Steady State and Dynamic Photophysical Properties of 2-Benzoimidazoleacetonitrile-α-Phenylmethylenes and 1-Aryl-2,2-Dicyanoethenes

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The steady state and dynamic photophysical characteristics of newly synthesized 2-benzoimidazoleacetonitrile-α-phenylmethylenes (BIA's) and 1-aryl-2,2-dicyanoethenes (DCE's) have been investigated in solution at 300 K and in a frozen matrix at 77 K.

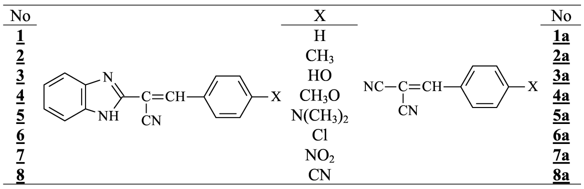
The compounds have a very low or no emission in solution at 300 K both in non-polar and polar solvents. While in BIA's a significant fluorescence ability is registered in a frozen ethanol matrix at 77 K, freezing solutions of DCE's at 77 K does not lead to the appearance of either fluorescence or phosphorescence at 77 K even in the presence of C_2H_5J. The comparison of the fluorescence ability in aprotic and protic solvents does not show any evidence for the specific influence of the proton-donating ability of the solvents on the weak fluorescence caused by the formation of intramolecular hydrogen bonds in excited states.

The high fluorescence quantum yield of BIA's in a frozen matrix at 77 K indicates that intramolecular libration of two heavy groups in the allyl chain is the reason for the weak fluorescence at 300 K. Quantum-chemical calculations support the hypothesis of quenching processes in the excited state of BIA's at 300 K.

Key words: 2-Benzoimidazoleacetonitrile-α-Phenylmethylenes; 1-Aryl-2,2-Dicyanoethenes; Fluorescence; Frozen Matrix.

1. Introduction

Scheme 1 shows the structure of the investigated compounds 2-benzoimidazoleacetonitrile-α-phenylmethylenes (BIA): compounds **1 – 8** and 1-aryl-2,2-dicyanoethenes (DCE): compounds **1a – 8a** with the corresponding substitutes. The practical interest on such structures containing strongly delocalized π-electrons with electron-donor and electron-acceptor groups on the opposite sides of the molecule is based mainly on their possible application as non-linear optical devices [1 – 9], as well as intermediates in the synthesis of heterocyclic compounds [10, 11], building blocks for numerous conventional and functional dyes [12, 13], e.g. color-formers and NIR dyes [14], suitable sensitizers for photographic halide emulsions [15 – 17], dyes for light-resistant thermal transfer recording [18] and fluorescence-based plasma viscometers [19].



No	X	No
1	H	1a
2	CH_3	2a
3	HO	3a
4	CH_3O	4a
5	$N(CH_3)_2$	5a
6	Cl	6a
7	NO_2	7a
8	CN	8a

Scheme 1. Structure and substituents of the investigated compounds.

The aim of the present paper is to study the effect of different substitutes on the X-position in both groups of compounds investigated (Scheme 1), and the influence of the polarity and proton-donating ability of the solvents at room temperature and 77 K on the characteristics of the electronic spectra. Quantum-chemical calculations are carried out to estimate the changes in the π-electron distribution in the ground and fluorescence excited state.

2. Experimental Details

The compounds are synthesized by Knoevenagel condensation of (2-benzimidazolyl)-acetonitrile or

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Table 1. Spectral characteristics of the investigated compounds (**1** – **8**) in ethanol (E) and benzene (B) at 300 K and 77 K. ν_{abs} and ν_{fl}: absorption and fluorescence Frank-Condon transitions in [cm^{-1}], ε: molar extinction coefficient in [lmol^{-1}cm^{-1}], Q_{fl}: fluorescence quantum yield, τ: natural lifetime in [ns], –: no fluorescence, /: no measurments.

