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Photophysical properties and quantum chemical calculations of differently substituted 2(2-phenylethenyl)-benzoxazoles and benzothiazoles

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Abstract

The low fluorescence quantum yield of 2(2-phenylethenyl)-benzoxazoles and benzothiazoles in solution at room temperature is attributed to intramolecular librations with great amplitude of the two heavy fragments at the both ends of the allyl chain. Freezing the solutions at 77 K leads to remarkable increase of fluorescence quantum yield up to three orders of magnitude. No phosphorescence at 77 K is observed. The analysis of the results from quantum-chemical calculations (AM1 approximation) supports the hypothesis for the quenching processes in excited sate. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: 2(2-Phenylethenyl)-benzoxazoles and benzothiazoles; Fluorescence; Quantum-chemical calculations — AM1 approximation

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1. Introduction

Scheme 1 shows the structure of the investigated compounds and the corresponding substituents. The practical interest upon 2(2-phenylethenyl)- benzoxazoles and benzothiazoles is based on their widespread application. They have been investigated to their clinical efficacy for use as an ophthalmic drug to lower intraocular pressure [1], anti-tumor [2] and anti-HIV-1 [3–5] activity. The presented compounds are also useful intermediates in the synthesis of heterocyclic compounds [6,7], suitable sensitizers for photographic halide emulsions [8–10] and have third-order nonlinear optical [11,12] effectiveness. Along with that there are spectroscopic data including IR spectra [13,14], mass spectra [15], NMR spectra [16,17] but there are not any detailed steady-state and dynamic photophysical study on the investigated compounds presented in Scheme 1. In [18] only the influence of OCH_3, Cl and $N(CH_3)_2$ substituents in phenyl fragment of 2-phenylbenzothazoles upon the fluorescence ability is followed. Absorption and fluorescence data on substituted 2-phenylbenzothiazoles and their vinylogues are presented in [19] without discussions.

The aim of the present paper is to follow the effect of different substituents on X, Y and Z-position in 2-(2-phenylethenyl) benzazole fragment (Scheme 1) and the influence of polarity and proton-donating ability of the solvents at room temperature and 77 K on the characteristics of electronic spectra. Quantum-chemical calculations are carried out to estimate the changes in the π-electron distribution in ground and in fluorescence excited state and to follow the energy of the molecule in relation to rotation of the phenyl fragment.

2. Experimental details

The compounds are synthesised by condensation of corresponding 2-alkylbenzazoles with aromatic aldehydes: **1–3** and **17–20** [20], **4–6** [21], **7–10** and **23–26** [22], **11–16** [23] and **21–22** [24].

The absorption spectra are recorded on Specord UV–VIS spectrophotometer (Carl Zeiss Jena). The corrected fluorescence spectra as well as corrected excitation spectra are recorded on a Perkin–Elmer MPF 44 spectrofluorimeter. The fluorescence quantum yields (Q_f) are measured relating to *p*-methoxy-benzylidenphtalide (Q_f=14 in ethanol) [25]. The low temperature luminescence measurements are performed at 77 K in the standard phosphorescence accessory to MPF 44 in quarts tubes of 4 mm diameter. Fluorescence-grade solvents are used. The fluorescence decay curves (10,000 counts in the maximum, time resolution=0.1 ns/chan) are

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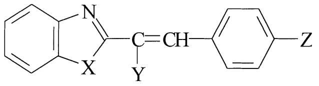

Comp. No	X	Y	Z	*Comp. No*	X	Y	Z
1	S	CH_3	OCH_3	***14***	S	CN	H
2	S	CH_3	CH_3	***15***	S	CN	Cl
3	S	CH_3	Cl	***16***	S	CN	NO_2
4	S	C_6H_5	OCH_3	***17***	O	CH_3	OCH_3
5	S	C_6H_5	CH_3	***18***	O	CH_3	CH_3
6	S	C_6H_5	Cl	***19***	O	CH_3	H
7	S	H	OCH_3	***20***	O	CH_3	Cl
8	S	H	CH_3	***21***	O	C_6H_5	CH_3
9	S	H	H	***22***	O	C_6H_5	Cl
10	S	H	Cl	***23***	O	H	$N(CH_3)_2$
11	S	CN	$N(CH_3)_2$	***24***	O	H	OCH_3
12	S	CN	OCH_3	***25***	O	H	H
13	S	CN	CH_3	***26***	O	H	Cl

Scheme 1. Structure and substituents of the investigated compounds.

collected at room temperature on a nanosecond single photon counting spectrofluorometer system PRA 2000, using a nitrogen filling flash lamp with λex=337 and emission wavelength corresponding to the maximum of the fluorescence band. The natural lifetime τ is estimated by a standard deconvolution procedure, the accuracy of the fit is controlled by the weight residuals, the autocorrelation function of the residuals and the reduced χ^2.

