

Fluorescence Properties and Dipole Moments of Novel Fused Thienobenzofurans. Solvent and Structural Effects

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Abstract The electronic absorption, fluorescence excitation and emission spectra, and fluorescence quantum yields of novel fused thienobenzofurans, including thieno[3,2-*b*] [1]benzofuran (**1**), [1]benzothieno[3,2-*b*]furan (**2**), and [1]benzothieno[3,2-*b*][1]benzofuran (**3**), were recorded in fourteen solvents of different polarities at room temperature. Compound **2** was not fluorescent. Experimental

ground-state dipole moments of compounds **1–3** were measured in benzene at 298 K and compared with the corresponding theoretical dipole moment values. The solvent effects on the electronic absorption and fluorescence spectra of these thienobenzofurans were quantitatively investigated by means of solvatochromic correlations based on the Kawski-Chamma-Viallet and McRae equations. A weak negative solvatochromic behavior was found for these compounds, showing that their dipole moments are slightly lower in the excited singlet-state than in the ground-state. Kamlet-Abboud-Taft multiparameter relationships were also established for electronic absorption and fluorescence wavenumbers, and fluorescence quantum yields in most solvents, demonstrating the occurrence of specific solute-solvent interactions.

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Introduction

In the last few years, novel sulfur- and oxygen-containing fused heterocycles such as benzothienothiophene (BTT) and benzothienoindole (BTI) derivatives have been shown to possess remarkable ferroelectric liquid crystal [1, 2] and luminescence properties [3–8], and also to lead to the electrosynthesis of conducting oligomers with interesting luminescent applications. In connection with our interest in the photophysical properties of these BTT and BTI derivatives and their potential use for the electrosynthesis of conjugated/aromatic oligomers and polymers with possible practical applications, we have decided to carry

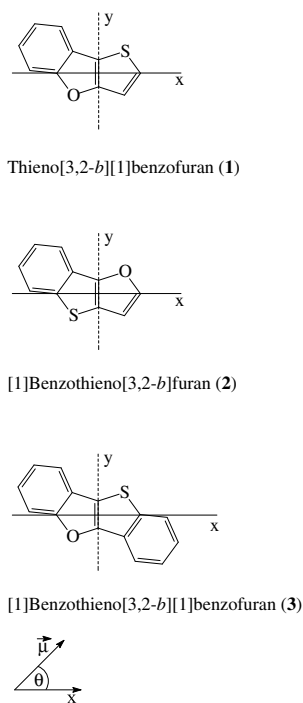
out electronic absorption and fluorescence spectral investigations of three recently-synthesized fused thienobenzofurans, namely thieno[3,2-*b*][1]benzofuran (**1**) [9, 10], [1]benzothieno[3,2-*b*]furan (**2**) [11], and [1]benzothieno[2,3-*b*][1]benzofuran (**3**) [12–14] (Scheme 1).

Examples of our previous photophysical studies of this type on various heterocycles include electronic absorption and emission (fluorescence, phosphorescence) spectra, solvent effects, excited-state lifetimes, ground- and excited-state dipole moments, solvatochromic correlations, Kamlet-Abboud-Taft multiparameter relationships, etc. [15–18].

As already stated, one can obtain, from functionalized fused heterocycles, conducting oligomers and/or polymers *via* electrosynthesis [3–5, 19]. These novel materials can be potentially used as conductors, for protection of metal surfaces, as ferroelectric liquid crystals, for development of luminescent devices, etc. This makes such compounds especially attractive for our studies [3–5, 19].

The main goal of the present work was to investigate the solvent and structural effects on the electronic absorption, fluorescence spectra and fluorescence quantum yields of the new thienobenzofurans **1**, **2** and **3** at room temperature. Therefore, we established Kawski-Chamma-Viallet and/or McRae solvatochromic correlations for these compounds in ten solvents of various polarities. Also, we determined the ground-state dipole moments, measured and/or calculated by means of the AM1 and the PM3 methods and a combination of the PPP method (Pariser-Parr-Pople, π -LCI-SCF-MO) and the σ -contribution, and we compared these dipole moments

Scheme 1 Structure of the thienobenzofurans under study



with the first excited singlet-state dipole moments. Moreover, in order to evaluate the contribution of the specific solute-solvent interactions in the singlet excited-state, we applied the Kamlet-Abboud-Taft multiparameter relationship to our electronic absorption and fluorescence spectral data.

Experimental

Chemicals

The synthesis of the compounds **1–3** has been previously reported [10, 11, 13, 14]. Analytical-grade solvents, including benzene, dioxane, carbon tetrachloride, toluene, chloroform, ethyl acetate, methyl acetate, 1,2-dichloroethane, 1-butanol, ethanol, methanol, acetonitrile, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), and de-ionized water were used to prepare the solutions employed in the spectral measurements and in the experimental determination of dipole moments.

