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A THEORETICAL STUDY OF 2- AND 3-ARYLBENZO[B]THIOPHENES. EVIDENCE OF AN INTRAMOLECULAR CHARGE TRANSFER STATE IN 3-α-NAPHTHYLBENZO[B]THIOPHENE§

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Abstract - PPP (LCI-SCF-MO) calculations were used to study the models of benzo[b]thiophene (1), 2-phenylbenzo[b]thiophene (2), 3-phenylbenzo[b]thiophene (3), 2-α-naphthylbenzo[b]thiophene (4), and 3-α-naphthylbenzo[b]thiophene (5). The results of the calculations were used to interpret the electronic absorption and fluorescence spectra of these compounds, to discuss their ground- and excited-state geometry, and to provide support for the existence of an intramolecular charge transfer state in 5, with a geometry different from that of the ground state.

INTRODUCTION

Within the framework of our systematic studies of photoreactions of benzo[b]furans, benzo[b]thiophenes, and their derivatives, we have investigated their photoaddition, photodimerization, and photocyclization reactions in the presence of aliphatic amines.[1-6] Recently, we have studied the photochemical behavior of four aryl derivatives of benzo[b]thiophene (1), *viz.*, 2-phenylbenzo[b]thiophene (2), 3-phenylbenzo[b]thiophene (3), 2-α-naphthylbenzo[b]thiophene (4), and 3-α-naphthylbenzo[b]thiophene (5).[7,8] Photophysical interactions between the arylbenzo[b]thiophenes 2-5 and tertiary amines have been found to lead to the formation of exciplexes in solvents of low dielectric constant.[9] Among these four substrates, 3-α-naphthylbenzo[b]thiophene (5) exhibits a rather unusual photochemical behavior. In contrast to 2-4, it is the only compound which gives photoaddition with primary aliphatic amines leading to the photoproduct 6 which

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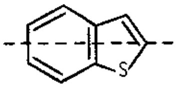

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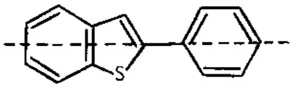

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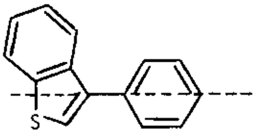

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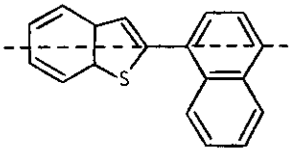

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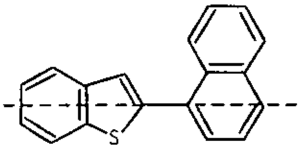

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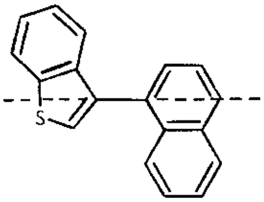

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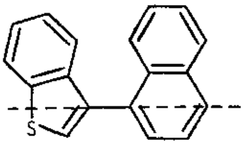
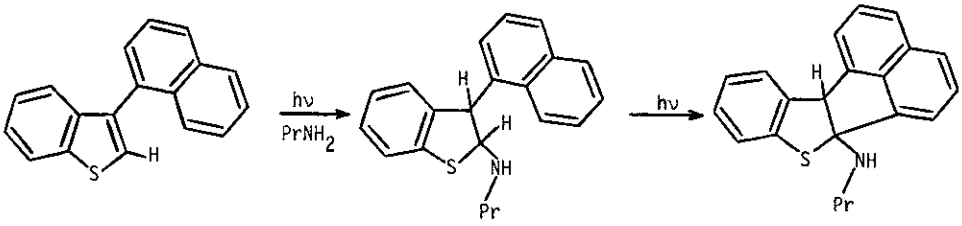


5, Geometry II

then undergoes further photocyclization with the formation of the final product **7** (Scheme 1).[7,8]