The quantum-chemical calculations are carried out using computational program VAMP 6.5 [26] with AM1 approximations. The calculations include geometry optimisation with optimiser Jon Baker's Eigenvector following (EF) [27], reaction path calculations, taking into consideration all single and double excited configurations among 10 molecular orbitals and simulating solvent effects in ground and excited state using the numerical self-consistent-reaction-field (SCRF) method [28].

3. Results and discussions

The absorption and fluorescence spectra of the investigated benzazoles (Scheme 1) are recorded in solvents of different polarity and proton-donating ability (hexane, heptane, cyclohexane, acetone, acetonitrile, methanol, *n*-propanol and *n*-butanol) at room temperature and frozen matrix at 77 K.

3.1. Absorption

In Table 1 the absorption and fluorescence characteristics of 2(2-phenylethenyl) benzazole derivatives are presented. Fig. 1 shows the absorption and corrected fluorescence spectra of compound 25 (X=O, Y=H, Z=H). Vertical lines specify the energy and intensity of the calculated oscillator strengths.

Absorption spectra of all compounds in the region 250–500 nm consist of one wide absorption band with

Table 1

Spectral characteristics of the investigated compounds (1–26) in cyclohexane and methanol at 300 K[a]

Compound No.	Cyclohexane			Methanol			
	λ_{abs}	λ_{fl}	Q_{fl}	λ_{abs}	ε	λ_{fl}	Q_{fl}
1	330	400	0.001	330	20.6	420	<0.001
2	320	390	0.003	325	20.8	400	0.001
3	320	390	0.03	320	22.9	400	0.005
4	350	400	<0.001	350	25.9	420	0.001
5	340	380	<0.001	345	24.5	410	<0.001
6	340	420	0.001	340	27.2	430	0.001
7	350	400	0.005	350	31.1	420	0.001
8	345	390	0.02	345	42.2	405	0.003
9	340	390	0.04	340	24.7	400	0.007
10	340	395	0.04	340	12.0	400	0.01
11	430	500	<0.001	450	13.0	520	<0.001
12	365	–	–	375	21.0	–	–
13	350	–	–	355	16.0	–	–
14	350	430	<0.001	350	19.0	–	–
15	350	390	<0.001	350	16.0	430	<0.001
16	360	450	<0.001	360	19.9	520	0.003
17	320	380	0.002	325	34.7	400	<0.001
18	315	370	0.004	315	16.2	380	0.002
19	315	370	0.007	315	24.3	380	0.002
20	320	375	0.02	320	25.7	380	0.003
21	325	380	0.008	330	31.3	385	0.004
22	330	–	–	330	30.7	420	0.002
23	380	430	0.005	390	22.5	490	0.007
24	330	390	0.006	340	37.4	420	0.001
25	320	380	0.05	320	21.8	380	0.006
26	325	380	0.14	330	32.8	385	0.02

[a] λ_{abs} and λ_{fl} — absorption and fluorescence Frank–Condon transitions in (nm), ε — molar extinction coefficient in ($l\,mol^{-1}\,cm^{-1}$), Q_f — fluorescence quantum yield.

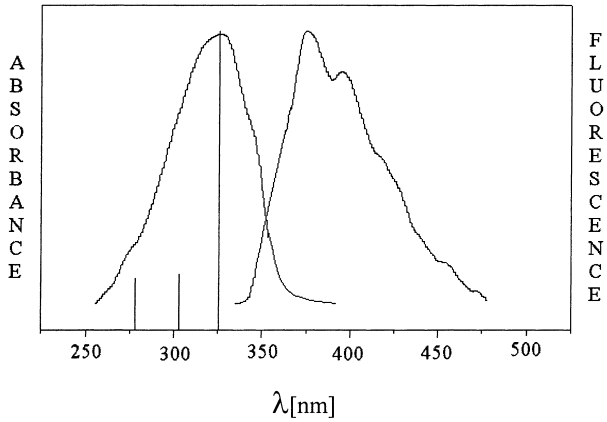

Fig. 1. Absorption and fluorescence spectra of compound **25** in cyclohexane at 300 K. The vertical lines denote the computed energies of the $\pi\pi^*$ transitions and the corresponding oscillator strengths.

molar extinction coefficient — ε at about 20,000 l mol^{-1} cm^{-1} (Table 1). The results from quantum-chemical calculations show that in the region of this band there are three overlapping electronic $\pi\pi^*$ transitions and this explains the large width of the absorption band (Fig. 1). In all solvents used the Franck–Condon absorption transition shifts batochromically with about 2000 cm^{-1} from compounds with X=O to compounds with X=S — see for instance the data for compounds **9** and **25** in Table 1. With increasing the electron-donating ability of the Y-substituents the absorption maximum shifts hypsochromically with about 1500 cm^{-1}, while the electron accepting CN group on Y-position shifts the absorption maximum to the red (refer to the corresponding data for compounds **1**, **4**, **7** and **12** in Table 1). The presence of CH_3, OCH_3, Cl, and NO_2 substituents in Z-position do not affect significantly the energy of the Franck–Condon absorption transition (Table 1). But similarly to 2-phenylbenzazoles [29] the presence of strongest electron donating $N(CH_3)_2$ group in Z-position — compounds **11** and **23**, shifts the absorption maximum strongly to the red with more than 5000 cm^{-1} in comparison to compounds with Z=H — **14** and **25**, respectively.