Electronic Absorption and Fluorescence Spectral Studies

The electronic absorption spectra of the three thienobenzofurans under study were recorded at 295 K in fourteen different solvents on a Perkin-Elmer Lambda 2 spectrophotometer. Excitation and emission fluorescence spectra were obtained at the same temperature with a Perkin-Elmer LS-50 spectrofluorometer. Fluorescence quantum yields were measured on a SLM Aminco-Bowman Series 2 spectrofluorometer, using quinine sulfate as a reference ($\Phi_F=0.58$) [20] in a 0.05 M H_2SO_4 aqueous solution.

Experimental Determination of the Ground-State Dipole Moments

The ground-state dipole moments of thienobenzofurans were measured in benzene at 298 K using a dipole meter DM-01 (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany) equipped with a DFL-2 cell as previously described [21]. The refraction indices, n , were measured on an Abbé refractometer (Bausch & Lomb, Rochester, NY).

The ground-state dipole moment (μ_g) values (expressed in Debye, D) were obtained by means of the classical, following formula [22–25], based on the measurement of the static dielectric constants:

$$\mu_g^2 = (27kT/4\pi N)[1/d(D + 2)^2](A_D - A_n)M \quad (1)$$

where k is the Boltzmann constant (1.381×10^{-16} erg deg $^{-1}$), T is the absolute temperature (in K), N is Avogadro's number (6.023×10^{23} mol $^{-1}$), d and D are the density and the dielectric constant of the solvent, respectively, A_D and

A_n are the numerical values obtained from the solute dielectric constant and refractive index measurements, and M is the molecular weight of the solute.

Results and Discussion

Solvent and Structural Effects on the Electronic Absorption and Fluorescence Spectra

The electronic absorption and fluorescence spectra of the three thienobenzofurans under study were recorded in fourteen solvents of different polarity (with their dielectric constants ranging from 2.209 to 78.54) and hydrogen-bonding ability, including dioxane, carbon tetrachloride, toluene, chloroform, ethyl acetate, methyl acetate, 1,2-dichloroethane, 1-butanol, ethanol, methanol, acetonitrile, dimethylformamide, dimethyl sulfoxide, and water.

Structural Effects

The electronic absorption spectral properties of the three compounds under study in different solvents are gathered in Table 1. As can be seen, in most solvents, the three thienobenzofurans are characterized by the presence of two relatively well-resolved main absorption bands in the wavelength regions of 240–260 and 280–300 nm for compound **1**, 230–250 and 280–310 nm for **2**, and 225–260 and 300–320 nm for **3**. Both bands possessed high molar absorption coefficients, with $\log \epsilon$ values ranging between 4.1 and 4.3 for compound **1**, 3.2 and 4.3 for **2**, and 4.1–4.6 for **3**. For the three compounds, the shortest-wavelength bands can be attributed to the $\pi \rightarrow \pi^*$ 1B electronic transitions, whereas the long-wavelength bands are due to the $\pi \rightarrow \pi^*$ 1L_a and 1L_b transitions. A similar interpretation of the absorption bands of related compounds has been proposed in the case of fused benzothiophene derivatives [5]. Moreover, in spite of the presence of thiophene and furan rings in the molecular structure of thienobenzofurans, no band resulting from $n \rightarrow \pi^*$ transitions was observed, probably because of their complete overlapping by the very strong π, π^* bands. Table 1 also shows that significant red-shifts of the absorption band maxima occurred in most solvents ($\Delta\lambda = 13$ –21 nm) upon going from compounds **1** and **2** to **3**, which may be attributed to the increase of π electronic conjugation in the molecular structure of **3** ([1]benzothieno[2,3-*b*][1]benzofuran). Indeed, compound **3** possesses a supplementary ring in its fused aromatic system relative to the two other thienobenzofurans.

The fluorescence excitation and emission spectra, and quantum yields of fused thienobenzofurans in various solvents, to the exception of **2** which is not fluorescent, are reported in Table 2. As can be seen, the excitation

spectra generally possess bands located at wavelength values very close to those of the absorption spectra, which indicates that the absorbing species is also the fluorescing one. According to the solvent, the emission spectra of compounds **1** and **3** exhibited one to three bands and/or shoulders in the 310–330 and 330–360 nm regions, respectively (Table 2 and Fig. 1). It is worthwhile to stress that the emission spectra of compounds **1** and **3** presented a marked structure in most solvents, which is probably due to the above-mentioned π^*, π 1B , 1L_a and 1L_b electronic transitions, whereas the long-wavelength bands are due to the $\pi^* \rightarrow \pi$ transitions. No well-defined mirror image was observed between the excitation and emission spectra of both thienobenzofurans. Notable red-shifts of the fluorescence emission maxima ($\Delta\lambda_{em} = 19$ –23 nm, according to the solvent) were observed upon going from compound **1** to **3**, in the same structural order than for the absorption spectra, which indicates an important increase of π electronic conjugation in the excited singlet-state of **3** relative to **1**, due to the presence of an additional aromatic ring in the fused system of the former compound.