5 **6** **7**

Scheme 1

The results obtained in a study of the fluorescent exciolexes of these substrates with tertiary aliphatic amines also indicate that compound **5** behaves differently and that it should possess a substantially increased dipole moment in its first excited singlet state.[9] This difference in the behavior of **5** was explained on the basis of the existence of an intramolecular charge transfer (ICT) state inferred for this compound.[9] In other recently studied aromatic systems, twisted internal charge transfer (TICT) states have been postulated.[10,11] The increase of the dipole moment in the excited state of 5 would be caused by an intramolecular charge transfer between the benzo[b]thienyl and the α-naphthyl portions of the molecule and related to a change of the twist angle between them. In the present paper we wish to report the PPP calculations on these systems and a comparison of the theory with the experimental electronic spectral data for 1-5. Furthermore, it will be shown that the results obtained in this study provide additional supporting evidence for the existence of an ICT state in 3-α-naphthylbenzo[b]thiophene (5).

RESULTS AND DISCUSSION

Calculations. The PPP (LCI-SCF-MO) calculations were carried out in the usual manner using sets of parameters for carbon and sulfur employed in our previous work[12] (Table 1). The results of the calculations include the transition energies, oscillator strengths, directions of the transition moments, and the predominant configurations involved in a particular transition, both for the singlet and triplet excited states.[13]

Two different conformations were used in the calculations of the naphthyl derivatives 4 and 5 and they are indicated in their respective formulas as Geometry I and Geometry II. Because of different steric hindrances in compounds 2-5, their equilibrium molecular geometries in the ground state and in the first excited singlet state can be expected to be different. The twist angle θ (torsional angle) which is the angle of internal rotation about the C(benzo[b]thienyl)-C-(aryl) bond in the molecule (which is formally represented as a single bond in the Kekulé structures) can be included in the calculation using a previously published formula (see Experimental).[11,14] The best equilibrium geometries for the ground and excited states can then be determined by comparison of a series of calculations carried out for various angles θ with the electronic spectral data.

Table 1. Parameters Used in PPP Calculations (in eV)[a]

Atom, μ	I_μ	A_μ	$\gamma_{\mu\mu}$	Z_μ	$\beta_{C-\mu}$
C	11.22	0.69	10.53	1	-2.318
S	20.27	10.47	9.80	2	-1.623

[a] For explanation of the symbols, see the text (Experimental, Calculations).

It is interesting to note that, according to the calculations, the contributions from the 1,-1 and 2,-1 transitions are reversed in the case of benzo[b]thiophene (1), i.e., the predominant configuration in the first transition is 2,-1. Another interesting result is that, for some geometries, the second transition in 2-α-naphthylbenzo[*b*]thiophene (**4**) and in 3-α-naphthylbenzo[*b*]thiophene (**5**) is a forbidden transition.

In 3-α-naphthylbenzo[*b*]thiophene (**5**), the wave function of the first excited singlet state assumes an almost nonbonding character on the carbon atoms 2-3 (in the benzo[*b*]thiophene portion of the molecule) on which the addition in the photochemical reaction takes place, whereas the same bond retains its bonding character in 2-α-naphthylbenzo[*b*]thiophene (**4**).^{13} This, of course, can be relevant to the different chemistry of compound **5** in its first excited singlet state as compared to compound **4**.

Spectra. The first experimental absorption and emission (fluorescence) bands of the five compounds under study (**1**-**5**) in hexane and the corresponding calculated positions of the 0-0 bands are presented in Table 2. Also, as an example, the absorption and fluorescence spectra of 3-α-naphthylbenzo[*b*]thiophene (**5**) are shown in Fig. 1 along with the calculated transitions and their intensities.

