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On the dependence of optical properties on conformational changes in oligothiophenes I. Electron absorption spectra

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Abstract

The geometries of 2,2'-bithiophene, 2,2':5',2''-terthiophene and 2,2:5',2'':5'',2'''-quaterthiophene molecules were optimized by using semiempirical AM1 method for fixed equidistant dihedral angles between neighboring thiophene rings. Corresponding electron spectra are calculated by semiempirical AM1 and ZINDO/S methods. The vibronic interaction between the low lying monoexcited electronic states is symmetry forbidden for any torsion coordinate in all planar oligothiophenes and similar compounds because these electron states are constructed from π molecular orbitals. Mutual orientation of torsion angles is not important for electronic structure of oligothiophenes. The dependence of maximal wavelength λ_{\max} on the torsion angle is of similar shape as its squared sine function. Using this dependence the torsional angles for some alkylated oligothiophenes in solution are estimated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oligothiophenes; Electron spectra; Torsional dependence; Conformations in solution

1. Introduction

Oligo- and polythiophenes are promising materials for a variety of applications in electronics and optoelectronics. They are unique for their high stability and non-linear optical properties. Whereas the polymers are obtained as highly amorphous materials, the oligomers can be synthesized as well defined compounds. Moreover, the oligothiophenes provide interesting models for understanding the structural and electronic peculiarities which control the charge transport and optical properties in polythiophenes [1,2].

Electrical and optical properties of thiophene chains are related with intramolecular delocalization of π electrons. This depends 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 about this bond. The degree of planarity directly determines the effective conjugation lengths [3].

Theoretical calculations can predict the preferred chain conformational structure at least in the gas phase. Electron diffraction study of the 2,2'-bithiophene molecule (T2) performed at 97–98°C in the gas phase has shown the coexistence of two conformations with the inter-ring torsion angles $\Theta \sim 148^\circ$ and $\Theta \sim 36^\circ$ with statistical weights of 56 and 44%, respectively. The *trans*-gauche conformation is 0.18 kcal mol⁻¹ more stable [4]. Whereas ab initio calculations using small basis sets (3-21G* and lower) indicate the planar conformations as the most stable [2,5–7], the use of sufficiently large basis sets with polarization functions enables the correct description of the qualitative nature of the torsion

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potential with *syn*-gauche and *anti*-gauche minima (the latter being more stable) and with *syn*, *anti* and orthogonal transition states at all levels of approximation [8–15]. Adding diffuse functions consistently lowers most of the potential curves whereas the relative energetics of the *syn* and *anti* conformations as well as the corresponding torsion angles are much less modified. MP2 and MP4 proved to be superior to all variants of DFT studied [14–17].

No experimental structure data are available on 2,2':5',2''-terthiophene (T3) and 2,2':5',2'':5'',2'''-quaterthiophene (T4) in the gas phase. Analogously to T2, ab initio calculations of T3 using STO-3G* and 3-21G* basis sets at SCF level indicate the all-*anti* planar conformation as the most stable one [18] whereas HF/6-31G* [19] and analogous DFT [20] calculations show the higher stability of non-planar conformation with similar torsion angles as in T2. The structures of T4 and higher oligomers have been calculated using semiempirical methods only [2,3,21–24]. It was found that internal rotational potentials obtained by semiempirical AM1 method are too flat but qualitatively in agreement with those found by the most advanced ab initio calculations. Semiempirical PM3 method does not give accurate conformations (wrong relative stabilities) and INDO method prefers planar conformations due to neglecting small steric interactions [3].

The situation in liquid and especially in solid-state systems is more complicated. The conformational potential curve of the chain may be separated into two terms: an intramolecular potential where steric repulsions and delocalization energy are taken into account and an intermolecular potential that involves all intermolecular forces between the chain and the environment. These three parameters depend upon the torsional angle between the adjacent rings. It is assumed that both the delocalization energy and the attractive intermolecular interactions favor a coplanar structure whereas, depending on the substitution pattern, the repulsive steric interactions can favor any conformation between 0 and 180°. The resulting overall conformational structure of the various oligothiophenes is determined by an energetic compromise between these three parameters [25–27].