Solvent Effects

Upon increasing the solvent polarity, very weak blue-shifts of the absorption bands were observed for the three compounds ($\Delta\lambda = -3$ –5 nm), which did not provide precise information on the type of solvatochromism (Table 1). Nevertheless, these small blue-shifts suggest a slight decrease of the thienobenzofurans dipole moments in the excited singlet-state relative to the ground-state. It also indicates that other, specific solute-solvent interactions might be involved in addition to the solvent polarity.

The emission maxima of both fluorescent thienobenzofurans were characterized by slight blue-shifts ($\Delta\lambda_{em} = -2$ –8 nm, according to the compound and solvent) upon increasing the solvent polarity, except for water. This behavior indicates the existence of a small negative solvatochromism. A typical example of this solvent effect on the fluorescence emission spectra of **3** is illustrated in Fig. 1 for four different solvents (two non polar solvents, *i.e.*, toluene and 1,2-dichloroethane, and two polar ones, namely 1-butanol and acetonitrile), which again shows a weak blue-shift of the maximum of the emission band with increasing solvent polarity, confirming a negative solvatochromism. This type of solvatochromic behavior has been also found in the case of several structurally-similar fused BTT and BTI derivatives [5].

Overall, the fluorescence quantum yield (Φ_F) values of **1** and **3** were found to be relatively weak and to vary rather notably from 0.0003 to 0.065, according to the nature of the solvent and the structure of the compound (Table 2). In most cases, an increase of Φ_F was observed in the polar

Table 1 Electronic absorption spectral properties of thienobenzofurans in various solvents

Compound ^a	Solvent ^b	λ (nm) (log ϵ) ^c
1	Dioxane	301 (4.28), 293 (4.24), 289 (4.28), 282 (4.30), 273 _{sh} (4.21), 243 (4.29)
	Carbon tetrachloride	303(4.23), 295 (4.20), 291 (4.22)
	Toluene	302 (4.27), 294 (4.23)
	Chloroform	302 (4.24), 294 (4.21), 290 (4.24), 283 (4.25)
	Ethyl acetate	300 (4.20), 292 (4.16), 288 (4.20), 281 (4.21)
	Methyl acetate	300 (4.20), 292 (4.17), 288 (4.20), 281 (4.22)
	1,2-Dichloroethane	301 (4.23), 293 (4.20), 289 (4.23), 282 (4.25)
	1-Butanol	301 (4.25), 293 (4.19), 289 (4.22), 282 (4.24), 272 _{sh} (4.12), 250 (4.20), 243 (4.15)
	Ethanol	300 (4.34), 293 (4.29), 288 (4.33), 281 (4.35), 250 (4.30), 243 (4.26)
	Methanol	299 (4.26), 292 (4.22), 288 (4.25), 280 (4.28), 250 (4.23), 243 _{sh} (4.18)
	Acetonitrile	299 (4.28), 292 (4.26), 288 (4.29), 280 (4.32)
	Dimethylformamide	301 (4.21), 293 (4.17), 289 (4.21), 282 (4.23)
	Dimethyl sulfoxide	302 (4.20), 294 (4.17), 290 (4.20), 282 (4.23)
	Water	299 (4.13), 291 (4.13), 287 (4.16), 280 (4.19), 249 (4.11), 243 (4.13)
2	Dioxane	306 (3.30), 296 (3.95), 283 (4.20), 253 (4.34), 245 (4.38)
	Carbon tetrachloride	308 (3.46), 299 (4.04), 286 (4.20)
	Toluene	307 (3.30), 297 (3.98), 284 (4.19)
	Chloroform	307 (3.34), 297 (3.97), 284 (4.19)
	Ethyl acetate	305 (3.17), 296 (3.85), 282 (4.21)
	Methyl acetate	305 (3.24), 295 (3.91), 282 (4.21)
	1,2-Dichloroethane	307 (3.28), 296 (3.94), 283 (4.18)
	1-Butanol	306 (3.13), 295 (3.89), 283 (4.15), 253 (4.29), 245 (4.35), 236 (4.31)
	Ethanol	305 (3.23), 296 (3.88), 282 (4.14), 252 (4.31), 244 (4.12), 233 (4.48)
	Methanol	305 (3.21), 295 (3.89), 282 (4.20), 252 (4.33), 244 (4.39), 236 (4.36)
	Acetonitrile	305 (3.22), 295 (3.87), 282 (4.18), 252 (4.31)
	Dimethylformamide	306 (3.26), 296 (3.93), 283 (4.18)
	Dimethyl sulfoxide	306 (3.33), 296 (3.95), 284 (4.16)
	Water	305 (3.26), 295 (3.82), 281 (4.14), 252 (4.25), 245 (4.30), 235 (4.30)
3	Dioxane	319 (4.38), 311 (4.40), 304 (4.47)
	Carbon tetrachloride	322(4.42), 313 (4.44), 308 (4.49), 302 _{sh} (4.40)
	Toluene	321 (4.37), 312 (4.39), 306 (4.44), 301 _{sh} (4.37)
	Chloroform	321 (4.46), 312 (4.50), 307 (4.55), 300 _{sh} (4.48)
	Ethyl acetate	318 (4.40), 310 (4.40), 303 (4.47), 298 _{sh} (4.42)
	Methyl acetate	317 (4.40), 310 (4.43), 303 (4.50), 298 _{sh} (4.45)
	1,2-Dichloroethane	320 (4.43), 311 (4.46), 306 (4.52), 300 _{sh} (4.45)
	1-Butanol	320 (4.38), 311 (4.38), 304 (4.44), 257 (4.41)
	Ethanol	318 (4.34), 311 (4.36), 304 (4.42), 299 _{sh} (4.38), 257 (4.39), 248 (4.26), 227 (4.21)
	Methanol	318 (4.29), 310 (4.34), 303 (4.40), 299 _{sh} (4.40), 256 (4.34), 248 (4.21), 228 (4.14)
	Acetonitrile	318 (4.34), 309 (4.40), 303 (4.47), 256 (4.43), 248 (4.32), 228 (4.26)
	Dimethylformamide	319 (4.39), 311 (4.43), 305 (4.47), 300 _{sh} (4.43)
	Dimethyl sulfoxide	320 (4.40), 311 (4.43), 306 (4.49), 300 _{sh} (4.44)
	Water	317 (4.41), 310 (4.49), 304 (4.56), 297 _{sh} (4.53), 256 (4.61), 248 (4.64),