3.2. Fluorescence

The Franck–Condon fluorescence transition of compounds with X=O is hypsochromically shifted in comparison to compounds with X=S both in non-polar and in polar solvent similarly to the absorption (Table 1). There is not effect of the Y and Z-substituents (Scheme 1) on the energy of the fluorescence maxima of the compounds investigated. The fluorescence spectrum is independent of the excitation wavelength and has a clear vibronic structure (Fig. 1). The corrected excitation spectrum is identical to the absorption spectrum in all solvents used. The Stockes shifts increase slightly from 4400 cm^{-1} in hexane to 5200 cm^{-1} in *n*-butanol for all compounds investigated. According the Lippert's model [30] the difference between the dipole moments in the ground and excited state is calculated about 1.5 D.

Most of the studied compounds have a weak fluorescence in solutions at room temperature with Q_f at about 10^{-2}–10^{-3} or lower. The exceptions are compounds **12**, **13** and **22** which practically do not fluoresce in any solvents (Table 1) and compound **26** (X=O Y=H Z=Cl) which has fluorescence quantum yield in cyclohexane (Q_f=0.14) in two orders higher than Q_f of other compounds. The observed high Q_f in compound **26** could be attributed to the presence of the halogen substituent Cl on *p*-position in the phenyl fragment. According to the literature [31] the influence of Cl-substituent can lead either to increasing of the fluorescence quantum yield or to its decreasing without any changes in the position of the fluorescence maximum.

Increasing of the solvent polarity leads to decreasing of the fluorescence quantum yield up to one order of magnitude (Table 1) for all compounds. There is no evidence for the specific influence of the proton-donating ability of the solvents upon lowering of Q_f caused by forming of intramolecular hydrogen bonds in excited state [32].

Table 2
Spectral characteristics in methylcyclohexane and ethanol at 300 and 77 K

Comp. No.	Methylcyclohexane			Ethanol		
	λ_{fl} (77 K)	Q_f (300 K)	Q_f (77 K)	λ_{fl} (77 K)	Q_f (300 K)	Q_f (77 K)
1	400	0.001	0.28	420	<0.001	0.56
3	378	0.03	0.28	395	0.005	0.17
6	455	0.001	0.37	466	0.001	0.43
8	397	0.02	0.31	400	0.003	0.24
9	389	0.04	0.27	393	0.007	0.36
11	490	<0.001	0.3	500	<0.001	0.3
16	500	<0.001	0.07	527	0.003	0.11
18	378	0.004	0.92	385	0.002	0.66
19	370	0.007	0.86	383	0.002	0.89
21	428	0.008	0.87	418	0.004	0.47
25	378	0.05	0.9	380	0.006	0.7
26	384	0.14	0.88	386	0.02	0.99

Table 3
Natural lifetime τ, constants of radiative K_f and non-radiative K_{nf} transitions, calculated from τ and Q_f in cyclohexane and methanol at 300 K

Comp. No.	Cyclohexane			Methanol		
	τ	K_f	K_{nf}	τ	K_f	K_{nf}
9	0.17	0.23	5.65	–	–	–
10	0.35	0.11	2.67	0.3	0.032	3.19
25	0.16	0.29	5.59	0.31	0.02	3.1
26	0.2	0.67	4.1	0.16	0.11	5.76

Baring in mind the structure of the investigated compounds — two heavy fragments connected by allyl chain, the most probable explanation for the low Q_f in solvents at room temperature are intramolecular librations with great amplitude in the fluorescent excited state. This hypothesis is supported by the results in frozen matrix at 77 K where the fluorescence quantum yield of the investigated compounds in all solvents used increases with more than two orders of magnitude, for compound **25** Q_f in cyclohexane increases in two times — Table 2. In the literature such effect is considered as strong evidence that the quenching of the fluorescence intensity is caused by intramolecular motions of great amplitude in the fluorescence excited state [33]. In frozen solutions at 77 K the Franck–Condon fluorescence transitions are hypsochromically shifted with at about 500–1000 cm^{-1} against the corresponding data at room temperature similarly to literature [34]. No phosphorescence at 77 K for all of the compounds is recorded.