NMR spectra [28,29] of bithiophene partially oriented in a nematic phase of a liquid crystalline solvent indicate the existence of two rotamers with

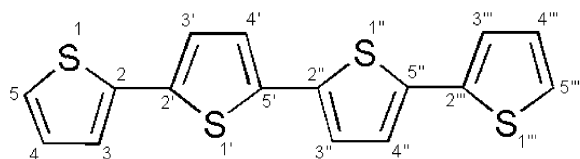
the *anti* structure more stable than the *syn* one by 0.2 kcal mol⁻¹ and separated by a barrier of 5 ± 2 kcal mol⁻¹. The relative concentration of the two isomers at room temperature is 64% *anti* to 36% *syn*. However, the observed absorption maxima in UV–Vis spectra are at 3.49 eV in the solid state and at 4.05 eV in the solution [30].

The first electronic transition of bithiophene absorption spectrum in the gas phase is centered at 34 600 cm⁻¹ with the shoulder at ~30 900 cm⁻¹ that has been assigned to the (0,0) electronic transition. An experimental evaluation of the gas phase transition energy can be done by measuring the absorption spectrum in a series of *n*-alkanes. The wavenumber of the absorption peak should vary linearly with the solvent polarizability function, $f = 2(n^2 - 1)/(2n^2 + 1)$ where *n* represents the solvent refractive index. From a good linear correlation of the above-mentioned electronic transition for bithiophene a value of 32 200 cm⁻¹ has been obtained at *n* = 1. This discrepancy might be explained by the conformational change between the gas phase and the solution. The dependence of ZINDO/S calculated electron spectra on the inter-ring torsion angle for AM1 optimized geometry gives a torsion angle close to 150° (30°) for the first and 140° (40°) for the latter (0,0) peak position [3,31].

Some studies [2,5,6] on the deviations from the oligothiophenes planarity (up to 30°) concluded no significant consequences on optical properties in real systems and postulated the use of (more simple) planar model systems for their description. We do not agree with this conclusion and the aim of this study is a deeper insight into the dependence of electron absorption spectra on the conformation of the oligothiophene chain. This information might be useful for the torsion angles estimation as the optimal conformation is much more influenced by the environment than the corresponding electron absorption spectra originating in π – π transitions.

2. Method

The standard semiempirical AM1 (Austin Model 1) method of quantum chemistry (AMPAC program package) [32–34] has been used in order to find the optimal geometries of neutral 2,2'-bithiophene (T2),



Scheme 1. The schematic structure of 2,2':5',2'':5'',2''':5'''-quaterthiophene.

2,2':5',2''-terthiophene (T3) and 2,2':5',2'':5'',2'''-quaterthiophene (T4 — see Scheme 1) molecules for fixed dihedral angles between neighboring thiophene rings. The dihedral angles were scanned with 15° steps. For these geometries electronic spectra (maximal wavelengths) are calculated by AM1 as well as by ZINDO/S method (using standard values of 1.267 and 0.585 for σ – σ and π – π overlap weighting factors, respectively) [35,36] for single excitations from 10 highest occupied to 10 lowest unoccupied molecular orbitals in SCI approximation.

3. Results and discussion

The atoms in T2, T3 and T4 molecules are

numbered according to Scheme 1. The inter-ring torsion angles are described by dihedral angles θ_1 (S(1)–C(2)–C(2')–S(1')) in T2, T3 and T4), θ_2 (S(1')–C(5')–C(2'')–S(1'')) in T3 and T4) and θ_3 (S(1'')–C(5'')–C(2''')–S(1''')) in T4). We may restrict to equal values for all the dihedral angles $\theta_1 = \theta_2 = \theta_3 = \theta$. The values of $\theta = 0^\circ$ and $\theta = 180^\circ$ correspond to all-*syn* and all-*anti* planar conformations, respectively. The remaining θ values correspond to non-planar structures. The deviations of the neighboring thiophene rings from planarity may be either of the same or opposite orientations. The independent linear combinations Q of individual torsions as well as the symmetries of individual conformations of the systems under study are presented in Table 1. It is evident that any torsion may be constructed as a linear combination of resulting Q coordinates.