^a **1** = thieno[3,2-*b*][1]benzofuran; **2** = [1]benzothieno[3,2-*b*]furan; **3** = [1] benzothieno [2,3-*b*][1]benzofuran. The concentrations of thienobenzofurans were between 2×10^{-6} and 5×10^{-5} M

^b Solvents are listed in order of increasing dielectric constant

^c Absorption maxima. Wavelength precision = ± 1 nm. sh = shoulder. The logarithm of the molar value coefficient ($M^{-1} \text{ cm}^{-1}$) is given in parentheses

Table 2 Fluorescence excitation and emission spectral properties and fluorescence quantum yields of thienobenzofurans **1** and **3** in various solvents

Compound N°	Solvent ^a	λ_{ex} (nm) ^b	λ_{em} (nm) ^b	Φ_{F} ^c
1	Dioxane	294, 290 _{sh} , 272	321	0.016
	Carbon tetrachloride	295, 287, 284 _{sh}	324	0.0003
	Toluene	301	322	0.024
	Chloroform	296, 288	309 _{sh} , 319	0.004
	Ethyl acetate	298, 291, 288, 281	318	0.015
	Methyl acetate	299, 290 _{sh}	310 _{sh} , 318, 329 _{sh}	0.030
	1,2-Dichloroethane	302, 299 _{sh} , 296, 290 _{sh}	312 _{sh} , 321	0.065
	1-Butanol	300, 291, 286 _{sh} , 257, 242	310 _{sh} , 318, 325 _{sh}	0.043
	Ethanol	299, 287, 251	317	0.014
	Methanol	297, 291, 271, 253, 287	310, 316, 329 _{sh}	0.015
	Acetonitrile	298, 290 _{sh} , 286	310, 318	0.010
	Dimethylformamide	300, 297, 291 _{sh} , 286, 284 _{sh}	312 _{sh} , 319, 333 _{sh}	0.073
	Dimethyl sulfoxide	302, 297, 292, 288, 283 _{sh}	313 _{sh} , 322	– ^d
	Water	285, 273, 243 _{sh} , 222 _{sh}	333	0.015
3	Dioxane	319, 309, 304 _{sh}	329 _{sh} , 341, 357 _{sh}	0.014
	Carbon tetrachloride	322, 313	343	0.0004
	Toluene	321, 312	330 _{sh} , 343, 359 _{sh}	0.011
	Chloroform	320, 309, 297, 289 _{sh} , 259	331 _{sh} , 343, 357 _{sh}	0.005
	Ethyl acetate	317, 309, 304 _{sh}	327 _{sh} , 338, 354 _{sh}	0.022
	Methyl acetate	316 _{sh} , 308, 303, 296	328 _{sh} , 341, 355 _{sh}	0.006
	1,2-Dichloroethane	319, 308, 283	330 _{sh} , 342, 356 _{sh}	0.031
	1-Butanol	319, 309, 251 _{sh} , 247	326 _{sh} , 339, 354 _{sh}	0.016
	Ethanol	314 _{sh} , 305, 254, 221	326 _{sh} , 338, 355 _{sh}	0.012
	Methanol	316, 308, 303 _{sh} , 255	326 _{sh} , 337, 353 _{sh}	0.010
	Acetonitrile	316, 308, 255, 226	329 _{sh} , 340, 355 _{sh}	0.007
	Dimethylformamide	319, 309, 291, 282, 274 _{sh}	329 _{sh} , 342, 356 _{sh}	0.017
	Dimethyl sulfoxide	320, 309, 287	331 _{sh} , 342, 358 _{sh}	– ^d
	Water	316, 304, 285 _{sh} , 255, 224	329 _{sh} , 339	0.007