When comparing the spectra with the calculated transition energies, it is important to remember that the latter correspond to vertical transitions. It can be seen that the electronic absorption spectrum of 3-phenylbenzo[*b*]thiophene (**3**) resembles that of the unsubstituted benzo[*b*]thiophene (**1**) itself.^{16} This is due to the steric interaction between the *o*-hydrogens of the phenyl group and the H-4 in the benzo[*b*]thiophene moiety which prevents complete conjugation of the phenyl group with the rest of the molecule,^{17,18} even if **3** is essentially planar. A similar situation is observed with 3-α-naphthylbenzo[*b*]thiophene (**5**). On the other hand, such steric effects are absent in 2-phenybenzo[*b*]thiophene (**2**) and 2-α-naphthylbenzo[*b*]thiophene (**4**) and, indeed, their spectra are considerably different from that of benzo[*b*]thiophene (**1**).$^{17-19}$

A comparison of the experimental absorption and fluorescence bands with the calculations carried out for different twist angles θ varied from 0° to 90° (see Experimental) indicates that both phenyl derivatives are essentially planar ($\theta = 0^\circ$) or close to planar both in the ground and in the first excited singlet states. On the other hand, in the case of 2-α-naphthylbenzo[*b*]thiophene (**4**) the best fit for the ground state is obtained for $\theta = 75^\circ$ and in the case of 3-α-naphthylbenzo[*b*]thiophene (**5**) for $\theta = 60^\circ$, determined on the basis of their electronic absorption spectra. Both molecules appear to be essentially planar in their first excited singlet state ($\theta = 0^\circ$), based on a comparison of the calculated quantities with the experimental fluorescence spectra. This result is similar to that obtained for 1-phenylnaphthalene and 2-phenylnaphthalene, where both molecules were found to be nonplanar in the ground state ($\theta = 50^\circ$ and 23°, respectively), whereas the twist angle for 1-phenylnaphthalene was smaller in the first excited

Table 2. Experimental and Calculated First Electronic Transitions for the Benzo[b]thiophenes 1-5

No.	Compound	Experimental[a]			Calculated		τ_0[b]
		λ_{max}, nm	$\tilde{\nu}$, kK	log ε	$\tilde{\nu}$, kK	log f	
1	Benzo[b]thiophene	300[c]	33.33	-	34.94	-1.463	-
		298[d]	33.60	3.53	34.94	-1.463	
2	2-Phenylbenzo[b]-thiophene[e]	327[c]	30.58	-	31.52	0.060	1
		318 sh	31.45	4.17	31.52	0.060	
3	3-Phenylbenzo[b]-thiophene[e]	334[c]	29.94	-	34.04	-0.393	2.6
		302	33.11	3.82	34.04	-0.393	
		293	34.13	3.82			
4	2-α-Naphthylbenzo-[b]thiophene[f]	380[c]	26.32	-	27.52	0.042	1.5
		303	33.00	4.19	33.16	-0.213	
5	3-α-naphthylbenzo-[b]thiophene[g]	337[c] sh	29.67	-	29.51	-0.194	2
		352[c]	28.41	-			
		304	32.89	4.04	32.64	-0.374	

[a] In hexane, at 25°. [b] Fluorescence lifetime, ns.[9] [c] Fluorescence. [d] Absorption spectrum in light petroleum ether, taken from ref.[16] [e] θ for S_0 and for S_1: 0°. [f] θ for S_0, 75°, for S_1, 0°; geometry I. [g] θ for S_0, 60°, for S_1, 0°; geometry I.

singlet state (θ = 32°) and 2-phenylnaphthalene was practically planar (θ = 1°).[14] Several other papers devoted to the excited states of arylsubstituted aromatics and heteroaromatics, to their geometries, and to twisted states provide important information as well.[20-22] Depending on whether the twist angle θ is applied to compounds 4 and 5 in geometry I or II, one could, in principle, expect a variation of γ_μ . However, it turns out that, even when the same value of γ_μ is used, the differences between the results obtained for the two geometries are very small and negligible from the practical point of view.