As the C_2 axis is coincident with the Cartesian z coordinate, the planar conformers of C_{2v} and C_{2h} symmetries are positioned in xz and xy Cartesian planes, respectively [37]. Molecular π -orbitals must be antisymmetric to these planes (see Table 1 for their symmetries). As the main contributions to electron spectra originate in single electron excitations from several highest occupied π orbitals to several lowest

Table 1
Symmetry properties of the systems under study

Model system	Torsion coordinate Q definition	Conformation	Conformation point group	Torsion coordinate Q representation	π -MO representations	Monoexcited π -electron states representations
T2	θ_1	<i>Syn</i>	C_{2v}	a_2	a_2, b_2	A_1, B_1
		Non-planar	C_2	a	a, b	A, B
		<i>Anti</i>	C_{2h}	a_u	a_u, b_g	A_g, B_u
T3A	$\theta_1 + \theta_2$	All- <i>syn</i>	C_{2v}	a_2	a_2, b_2	A_1, B_1
		Non-planar	C_2	a	a, b	A, B
		All- <i>anti</i>	C_{2v}	a_2	a_2, b_2	A_1, B_1
T3B	$\theta_1 - \theta_2$	All- <i>syn</i>	C_{2v}	a_2	a_2, b_2	A_1, B_1
		Non-planar	C_s	a'	a', a''	A', A''
		All- <i>anti</i>	C_{2v}	a_2	a_2, b_2	A_1, B_1
T4A	$\theta_1 + \theta_2 + \theta_3$	All- <i>syn</i>	C_{2v}	a_2	a_2, b_2	A_1, B_1
		Non-planar	C_2	a	a, b	A, B
		All- <i>anti</i>	C_{2h}	a_u	a_u, b_g	A_g, B_u
T4B	$\theta_1 - \theta_2 + \theta_3$	All- <i>syn</i>	C_{2v}	a_2	a_2, b_2	A_1, B_1
		Non-planar	C_2	a	a, b	A, B
		All- <i>anti</i>	C_{2h}	a_u	a_u, b_g	A_g, B_u
T4C	$\theta_1 + \theta_2 - \theta_3$	All- <i>syn</i>	C_{2v}	$a_2 + b_2$	a_2, b_2	A_1, B_1
		Non-planar	C_1	a	a	A
		All- <i>anti</i>	C_{2h}	$a_u + b_g$	a_u, b_g	A_g, B_u

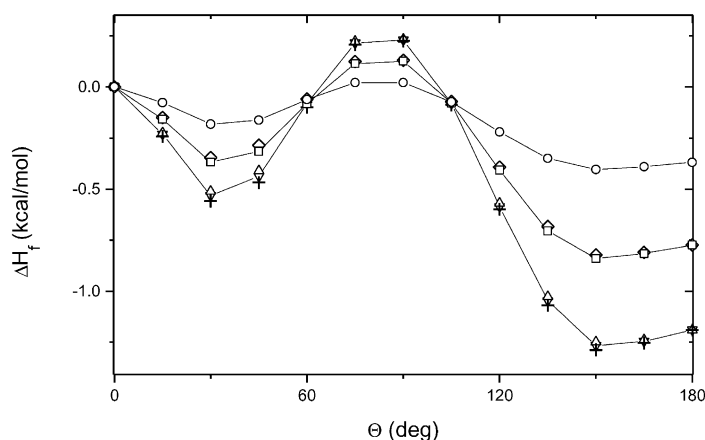


Fig. 1. The dependence of the relative heat of formation, $\Delta H_f = H_f(\Theta) - H_f(0)$, on the torsion angle Θ of T2 (circles), T3A (squares), T3B (diamonds), T4A (crosses), T4B (up triangles) and T4C (down triangles) systems.

unoccupied ones, the symmetries of corresponding excited electronic states (i.e. the direct product of their (irreducible) representations [37]) are presented in the last column of Table 1. Analogous two (and more) electron excitations, which may be constructed as direct products of the representations of these single electron excitations, span the same symmetries. The integrals describing the interaction of two electron states mediated by any operator of the vibration coordinate symmetry are necessarily zero unless the direct product of electron states representations spans the coordinate symmetry representation [37]. It is evident that the electron state symmetries as well as their products are different from the torsion coordinate Q symmetry for planar structures only. This means that the direct (1st order) vibronic interaction between the low lying monoexcited electronic states is symmetry forbidden for any torsion coordinate in all planar oligothiophenes and similar compounds because these electronic states are constructed from π molecular orbitals. This restriction is removed in non-planar structures. It may be supposed that the vibronic interaction increases with the deviation from planarity. These conclusions are important for relaxation processes in excited electronic states.

Fig. 1 illustrates the shape of AM1 inter-ring torsional potential in the systems under study. Our results confirmed that it is qualitatively the same for all the systems under study (independent on the symmetry of torsion coordinate Q). The maximal

energy differences between individual torsional systems corresponding to the same molecule (T3A and T3B as well as T4A, T4B and T4C) are negligibly small in comparison with the differences between individual oligothiophenes (T2, T3, T4).