1 = thieno[3,2-*b*][1]benzofuran;
3 = [1]benzothieno[2,3-*b*][1]benzofuran. The concentrations of thienobenzofurans were between 2×10^{-6} and 5×10^{-5} M. Compound **2** is not fluorescent

^a Solvents are listed in order of increasing dielectric constant

^b Fluorescence excitation (λ_{ex}) and emission (λ_{em}) maxima. Wavelength precision = ± 1 nm

^c Fluorescence quantum yields (Φ_{F}) values measured relative to quinine sulfate (see Experimental)

^d Φ_{F} value not available

solvents relative to the non polar ones. An analogous behavior has been described for the Φ_{F} values of some fused BTT and BTI derivatives [5].

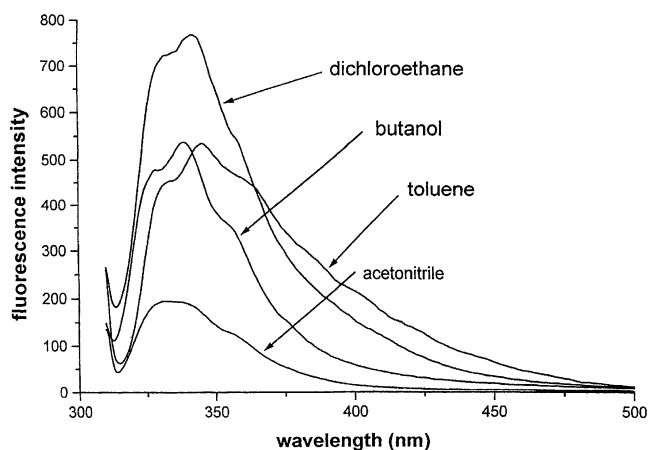


Fig. 1 Solvent effect on the fluorescence emission spectra of compound **3** ([1]benzothieno[2,3-*b*][1]benzofuran) (5×10^{-6} M) recorded at 295 K in toluene, 1,2-dichloroethane, 1-butanol and acetonitrile. $\lambda_{\text{ex}} = 300$ nm

Theoretical and Experimental Ground-State Dipole Moments

The theoretical and experimental ground-state dipole moments (μ_{g}) of the thienobenzofurans under study, **1–3**, are presented in Table 3, together with the angles showing their direction.

The experimental μ_{g} values, determined in benzene, are quite similar for all the three compounds since they range from 1.26 D to 1.41 D ($\pm 10\%$). They are very close to the dipole moments of some analogous benzothiophene derivatives [26]. Two sets of calculated dipole moments are given. The first set of the calculated dipole moments was obtained as a vector sum of the π -moment (PPP method) [27, 28] and the σ -moment (from the σ -bond and group moments) [24, 29–31]. The second set represents the values obtained by the AM1 and PM3 methods [32]. There is an acceptable agreement between the experimental and calculated values for compounds **1** and **2**, but not for **3**. Indeed, the experimental value for **1**, 1.28 D, compares favorably with the average theoretical value from the two calculations, *i.e.*

Table 3 Comparison of the ground-state dipole moments (μ_g) and first excited singlet-state dipole moments (μ_e) of thienobenzofurans (in Debye units, D)

Compound ^a N ^o	μ_g exp ^b	μ_g calc ^c			μ_e calc ^d	
		I ^e	II ^f	θ^g	II ^h	θ^g
1	1.28	1.464	1.048	140°	3.413	136°
2	1.41	0.862 ⁱ	1.130	180°	2.830	138°
3	1.26	0.789	0.719	3°	0.580	354°

^a **1** = thieno[3,2-*b*][1]benzofuran; **2** = [1]benzothieno[3,2-*b*]furan; **3** = [1] benzothieno [2,3-*b*][1]benzofuran

^b μ_g exp = experimental ground-state dipole moments measured in benzene. See [Experimental](#)

^c μ_g calc = calculated ground-state dipole moments

^d μ_e calc = calculated first excited singlet-state dipole moments. Only negative experimental μ_e values are obtained by using the Kawski-Chamma-Viallet and Mc Rae correlations

^e AM1 method (HyperChem)

^f A combination of the π -moment (PPP method) and the σ -moment (σ -bond contributions)

^g Angle between the positive direction of the x-axis and the positive directions of the dipole moment (from + to -) read counterclockwise

^h A combination of the first excited singlet state π -moment and the σ -moment (the same as in the ground state)

ⁱ PM3 method (HyperChem). AM1 method gives 0.379 D

1.26 D. Similarly, for **2**, the experimental value is 1.41 D, the average of the two calculated values is 1.00 D. In contrast, for **3**, the experimental value is 1.26 D, whereas the average of the two calculated values is 0.75 D. One possible explanation of the later discrepancy is that no solute-solvent interactions are taken into account in the theoretical calculations. Moreover, while **1** and **2** are very similar in size, compound **3**, a four-ring system, is considerably larger than the two other thienobenzofurans.

