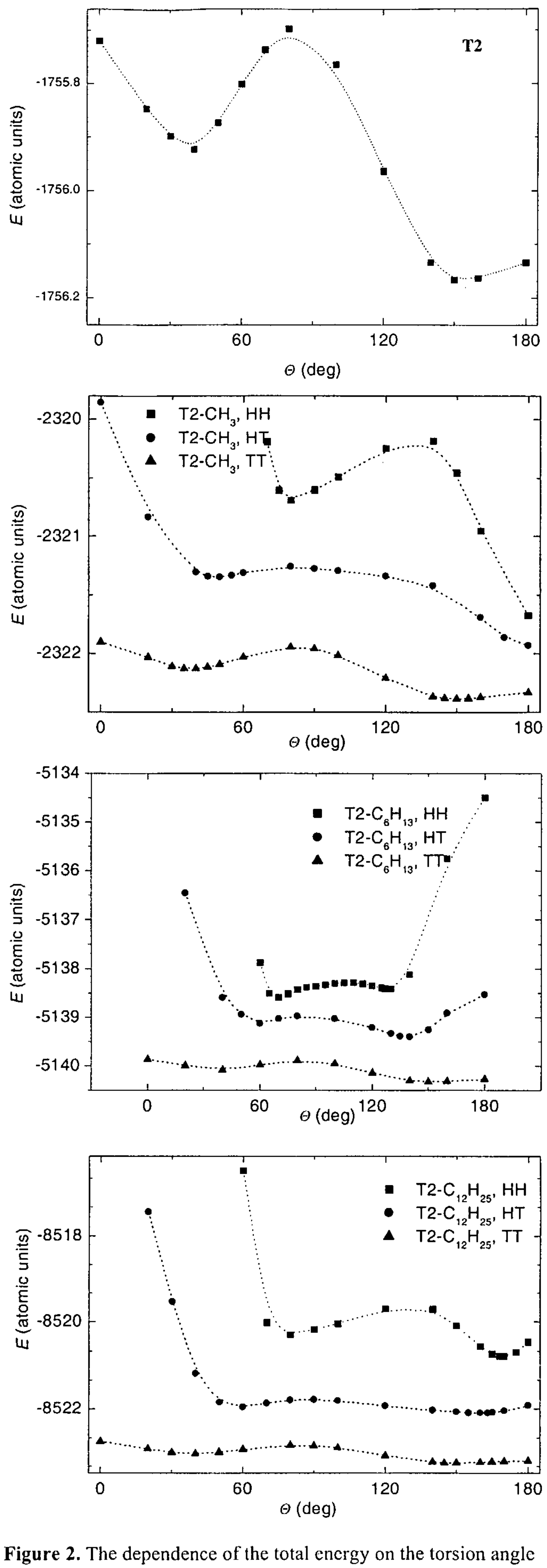


Figure 2. The dependence of the total energy on the torsion angle Θ of the systems under study.

by the thiophene rings twisting. Although the position of the maxima cannot be directly related to the total energy minima, the all-cis planar geometries for the HH conformation show about 18% greater values than the all-trans planar ones. The dependence on the mutual torsion orientation within the unsubstituted and HT, TT alkyloligothiophene conformers is vanishing (the data differ less than 2 %).

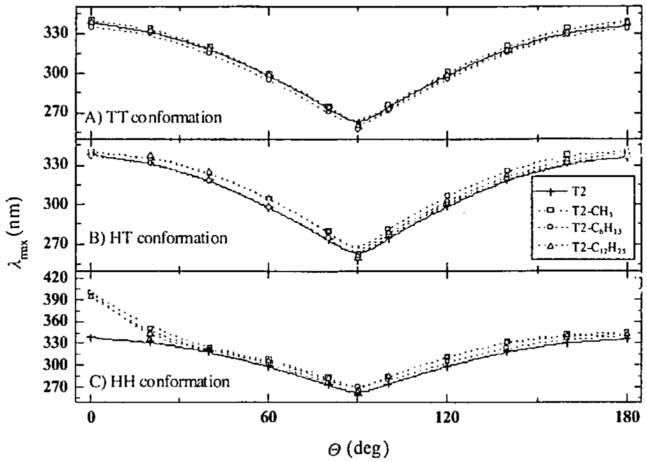
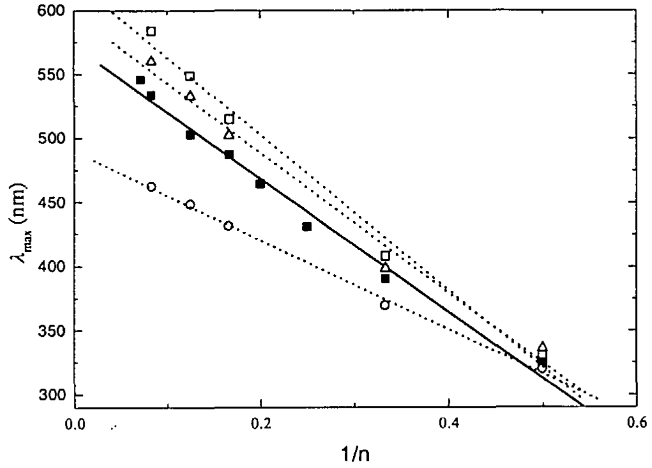