Electron spectra of oligothiophenes are usually calculated by semiempirical ZINDO/S method [1–3,31]. Due to its parametrization (for planar conjugated compounds) as well as other approximations, it might work less well for non-planar structures. On the other hand, ab initio treatment may produce reliable spectral data using large basis sets and huge multi-configurational treatment only. Consequently, only few data of this type are known for oligothiophenes. Using multiconfigurational second-order perturbation theory (CASPT2) and a basis set of ANO type, with split valence quality and including polarization functions, the first singlet-singlet excitation of *trans* 2,2'-bithiophene is 3.88 eV for the planar and 4.36 eV for the twisted (with inter-ring angle of 38°) geometry, respectively [38]. Analogous calculations for planar 2,2':5',2''-terthiophenes [39] estimate this transition to 2.86 eV.

As a consequence of great computational requirements of above-mentioned ab initio calculations and shortages of ZINDO/S treatments, the AM1 method represents a reasonable compromise for the study of the torsional dependence of electron spectra (despite missing spectral parameterization). The dependence of the maximal wavelengths calculated by ZINDO/S

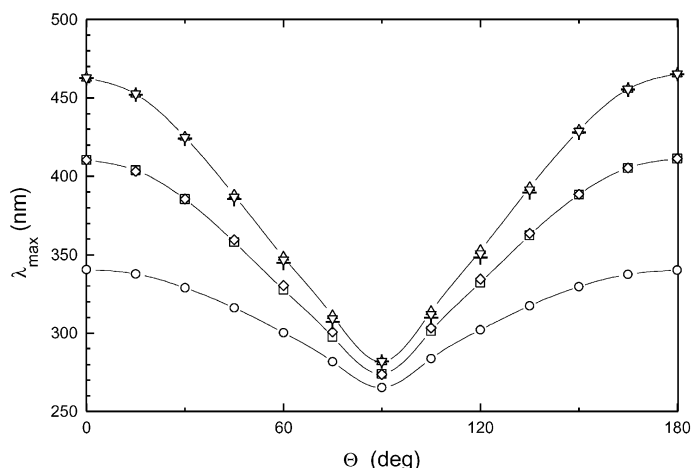


Fig. 2. The dependence of the λ_{\max} wavelength obtained by ZINDO/S method on the torsion angle Θ of T2 (circles), T3A (squares), T3B (diamonds), T4A (crosses), T4B (up triangles) and T4C (down triangles) systems.

and AM1 methods on Θ torsion is shown in Figs. 2 and 3 for all the systems under study. It is evident that there are only small differences between Θ and $180^\circ - \Theta$ torsions in all the systems under study. Vanishing differences between various torsional systems corresponding to the same molecule (T3A and T3B as well as T4A, T4B and T4C) indicate that mutual torsion orientation (but not its magnitude) of individual thiophene rings cannot be deduced from real electron absorption spectra. The calculated curves have similar shape as the sine function (or its n -th power). The results of the simplest binomial regres-

sion (with minimal number of parameters)

$$\lambda_{\max} = A - B(\sin \Theta)^n \quad (1)$$

where A corresponds to the (averaged) λ_{\max} value for planar conformations and B to its (negative) correction for the perpendicular ones, are shown in Table 2 (ZINDO/S data) and Table 3 (AM1 data). According to the statistical characteristics presented, the optimal power value in Eq. (1) is between $n = 3$ (ZINDO/S data) and $n = 2$ (AM1 data). As there are no significant differences in standard deviations and AM1 method is more accomplished, we can use the squared

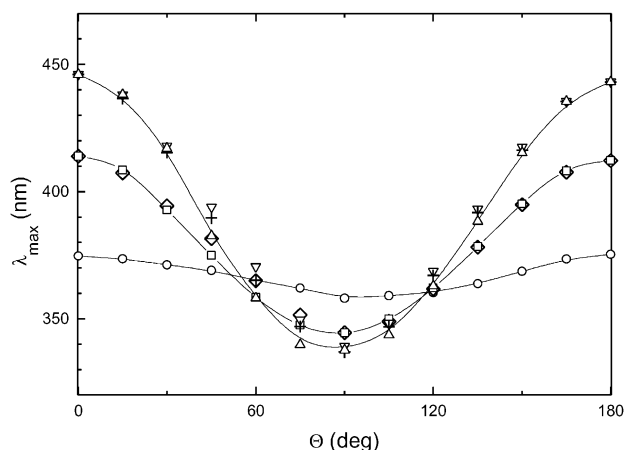


Fig. 3. The dependence of the λ_{\max} wavelength obtained by AM1 method on the torsion angle Θ of T2 (circles), T3A (squares), T3B (diamonds), T4A (crosses), T4B (up triangles) and T4C (down triangles) systems.