Solvatochromic Correlations and First Excited Singlet-State Dipole Moments

In order to determine the relative changes of the dipole moment upon going from the ground-state to the first excited singlet-state of thienobenzofurans, we applied the solvatochromic method, by using the Kawski-Chamma-Viallet equation [33–35] and the McRae equation [36, 37]. The later equation can be utilized only in the case of non-fluorescent compounds.

Kawski-Chamma-Viallet equation [33–35]:

$$\frac{\tilde{\nu}_A + \tilde{\nu}_F}{2} = \frac{-2(\mu_e^2 - \mu_g^2)}{a_0^3 h} \left[\frac{2n^2 + 1}{2(n^2 + 2)} \cdot \left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right) + \frac{3(n^4-1)}{2(n^2+2)^2} \right] \quad (2)$$

where $\tilde{\nu}_A$ and $\tilde{\nu}_F$ are the wavenumbers of the absorption and emission maxima (in cm^{-1}), respectively, μ_g and μ_e are the

permanent dipole moments in the ground-state and the first excited singlet-state, respectively, a_0 is the Onsager cavity radius, D is the solvent dielectric constant, n is the solvent index of refraction, and the term in bracket corresponds to the solvent function F_2 .

McRae equation [36, 37]:

$$\tilde{\nu}_A = -\frac{\mu_g(\mu_e - \mu_g)}{a_0^3 h c} \left[\frac{2(D-1)}{D+2} \right] \quad (3)$$

where the meaning of the symbols is the same as in Eq. (2), and the term in bracket is the solvent function F_3 .

The values of the solute cavity radii, a_0 , were calculated from the molecular volume of the thienobenzofurans according to the Suppan's formula [38]:

$$a_0 = (3M/4\pi\delta N)^{1/3} \quad (4)$$

where M is the molecular weight of the solute, δ is the density of the solute molecule, and N is Avogadro's number. The solid-state densities of **1** and **2** were determined pycnometrically in a suspension in kerosene, the δ value measured for **2** being also used for **3**. The obtained a_0 values were (in Å): **1**, 4.62; **2**, 4.16; **3**, 4.52.

The solvatochromic correlations were established as the plots of $(\tilde{\nu}_A + \tilde{\nu}_F)/2$ (Kawski-Chamma-Viallet), for compounds **1** and **3**, and $\tilde{\nu}_A$ (McRae) for compounds **1–3**, against the solvent functions F_2 and F_3 , respectively. The values of solvent functions F_2 and F_3 were taken from our previous publications (cf., e.g. [18, 39–41]). For all solvents, the $\tilde{\nu}_A$ and $\tilde{\nu}_F$ values were obtained from the absorption and fluorescence maxima wavelengths of thienobenzofurans given in Tables 1 and 2. The results of the statistical treatment of the Kawski-Chamma-Viallet and McRae correlations of solvent spectral shifts can be considered as rather satisfactory for the three compounds under study (Table 4). Indeed, as can be seen, both types of relationships were found to be linear, with correlation coefficient values close to or larger than 0.90. The correlations are obeyed by ten solvents for all the three compounds under study. The linearity of these solvatochromic curves suggests the dominant importance of the general polarity effects on the observed spectral shifts, which is confirmed by the Stokes shift values obtained in these solvents. An example of a Kawski-Chamma-Viallet plot for **3** is shown in Fig. 2. The correlation slopes exhibited weakly positive values, ranging from about 270 to 960 cm^{-1} , which demonstrates the existence of a small negative solvatochromism. Consequently, it can be expected that the first excited singlet-state dipole moments (μ_e) of the thienobenzofurans under study should be slightly smaller than their ground-state counterparts (μ_g).

Theoretical excited singlet-state dipole moments of thienobenzofurans were obtained as a combination of

Table 4 Statistical treatment of the solvatochromic correlations of Thienobenzofurans

Compound ^a N ^o	Slope (cm ⁻¹)	Intercept (cm ⁻¹)	r ^b	n ^c
Mc Rae Equation				
1	274	32 877	0.832	10
2	326	34 845	0.884	10
3	275	30903	0.904	10
Kawski-Chamma-Viallet Equation				
1	926	32 007	0.797	10
2 ^d	–	–	–	–
3	961	30 054	0.921	10

^a **1** = thieno[3,2-*b*][1]benzofuran; **2** = [1]benzothieno[3,2-*b*]furan; **3** = [1]benzothieno[2,3-*b*][1]benzofuran