The fluorescence decay curves in methanol and cyclohexane solutions are monoexponential. The natural lifetimes of the fluorescence $S_1(\pi\pi^*)$ state, the radiative and nonradiative rate constants K_f and K_{nf} for some of the studied compounds — **9** (X=S Y=H Z=H), **10** (X=S Y=H Z=Cl), **25** (X=O Y=H Z=H) and **26** (X=O Y=H Z=Cl) are given in Table 3. With increasing of Q_f the calculated K_f values increase and K_{nf} values decrease simultaneously both in cyclohexane and methanol.

4. Quantum-chemical calculations

The hypothesis for the quenching of the emission by intramolecular motions is supported also by the quantum-chemical calculations. The data in Fig. 2 show that upon excitation to the S_1 state the bond order of the central double bond decreases, while that of the neighbouring single bonds increases similarly as in [35,36] and this leads to a considerable smoothing of bond alternation (Fig. 2). This result is in line with the high fluorescence ability of the compounds at 77 K as it is seen from the data in Table 2. But at the same time diminishing the bond order of the double bond in the S_1 $(\pi\pi^*)$ state makes the non-radiating processes due to intramolecular librations with great amplitude along it more probable and it is in accordance with the low Q_f at room temperature. The results from the reaction path calculations with rotation of the phenyl fragment (Fig. 3) show that the most stable structure in the lowest excited singlet state $(\pi\pi^*)$ of compound 25 (X=O, Y=H, Z=H) is that in which the two heavy fragments at the ends of the allyl chain are situated in one plane. This is in agreement with the pronounced conjugation of the π-electronic structure — see bond orders values in S_1 in Fig. 2. The calculated energy diagram (Fig. 3) indicates for the significant difference between the energies of S_0 and fluorescence excited state and this fairly corresponds to the experimentally observed large value of Stockes shift (Table 1).

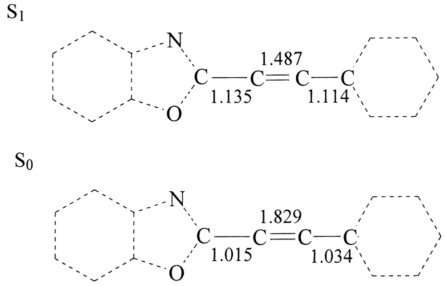

Fig. 2. Calculated π — bond orders in allyl chain for compound **25** in S_0 an S_1 $(\pi\pi^*)$ state.

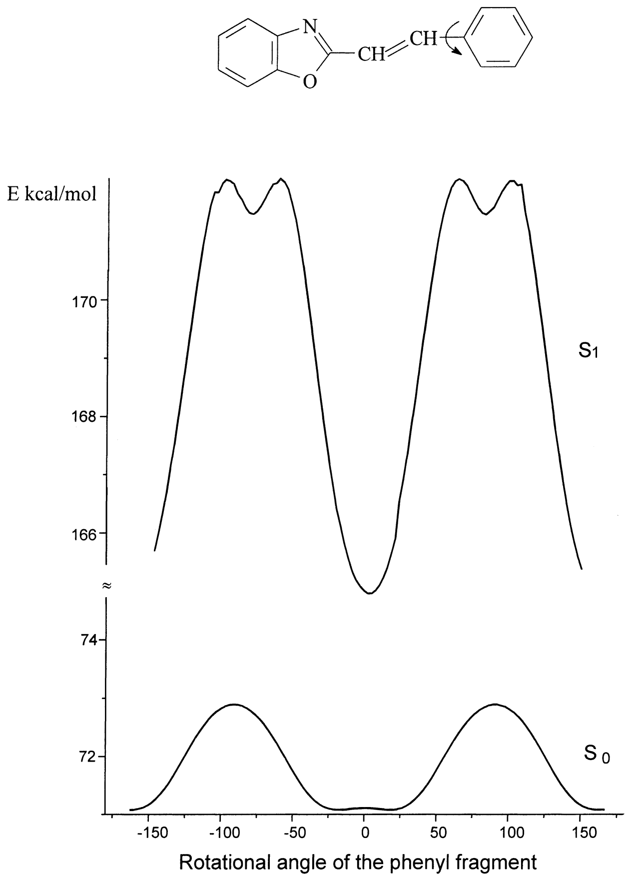

Fig. 3. The molecular energy of compound **25** in relation to rotation of the phenyl fragment.

5. Conclusions

The experimental results for the luminescence characteristics of 2(2-phenylethenyl)-benzoxazoles and benzothiazoles in solution at room temperature and in frozen matrix at 77 K indicate that the low fluorescence quantum yield of these structures at 300 K is connected with intramolecular motions with great amplitude. This hypothesis is supported by the analysis of the quantum-chemical calculations (AM1 approximation) of model structure in ground and excited state.

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