Table 2

The values of parameters of $\lambda_{\max} = A - B(\sin \Theta)^n$ expansion (see Fig. 2) obtained by ZINDO/S method

System	n	A (nm)	B (nm)	R -squared	Standard deviation (nm)
T2	1	353.1 ± 6.0	63.6 ± 8.8	0.82692	11.0
	2	343.9 ± 2.6	64.9 ± 4.4	0.95267	5.7
	3	339.5 ± 1.4	65.4 ± 2.7	0.98165	3.6
	4	336.8 ± 1.4	66.0 ± 2.7	0.98166	3.6
T3A	1	429.6 ± 9.8	120.0 ± 15.0	0.85907	18.0
	2	415.3 ± 3.6	121.4 ± 6.2	0.97214	8.2
	3	406.8 ± 2.2	121.6 ± 4.2	0.98724	5.5
	4	401.4 ± 2.9	122.0 ± 5.7	0.97634	7.5
T3B	1	430.1 ± 9.8	123.0 ± 14.0	0.86857	18.0
	2	415.4 ± 3.3	123.8 ± 5.7	0.97743	7.5
	3	406.8 ± 2.0	123.7 ± 5.7	0.99022	4.9
	4	401.2 ± 2.9	124.0 ± 5.8	0.97686	7.6
T4A	1	488.0 ± 12.0	169.0 ± 17.0	0.89560	22.0
	2	467.5 ± 3.2	168.3 ± 5.4	0.98895	7.1
	3	455.3 ± 2.8	167.2 ± 5.2	0.98937	6.9
	4	447.5 ± 4.7	166.8 ± 9.3	0.96682	12.0
T4B	1	488.0 ± 12.0	170.0 ± 17.0	0.89977	21.0
	2	454.8 ± 2.9	170.0 ± 4.9	0.99106	6.4
	3	454.8 ± 2.8	168.7 ± 5.2	0.98951	6.9
	4	446.9 ± 4.8	168.1 ± 9.6	0.96529	13.0
T4C	1	488.0 ± 12.0	167.0 ± 18.0	0.89138	22.0
	2	467.7 ± 3.4	166.8 ± 5.9	0.98661	7.7
	3	455.7 ± 2.8	165.9 ± 5.2	0.98893	7.0
	4	448.0 ± 4.6	165.6 ± 9.1	0.96804	12.0

Table 3

The values of parameters of $\lambda_{\max} = A - B(\sin \Theta)^n$ expansion (see Fig. 3) obtained by AM1 method

System	n	A (nm)	B (nm)	R -squared	Standard deviation (nm)
T2	1	376.6 ± 1.4	15.6 ± 2.1	0.83180	2.6
	2	374.5 ± 1.0	15.2 ± 1.7	0.87603	2.3
	3	373.4 ± 1.0	14.9 ± 1.9	0.88718	2.5
T3A	1	421.6 ± 3.6	70.4 ± 5.2	0.94286	6.5
	2	412.24 ± 0.73	68.8 ± 1.2	0.99648	1.6
	3	406.8 ± 2.1	67.3 ± 3.8	0.96535	5.1
T3B	1	422.2 ± 3.9	68.9 ± 5.7	0.92881	7.2
	2	413.26 ± 0.80	67.7 ± 1.4	0.99527	1.9
	3	407.3 ± 1.6	65.5 ± 3.1	0.97636	4.1
T4A	1	458.4 ± 5.7	112.1 ± 8.4	0.94175	11.
	2	443.5 ± 1.2	109.5 ± 2.1	0.99596	2.8
	3	434.8 ± 3.4	107.0 ± 6.2	0.96387	8.3
T4B	1	457.6 ± 5.8	103.8 ± 8.5	0.93128	11.0
	2	444.09 ± 0.74	102.1 ± 1.3	0.99832	1.7
	3	436.3 ± 2.4	100.5 ± 4.4	0.97929	5.8
T4C	1	457.4 ± 5.6	106.6 ± 8.2	0.92177	8.2
	2	443.35 ± 0.68	104.4 ± 1.1	0.99868	6.7
	3	435.3 ± 2.7	102.4 ± 5.0	0.94175	6.7