Generally, there is a good agreement between the calculated transitions and the major bands in the electronic absorption spectra of the compounds under study, as well as between the first

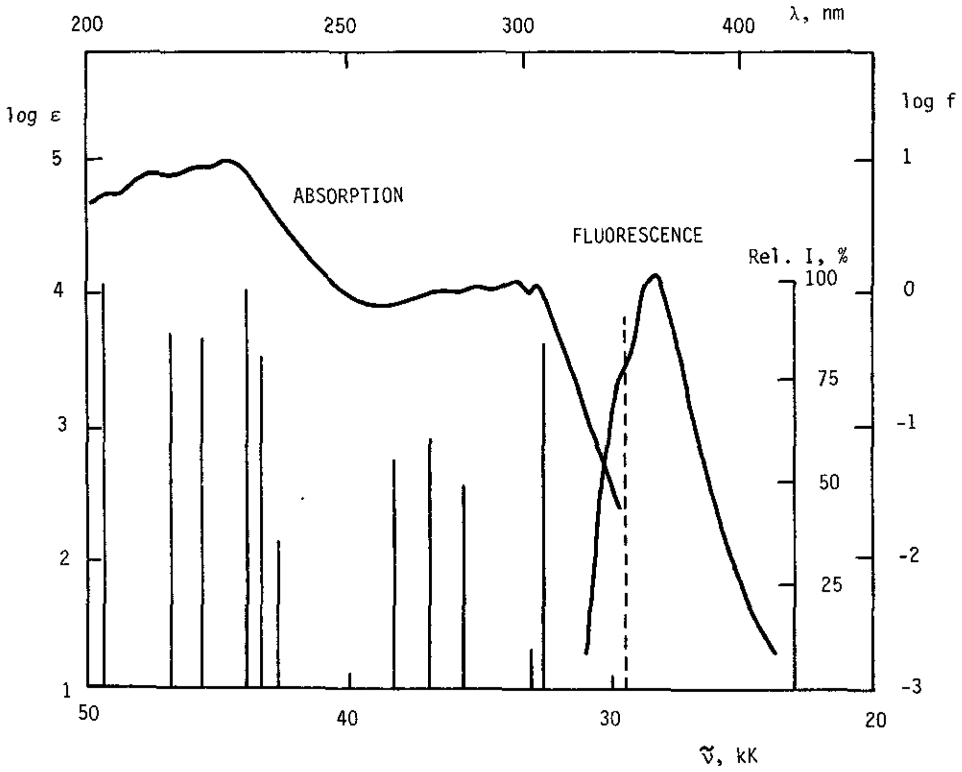


Fig. 1. Electronic absorption and fluorescence spectra of 3-α-naphthylbenzo[b]thiophene (5) in hexane. Calculated LCI transition energies and intensities are shown as full straight lines (broken line in the case of fluorescence). The scale for the calculated oscillator strengths is shown on the right-hand side (log ε ≐ log f + 4). The relative intensity scale is for the fluorescence spectrum.

fluorescence band and the corresponding calculated transition (Table 2 and Fig. 1). Additional bands, observed in the case of benzo[b]thiophene, are due to the fine vibrational structure. For many transitions, a considerable mixing of configurations is predicted, even for those of low energy.

Electronic distribution. For the selected geometries of the compounds under study, changes in the distribution of π-electrons in the ground and in the first excited singlet states are summarized in Table 3. It can be seen that in the case of 3-α-naphthylbenzo[b]thiophene (5) there is a substantial charge transfer from the heterocyclic ring to the naphthyl group upon excitation to the first excited singlet state. This charge transfer is less pronounced in compounds 2 and 4 and is negligible in the case of 3.

Table 3. Differences between the Overall π-Electron Densities, Σq, in the Benzo[b]thienyl and Aryl Moieties of Arylbenzo[b]thiophenes **2**-**5** in Their Ground (S_0) and the First Excited Singlet (S_1) States[a]