^b r = correlation coefficient

^c n = number of solvents

^d Compound not fluorescent

the π -contribution to the first excited singlet-state (PPP calculation) and the σ -moment which was assumed to be the same as in the ground-state (Table 3). As can be noted in Table 3, the calculated μ_e values were significantly higher than the ground-state dipole moments for compounds **1** and **2**, whereas, in the case of compound **3**, the calculated μ_e value was smaller than its ground-state counterpart. This behavior was rather unexpected, since the experimental results of solvatochromic correlations predicted for all three compounds a decrease of dipole moments upon excitation. A possible explanation of this discrepancy is that solute-solvent specific interactions are not taken into account in the theoretical calculations. Moreover, it is well known that the PPP calculations of the excited singlet-state dipole moments are often subject to important uncertainties due to the incomplete evalua-

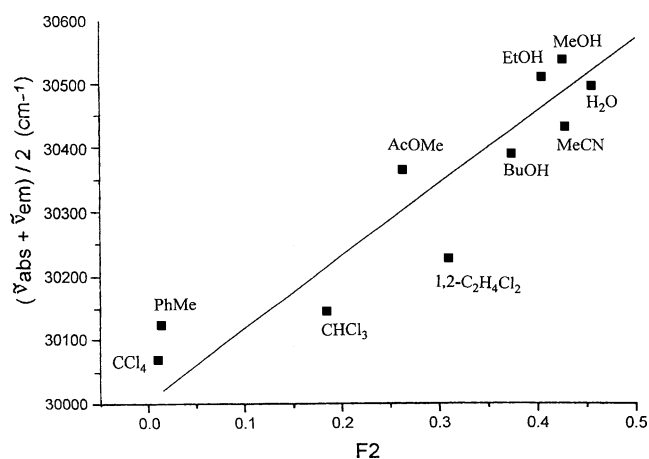


Fig. 2 Example of Kawski-Chamma-Viallet solvatochromic correlation plot for **3** in ten solvents of different polarities (carbon tetrachloride, toluene, chloroform, methyl acetate, 1,2-dichloroethane, 1-butanol, ethanol, methanol, acetonitrile, and water)

tion of the charge distribution of molecules in their excited state [41].

Also, attempts to determine experimental first excited singlet-state dipole moments on the basis of the Kawski-Chamma-Viallet and McRae solvatochromic correlations, and using the experimental μ_g values, were unsuccessful. Indeed, only negative values of excited singlet-state dipole moments were obtained for the three thienobenzofurans under study, which might be explained by the too weak values of the ground-state dipole moments and/or of the solvatochromic correlation slopes [15]. Specific solute-solvent interactions, such as hydrogen bond formation with protic solvents (in the solvatochromic correlations), undoubtedly also contributed to this anomalous behavior.

Kamlet-Abboud-Taft Multiparameter Solvation Energy Relationships

In order to obtain more precise information about the various, specific solute-solvent interactions, including the solvent polarity/polarisability, the solvent hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) abilities in the ground- and the excited singlet-state, we also carried out Kamlet-Abboud-Taft multiparameter relationships for the three thienobenzofurans. The electronic absorption ($\tilde{\nu}_A$) and fluorescence ($\tilde{\nu}_F$) wavenumbers of the respective maxima, and the fluorescence quantum yields (Φ_F) were plotted using the simplified form of the Kamlet-Abboud-Taft Eq. (5) [42, 43].

$$XYZ = (XYZ)_0 + s\pi^* + a\alpha + b\beta \quad (5)$$

where XYZ is a solvatochromic property, π^* is the solvent polarity/polarizability, α and β are the solvent HBD and HBA abilities, and s , a and b are the corresponding regression coefficients.

For performing the calculations, we applied the method of multiple regression analysis, which is known to provide results analogous to those obtained with the stepwise method, and we used π^* , α and β parameter values taken from literature [42, 43].

The statistical results of the Kamlet-Abboud-Taft multiparameter correlations are presented in Table 5. In the case of $\tilde{\nu}_A$ and $\tilde{\nu}_F$, the relationships exhibit a satisfactory precision, as indicated by the correlation coefficient values larger than or very close to 0.90. The majority of solvents obeyed to the correlations. It suggests that this model, based on specific solute-solvent interactions, provides a satisfactory quantitative description of the solvatochromic effects for the thienobenzofurans under study.

The s regression coefficients for compounds **1–3** possess positive values for the absorption and fluorescence wavenumbers, which indicates that the increase of the solvent

Table 5 Statistical treatment of the Kamlet-Abboud-Taft multiparameter correlations for the absorption and fluorescence spectral data of thienobenzofurans

Compound ^a N ^o	s (cm ⁻¹) ^b	a (cm ⁻¹) ^c	b (cm ⁻¹) ^d	Intercept (cm ⁻¹)	r^e	n^f
Absorption ($\tilde{\nu}_A$)						
1	316	142	109	32 917	0.897	9
2	457	109	181	34 897	0.905	9
3	279	158	149	31 002	0.954	9
Fluorescence ($\tilde{\nu}_F$)						
1	31	-18	537	30 979	0.893	9
2^g	–	–	–	–	–	–
3	55	273	217	29 116	0.929	9
Fluorescence (Φ_F) ^h						
1	-0.71	-0.032	1.36	3.85	0.985	6
2^g	–	–	–	–	–	–
3	-0.27	-0.02	-1.21	5.30	0.976	7