Table 4

Maximal wavelength values of alkylated oligothiophenes measured in CHCl_3 solution [1], λ_{exp} , as well as calculated by ZINDO/S and AM1 methods, λ_{calc} , in the estimated conformations (see text for the discussion of $\Theta_1 = \text{S}(1)-\text{C}(2)-\text{C}(2')-\text{S}(1')$, $\Theta_2 = \text{S}(1')-\text{C}(5')-\text{C}(2'')-\text{S}(1'')$ and $\Theta_3 = \text{S}(1'')-\text{C}(5'')-\text{C}(2''')-\text{S}(1''')$ torsion angles)

Code	Compound	λ_{exp} (nm)	Θ_i angles		λ_{calc} (nm)	
			Assumed	Estimated	ZINDO	AM1
Bithiophenes						
T2	2,2'-Bithiophene	302		$\Theta_1 = 148 - 155^\circ$	328–333	368–371
T2m1	3-Methyl-2,2'-bithiophene	299		$\Theta_1 = 147 - 151^\circ$	335–337	375–376
T2m2	4-Methyl-2,2'-bithiophene	309	$\Theta_1 = 180 \pm 15^\circ$		339–342	373–375
T2m3	3,3'-Dimethyl-2,2'-bithiophene	270	$\Theta_1 = 90 \pm 15^\circ$		269–297	324–320
		268				
T2m4	4,4'-Dimethyl-2,2'-bithiophene	310	$\Theta_1 = 180 \pm 15^\circ$		340–343	373–374
		311				
T2m5	3,4'-Dimethyl-2,2'-bithiophene	302		$\Theta_1 = 144 - 155^\circ$	333–340	373–376
		299				
T2e1	3-Ethyl-2,2'-bithiophene	295		$\Theta_1 = 141 - 145^\circ$	332–335	371–373
T2e2	3,3'-Diethyl-2,2'-bithiophene	279		$\Theta_1 = 113 - 135^\circ$	309–335	365–376
T2h1	3,3'-Dihexyl-2,2'-bithiophene	270	$\Theta_1 = 90 \pm 15^\circ$		267–293	313–318
T2h2	3,4'-Dihexyl-2,2'-bithiophene	298		$\Theta_1 = 142 - 149^\circ$	322–327	357–359
T2h3	4,4'-Dihexyl-2,2'-bithiophene	310	$\Theta_1 = 180 \pm 15^\circ$		337–340	363–365
Terthiophenes						
T3	2,2':5',2''-Terthiophene	355	$\Theta_1 = \Theta_2$	$\Theta_1 = 151 - 160^\circ$	390–400	396–403
T3m1	3,3''-Dimethyl-2,2':5',2''-terthiophene	344	$\Theta_1 = \Theta_2 = 150^\circ$		402	414
T3m2	3,4',3''-Trimethyl-2,2':5',2''-terthiophene	324	$\Theta_2 = 90 \pm 15^\circ$	$\Theta_1 = 157 - 166^\circ$	356–367	376–381
T3b1	3',4'-Dibutyl-2,2':5',2''-terthiophene	350	$\Theta_1 = \Theta_2$	$\Theta_1 = 151 - 160^\circ$	394–403	404–411
T3e1	4'-ethyl-3,3''-Dimethyl-2,2':5',2''-terthiophene	321	$\Theta_2 = 90 \pm 15^\circ$	$\Theta_1 = 151 - 159^\circ$	353–366	373–397
T3h1	4,4',3''-Trihexyl-2,2':5',2''-terthiophene	326	$\Theta_1 = 180 \pm 15^\circ$		352–362	363–368
			$\Theta_2 = 90 \pm 15^\circ$			
T3h2	3,4',3''-Trihexyl-2,2':5',2''-terthiophene	316	$\Theta_2 = 90 \pm 15^\circ$	$\Theta_1 = 141 - 150^\circ$	348–362	365–387
T3h3	4,4',4''-Trihexyl-2,2':5',2''-terthiophene	348	$\Theta_1 = 180 \pm 15^\circ$	$\Theta_2 = 137 - 142^\circ$	392–395	388–391
Quaterthiophenes						
T4	2,2':5',2'':5'',2'''-Quaterthiophene	390	$\Theta_1 = \Theta_2 = \Theta_3 = 150 - 160^\circ$		427–445	415–428
T4m1	4',3''-Dimethyl-2,2':5',2'':5'',2'''-quaterthiophene	348	$\Theta_1 = \Theta_3$	$\Theta_1 = 133 - 137^\circ$	346–363	369–378
		346	$\Theta_2 = 90 \pm 15^\circ$			
T4m2	3,3',4'',3'''-Tetramethyl-2,2':5',2'':5'',2'''-quaterthiophene	346	$\Theta_1 = \Theta_3 = 90 \pm 15^\circ$	$\Theta_2 = 159 - 180^\circ$	366–384	378–390
T4m3	4,4',3'',4'''-Tetramethyl-2,2':5',2'':5'',2'''-quaterthiophene	348	$\Theta_1 = \Theta_3$	$\Theta_1 = 133 - 137^\circ$	344–364	375–380
			$\Theta_2 = 90 \pm 15^\circ$			