Compound No.	Benzo[b]thienyl			Aryl		
	$\Sigma q_B S_0(\theta)$	$\Sigma q_B S_1(\theta)$	Δq_B[b]	$\Sigma q_A S_0(\theta)$	$\Sigma q_A S_1(\theta)$	Δq_A[b]
1	10.000(-)	10.000(-)	0.000	-	-	-
2	9.987(0°)	9.875(0°)	-0.112	6.013(0°)	6.125(0°)	0.112
3	9.978(0°)	9.994(0°)	0.016	6.022(0°)	6.006(0°)	-0.016
4[c]	9.999(75°)	9.806(0°)	-0.193	10.001(75°)	10.194(75°)	0.193
4[d]	9.999(75°)	9.827(0°)	-0.172	10.001(75°)	10.173(0°)	0.172
5[c]	9.992(60°)	9.752(0°)	-0.240	10.008(60°)	10.248(0°)	0.240
5[d]	9.992(60°)	9.774(0°)	-0.218	10.008(60°)	10.226(0°)	0.218

[a] Index A refers to the aryl group attached to the benzo[b]thiophene ring, index B refers to the benzo[b]thiophene moiety. [b] $\Delta q_B = \Sigma q_B S_1 - \Sigma q_B S_0$; $\Delta q_A = \Sigma q_A S_1 - \Sigma q_A S_0$. [c] Geometry I. [d] Geometry II.

Dipole moments. Table 4 contains the calculated π-dipole moments for compounds **1**-**5** in their ground and the first excited singlet states and the corresponding differences. In the case of 3-α-naphthylbenzo[b]thiophene (**5**) there is an enormous difference in both dipole moments (even if one keeps in mind that the π-dipole moments in the PPP method are usually exaggerated), 1.720 D (or 1.837 D) in the ground state vs. 5.412 D (or 5.437 D) in the first excited singlet state. This clearly indicates a substantial redistribution of π-electrons in the excited state and a change of molecular geometry (Fig. 2). Changes in dipole moments are noticeably less pronounced for the other compounds **1**-**4**. It can be reasonably assumed that the σ-contribution to the overall dipole moments is small.

Thus, the results obtained in this study (changes in the distribution of π-electrons, change of the π-dipole moment) provide additional supporting evidence for the existence of an ICT state in 3-α-naphthylbenzo[b]thiophene (**5**), with a geometry different from that of the ground state. It is worth mentioning that in this case it is the excited ICT state which is planar or nearly planar, whereas the ground state is twisted about the C(benzo[b]thienyl)-C(α-naphthyl) bond. It is just the opposite of the situation found by Grabowski and co-workers[11] and Okada and co-workers[10] where the excited TICT state of their systems is twisted.

Table 4. π-Dipole Moments of Benzo[b]thiophenes (1-5), μ_π, in Their Ground (S_0) and the First Excited Singlet (S_1) States[a]

No.	S_0				S_1				μ_π[b]
	μ_π	cos α	sin α	α	μ_π	cos α	sin α	α	
1	1.675	-0.597	0.802	126°	1.799	-0.640	0.768	130°	0.124
2	1.408	-0.529	0.848	122°	1.270	0.848	0.530	32°	-0.138
3	1.964	0.741	0.672	42°	0.965	0.893	0.450	27°	-0.999
4[c]	1.634	-0.665	0.747	132°	2.669	0.997	-0.074	356°	1.035
4[d]	1.527	-0.626	0.779	129°	2.740	0.846	0.533	32°	1.213
5[c]	1.720	0.694	0.720	46°	5.412	0.976	-0.217	347°	3.692
5[d]	1.837	0.675	0.737	47°	5.437	0.914	0.405	24°	3.600

[a] Twist angles θ used for S_0 and S_1 are the same as in Table 3; μ_π are in D (Debye units). The angle α refers to the direction of the dipole moment. It is defined as the angle formed by the positive direction of the axis shown in the formula (see the structural formulas) and the direction of the dipole moment read counterclockwise. The angles are rounded off to the nearest full degree. [b] $\mu_\pi = \mu_\pi(S_1) - \mu_\pi(S_0)$. [c] Geometry I. [d] Geometry II.