^a **1** = thieno[3,2-*b*][1]benzofuran; **2** = [1]benzothieno[3,2-*b*]furan; **3** = [1]benzothieno[2,3-*b*][1]benzofuran

^b s = solvent polarity/polarisability regression coefficient [see Eq. (5)]

^c a = solvent HBD ability regression coefficient [see Eq. (5)]

^d b = solvent HBA ability regression coefficient [see Eq. (5)]

^e r = correlation coefficient

^f n = number of solvents

^g Compound not fluorescent

^h In the case of fluorescence quantum yields (Φ_F), the Kamlet-Abboud-Taft multiparameter correlations obey an equation of the form: $\ln([1/\Phi_F] - 1) = s\pi^* + aa + b\beta$. In this equation, the regression coefficients s , a , b and intercept are without units

polarity/polarisability (π^*) yields a blue-shift in $\tilde{\nu}_A$ and $\tilde{\nu}_F$. The observed blue-shifts of the fluorescence emission spectra can be attributed to the excited singlet-state weaker stability (higher energy level), in polar solvents relative to non-polar ones. Therefore, our results demonstrates that, when the solvent polarity/polarisability increases, the ground-state of thienobenzofurans becomes more stabilized whereas, as already stated, their excited singlet-state become less stabilized, which seems in agreement with the weakly negative solvatochromism observed on the basis of the results of the previous paragraph (solvatochromic correlations).

The a and b regression coefficients, obtained for absorption and fluorescence wavenumbers, also present positive values, to the exception of the negative sign of the a coefficient for the fluorescence wavenumbers of compound **1** (Table 5). These positive values indicate that increasing HBD and HBA solvent ability leads to a blue shift in $\tilde{\nu}_A$ and $\tilde{\nu}_F$, and, therefore, to a decrease in the formation of solute-solvent hydrogen bonding in the excited singlet-state relative to the ground-state. Moreover, the a and b coefficient values are generally smaller than the corresponding s coefficients for $\tilde{\nu}_A$, and greater than the s values for $\tilde{\nu}_F$. These differences probably indicate that the ability of the solvents to donate or to accept hydrogen bonds from the thienobenzofurans under study is weaker than the solute-solvent dipole-dipole interactions in the

ground-state and stronger in the excited singlet-state of these thienobenzofurans. A comparable behavior has been observed in the case of series of benzo[*a*]phenothiazines [44] and of fused benzothienothiophenes [5].

For the Kamlet-Abboud-Taft correlations of the fluorescence quantum yields, we applied the approach of Burget and Jacques [45], based on a successful relationship established between $\ln([1/\Phi_F] - 1)$ and the Kamlet-Abboud-Taft solvatochromic parameters for thioxanthone. In the case of the fluorescence quantum yields of thienobenzofurans, we obtained relationships presenting a good linearity with correlation coefficients close to 0.98 for most solvents (Table 5). Most s , a and b regression coefficients present negative values, which suggest an increase of the fluorescence quantum yield of thienobenzofurans with the solvent polarity/polarizability and hydrogen-bond donor and acceptor abilities. We have found similar results for the solvent effect on the fluorescence quantum yields of fused BTT and BTI derivatives [5], and of poly(3-methoxythiophene) [46].

Conclusion

In this work we have investigated the solvent and structural effects upon the electronic absorption and fluorescence

spectra and fluorescence quantum yields of three new fused benzothienofurans. We have established satisfactory linear Kawski-Chamma-Viallet and McRae solvatochromic correlations characterized by slope small positive values, which allows us to demonstrate the existence of a weak negative solvatochromism, and to predict that the benzothienofurans under study should be weakly less polar in the excited singlet-state than in the ground-state. We have also found that there is an acceptable agreement between the experimental and theoretical ground-state dipole moments of benzothienofurans. The solvatochromic correlations indicate that these compounds should possess slightly smaller dipole moment values in their first excited singlet-state than in the ground-state. This suggests a significant electronic redistribution in the excited singlet-state. In addition, we have obtained, for the three benzothienofurans, precise Kamlet-Abboud-Taft multiparameter relationships. The characteristics of the later relationships indicate that the ability of the solvents to donate or to accept hydrogen bonds is weaker than the solute-solvent dipole-dipole interactions in the ground-state and stronger in the singlet excited-state of thienobenzofurans. Finally, our study of the solvent effects on fluorescence quantum yields allowed us to conclude that, in most case, an increase of Φ_F was observed in the polar solvents relative to the non polar ones, and that satisfactory Kamlet-Abboud-Taft solvatochromic relationships were also established for the fluorescence quantum yields of thienobenzofurans.

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