Figure 3. The dependence of the λ_{max} on the torsion angle Θ of the systems under study.

Chain length dependences. The evaluation of the ZINDO/S calculated λ_{max} as a function of the inverse of the number (n) of thiophene units (λ_{max} = A + B/n) can help us to estimate the limit values for the studied compounds. In this model, the inter-ring torsion angles are kept in optimal values (see Table 1). We have used the all-anti conformations, where the deviations of the neighbouring thiophene rings from planarity are in opposite orientations. The depicted dependencies are linear (see Figure 4) and the estimated theoretical polymer limits (n →∞) are 572 nm for T∞, 620 nm for T∞–CH$_3$, 490 for T∞–C$_6$H$_{13}$ and 598 nm for T∞–C$_{12}$H$_{25}$. We can see that the effect of the increasing side alkyl chains is not proportional. The minimal value of λ_{max} appears in the case of hexyl group while the red shift in relation to the T∞ compound is indicated for methyl and dodecyl groups. This trend agrees very well with experimental observations [3].

A direct comparison of our theoretical results with the published experimental ones is still problematic. Experiments depend on the temperature as well as the solvent used and vibronic contributions cannot be fully extracted from the readings. The experimental value represents the average of the contributions from all the possible conformers and the experimental error could affect the reading. Evaluation of the ZINDO/S calculated λ_{max} values (from Figure 5) as a function of the experimental data (oligothiophenes measured in tetrahydrofurane solutions [28]) represents the suitable compromise. The perfect linearity of this dependence (correlation coefficient R = 0.998) reveals the good agreement of our theoretical data with experimental ones [3]. In agreement with these results, we may extent our estimations to substituted systems. If we suppose the same slope (1.23 nm) and y-intercept (-43 nm) for the alkylsubstituted compounds, than the obtained corrected polymer limits are 500 nm for T∞, 539 nm for T∞–CH$_3$, 433 nm for T∞–C$_6$H$_{13}$, 521 nm for T∞–C$_{12}$H$_{25}$.



Linear Regression: $\lambda_{max} = A + B * (1/n)$

Comp.	Symbols	A (nm)	B (nm)	R
Tn	■	572 ± 6	-520 ± 20	-0.993
Tn-CH_3	□	620 ± 10	-600 ± 40	-0.995
Tn-C_6H_{13}	○	490 ± 3	-348 ± 10	-0.999
Tn-$C_{12}H_{25}$	△	598 ± 11	-546 ± 40	-0.993

Figure 4. The dependence of the ZINDO/S λ_{max} values of oligothiophenes as a function of the experimental data (in tetrahydrofurane solutions [28]). See also Figure 4 (solid squares).

Conclusions

We have analysed torsional dependence of AM1 energies of unsubstituted and alkylsubstituted bithiophene isomers in terms of Fourier expansion. The obtained parameters (and their relationships for individual quantities) can be used in the theoretical description as well as modelling of large oligomer or polymer structures and their physico-chemical properties. The evaluation of the ZINDO/S calculated λ_{max} as a function of the inverse number of thiophene units reveal the linear dependences. Using the simple model based on the relations between experimental and calculated quantities, we obtained the polymer limits of electron spectra for unsubstituted and head-to-tail substituted polythiophenes. Progress toward practical applications of these materials depends on the understanding of the basic chemistry and physics that govern the optimisation and stability of electronic and optical properties in organic conjugated polymers and on the development of new material syntheses.

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