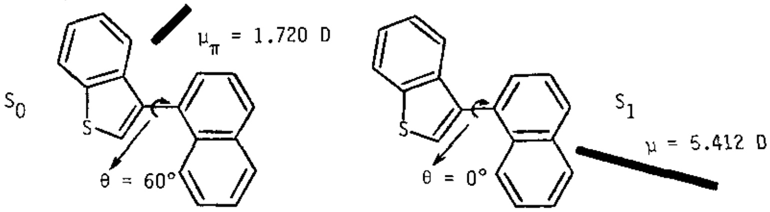


Fig. 2. π-Dipole moments of 3-α-naphthylbenzo[b]thiophene (5) in the ground state (S_0) and in the first excited singlet state (S_1). The dipole moments are shown for idealized geometries (planar ground and excited states).

EXPERIMENTAL

Compounds. Benzo[b]thiophene (1) was obtained from Fluka, Buchs, Switzerland, and from Aldrich-Europe, Beerse, Belgium. The four arylbenzo[b]thiophenes (2-5) were synthesized. The synthesis of 2-phenyl-benzo[b]thiophene (2), 2-α-naphthylbenzo[b]thiophene (4), and 3-α-naphthylbenzo[b]thiophene (5) has been reported in one of our previous publications,[7] as well as the synthesis of 3-phenylbenzo[b]thiophene (3).[9]

Spectra. The electronic absorption spectra of the compounds under study were measured in hexane (Merck, "For Fluorescence Spectroscopy" or "Uvasol") on a Jobin Yvon 201 spectrophotometer. The fluorescence spectra were recorded at room temperature in the same solvent using a FICA 55000 spectrofluorometer corrected both for excitation and emission measurements. The method of the determination of fluorescence lifetimes, τ_0, has been described previously.[9]

Calculations. The usual version of the PPP (LCI-SCF-MO) method was used.[23,24] Interactions between monoexcited configurations formed by promotion of one electron from one of the highest occupied MO's to one of the four lowest unoccupied MO's were considered. The systems studied were assumed to be planar and to have idealized geometry. All C-C and C-S bond lengths were assigned to be 1.40 Å and the rings were assumed to be regular hexagons and pentagons.[25-30] SCF MO's served as the basis for CI calculations. Only resonance integrals between nearest neighbors were considered. The parameters used in the calculations are summarized in Table 1.[12]

In Table 1, I_μ and A_μ are the ionization potential and electron affinity of atom μ in the atomic valence state, respectively. The monocentric electronic repulsion integrals and the core integrals between nearest neighbors are designated as $\gamma_{\mu\mu}$ and $\beta_{C-\mu}$, respectively, and Z_μ is the core charge at atom μ. The bicentric electronic repulsion integrals, $\gamma_{\mu\nu}$, have been calculated using the Mataga-Nishimoto formula,[31]

$$\gamma_{\mu\nu} = \frac{14.399}{r_{\mu\nu} + 1.328}\ \text{eV}$$

where $r_{\mu\nu}$ (Å) is the distance between atoms μ and ν.[13]

Structures Twisted about the Heteroaryl-Aryl Bond. In the case of the structures twisted about the single C(benzo[b]thienyl)-C(aryl) bond, standard bond lengths and bond angles were employed, with the twist angle θ (angle of internal rotation) varied from 0° to 90°. The calculations were carried out for seven different angles, θ = 0°, 15°, 30°, 45°, 60°, 75°, and 90°. The dependence of the resonance integral for the respective C-C bond, $\beta_{\mu\nu}$, upon the twist angle θ is given by equation:[11,14]

$$\beta_{\mu\nu}(\theta) = \beta_{\mu\nu}(0)\cos\theta$$

ACKNOWLEDGEMENT

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25. Although the C-S bond length is known to be 1.72 Å in thiophene,[26-28] our previous comparative PPP calculations on thiophene and other sulfur heterocycles using different geometries indicate that one should not expect considerable deviations when idealized geometry is used.[29] The actual numerical values are, of course, somewhat different. A detailed parameter study of models of sulfur heterocycles with different C-S bond lengths has been carried out by Fabian, Mehlhorn, and Zahradník and their results also show that changes of the C-S bond length in benzo[b]thiophene do not lead to significant differences in electronic spectral transitions.[30]

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