sine function in our studies. Using the above mentioned ab initio data for bithiophene [38], we obtain $A = 320$ nm and $B = 92$ nm. This is in better agreement with ZINDO/S than with AM1 data (see Tables 2 and 3).

A common way [3] to judge the theoretical transition energies calculated by semiempirical ZINDO/S method is to compare the calculations with the

absorption band maximum in a non-polar solvent. This method uses the implicit (but not fully correct) assumption that the solvatochromic shift in the solvent compared to the gas phase is approximately equal to the difference in energy between the maximum and the (0,0) peak positions [3]. In bithiophene, however, these differences correspond to 1500 cm^{-1} (*n*-hexane solution) and

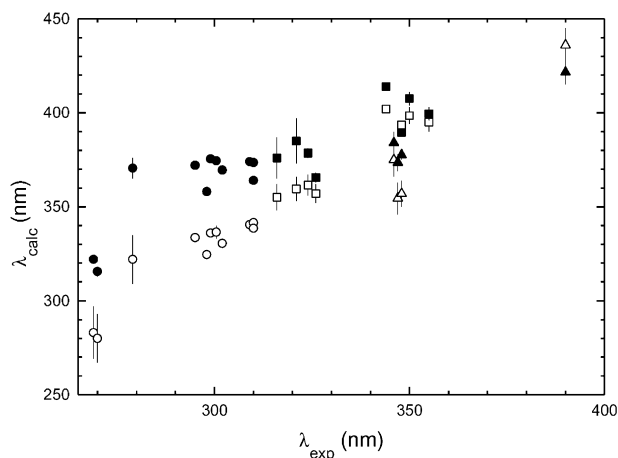


Fig. 4. The relation between maximal wavelengths, λ_{calc} , obtained by ZINDO/S (open symbols) and AM1 methods (full symbols) for the estimated conformations of alkylated bithiophenes (circles), terthiophenes (squares) and quaterthiophenes (triangles), respectively, and the corresponding values measured in CHCl_3 solution [1], λ_{exp} (see Table 4).

about 3000 cm^{-1} , respectively. This discrepancy should significantly affect the torsion angle evaluation ($\sim 125^\circ$). We propose another treatment to the torsion angles estimation where the above assumption is fulfilled because all the molecules studied are in the same solvent. We assume a vanishing influence of alkyl chains on π electrons of thiophene rings (very well fulfilled for β -alkylated oligothiophenes [1]). We do not suppose that a solvent shift equals to the difference between the vertical and adiabatic transition energy of the chromophore. We assume a similar dependence of both these quantities on the mutual chromophores orientation only. As a consequence, the parameters of Eq. (1) obtained from quantum-chemical calculations and experimental spectra should be different not only due to the solvent effect.

A series of geometry optimizations was carried out on alkyl-substituted bithiophenes [3,10,11,40,41] and terthiophenes [19,42]. The ground-state conformations are predicted to be quite independent of the alkyl chain length. A nearly planar ground-state conformation ($\theta = 180 \pm 15^\circ$) is predicted for 4,4'-dialkyl-2,2'-bithiophene while in 3,3'-coupled isomers, the thiophene rings are nearly perpendicular ($\theta = 90 \pm 15^\circ$). When comparing the data for T2m3 (nearly perpendicular) and T2m4 (nearly planar) in Table 4, we may estimate the parameters of Eq. (1): A is between 310 and 313 nm and B between 40 and

46 nm. Almost the same λ_{exp} values for T2m4, T2h3 and T2m2 compounds indicate not only the (quasi)-planarity of their backbone but also the transferability of A and B parameters to all β -alkylated bithiophenes. The same holds for (quasi)perpendicular T2m3 and T2h1 compounds (due to significantly different λ_{exp} , no perpendicularity for T2e2 is supposed). Using this parameters, we obtain the torsion angle values for T2 and its remaining alkylated derivatives that are presented in Table 4 (only trans isomers are presented).

In agreement with our theoretical results, we may extent our estimations to higher oligothiophenes but with lower accuracy. We suppose the same parameters values for all inter-ring torsions within the molecule (compare A and B values for various conformations of the same molecule in Tables 2 and 3) and arithmetic averaged squared sines. Suppose nearly planar and perpendicular thiophene pairs in T3h1 and $\theta_1 = \theta_2 = 150^\circ$ in T3m1, we obtain A between 360 and 365 nm and B between 63 and 83 nm for terthiophenes. Assuming equal torsion angles in the molecule, we obtain the θ_i values for T3 and T3b1 (see Table 4). Under (quasi)planarity or (quasi)perpendicularity assumptions we obtain the remaining torsion angle values for T3e1, T3h2 and T3h3 (see Table 4).

As λ_{exp} values for T4m1, T4m2 and T4m3 are practically the same, the equal values of averaged squared

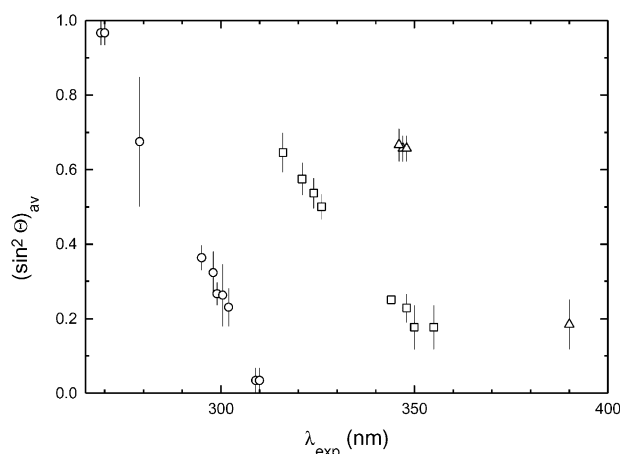


Fig. 5. The relation between the averaged values of $\sin^2\theta$ torsions for the estimated conformations of alkylated bithiophenes (circles), terthiophenes (squares) and quaterthiophenes (triangles), respectively, and the corresponding maximal wavelengths measured in CHCl_3 solution [1], λ_{exp} (see Table 4).

sines may be supposed for these compounds. For (quasi)perpendicular pairs of side rings in T3m2 ($\theta_1 = \theta_3 = 90 \pm 15^\circ$) the minimal values of $\sin^2\theta_2$ imply the central torsion angle value between 159 and 180° . The torsion angles obtained under appropriate (quasi)perpendicularity assumptions and the same averaged squared sine value for all these compounds are presented in Table 4. Supposing equal torsion angles between 150 and 160° in T4, we obtain the A value between 399 and 419 nm whereas the B one is between 76 and 116 nm.

Maximal wavelengths calculated by ZINDO/S and AM1 methods are presented in the last two columns of Table 4. Their correlation with experimental values (Fig. 4) corresponds to a nearly linear function. Significant deviations in systems with (quasi)perpendicular thiophene rings might be explained by problematic assignment of corresponding lines in the calculated spectra (vanishing oscillator strengths at higher wavelengths). Very good correlation between the averaged squared sine of estimated torsion angles (Fig. 5) and experimental wavelengths indicate that our treatment might produce reliable data on the geometries of alkylated oligothiophenes in solutions. The discrepancy between [3] and our results on T2 geometry might be ascribed to lower reliability of ZINDO/S method for non-planar structures. Nevertheless, further refinement of our assumptions as well as

of the sine function used is desirable. Very precise high level ab initio calculations of molecules in polar environment are necessary for this purpose.

Finally, it may be concluded that the inter-ring torsion plays an important role in oligothiophene chains. Their non-planar conformations are present in the gas phase as well as in the solution. Restricting to planar structures may lead to serious errors in the relaxation processes study. Mutual orientation of torsion angles is much less important for the electronic structure of oligothiophenes. Their electron spectra depend on the nearly squared sine function of the torsion magnitude independent on its orientation. This may be used for the torsion angle estimation. Nevertheless, this problem demands more exhaustive theoretical studies. In the next articles of this series, the non-linear optical properties of oligothiophenes will be studied in more details.

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