No		300 K					77 K		
		ν_{abs}	$\varepsilon \cdot 10^3$	ν_{fl}	Q_{fl}	τ (A%)	ν_{fl}	Q_{fl}	τ (A%)
1	E	28,655	15.5	22,730	< 0.001	/	23,700	0.39	/
	B	27,780	/	21,505	< 0.001	/	–	/	/
2	E	28,170	19.0	22,730	< 0.001	0.21 (96.6) 16.78 (3.4) $\chi^2 - 1.04$	23,475	0.87	1.97 (98.53) 9.18 (1.47) $\chi^2 - 1.11$
	B	27,030	/	20,830	< 0.001	/	–	/	/
3	E	26,680	26.3	21,280	< 0.001		22,320	0.72	/
	B	27,030	/	21,740	< 0.001	/	–	/	/
4	E	27,030	40.4	22,730	< 0.001		22,830	0.91	/
	B	26,315	/	21,280	< 0.001	/	–	/	/
5	E	23,255	8.2	20,000	< 0.001	/	20,475	0.85	/
	B	22,990	/	20,200	< 0.001	/	–	/	/
6	E	27,780	44.0	21,505	0.001	0.22 (97.19) 11.89 (2.81) $\chi^2 - 1.27$	23,255	0.89	1.94 (98.27) 9.10 (1.73) $\chi^2 - 1.31$
	B	27,030	/	21,280	< 0.001	/	–	/	/
7	E	26,315	11.0	17,545	0.004	0.32 (95.81) 14.65 (4.19) $\chi^2 - 1.6$	20,880	0.3	1.55 (87.52) 6.49 (7.11) $\chi^2 - 1.28$
	B	25,315	/	20,000	0.007	/	–	/	/
8	E	27,030	21.0	19,685	0.21	2.57 (96.03) 9.8 (3.77) $\chi^2 - 2.32$	22,575	0.93	2.15 (92.89) 6.67 (6.63) $\chi^2 - 1.04$
	B	26,315	/	20,410	0.11	/	–	/	/

malononitrile and the corresponding aldehydes in the presence of piperidine in ethanol.

The absorption spectra are recorded on a 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_{fl}) are measured in their relation to *p*-methoxybenzylidenphtalide ($Q_{\mathrm{fl}} = 0.14$ in ethanol) [20]. The low temperature luminescence measurements are performed at 77 K in the standard phosphorescence accessory to MPF 44 in quartz tubes of 4 mm diameter. In all experiments fluorescence-grade solvents are used. The fluorescence decay curves (10,000 counts in the maximum, time resolution = 0.1 nsec/chan) are collected at room temperature and 77 K on a nanosecond Single Photon Counting spectrofluorimeter System PRA 2000, using a nitrogen filling flash lamp with $\lambda_{\mathrm{ex}} = 356$ and an 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 chi-square. The quantum-chemical calculations are carried out with utilizing the AM1 semi-empirical method of the MOPAC 7.0 package, taking into consideration all single and double excited configurations among 10 molecular orbitals [21].

3. Results and Discussions

3.1. Absorption

In Tables 1 and 1a the absorption and fluorescence characteristics of BIA and DCE in ethanol and benzene at 300 K and 77 K are presented. Figures 1 and 1a show the absorption and corrected fluorescence spectra of compounds **1** (X = H) and **5** (X = $N(CH_3)_2$), and **1a** (X = H) and **5a** (X = $N(CH_3)_2$) in ethanol at 300 K. Vertical lines specify the energy and intensity of the calculated oscillator strengths.

The absorption spectra of all compounds in ethanol at 300 K are in the region 40,000 – 18,000 cm^{-1}, consisting of one longest wavelength absorption band with a molar extinction coefficient ε in the range 6,000 – 82,000 lmol^{-1}cm^{-1} (Tables 1 and 1a, Figures 1 and 1a). In the group of BIA the second absorption band at about 280 nm is due to the S_0-S_2 electronic transition, as is seen from the quantum-chemical calculations (Figure 1). The absorption

Table 1a. Spectral characteristics of the investigated compounds (**1a** – **8a**) in ethanol (E) and benzene (B) at 300 K and 77 K.

No		300 K				77 K	
		ν_{abs}	$\varepsilon \cdot 10^3$	ν_{fl}	Q_{fl}	ν_{fl}	Q_{fl}
1a	E	32,260	11.2	–	/	–	/
	B	31,745	/	–	/	–	/
2a	E	30,770	9.4	–	/	–	/
	B	30,300	/	–	/	–	/
3a	E	27,780	22.2	25,640	< 0.001	–	/
	B	28,820	/	–	/	–	/
4a	E	28,570	31.0	24,390	< 0.001	–	/
	B	28,170	/	–	/	–	/
5a	E	23,255	82.0	20,830	< 0.001	21,740	0.80
	B	23,255	/	21,980	< 0.001	–	/
6a	E	31,250	6.2	–	/	–	/
	B	30,770	/	–	/	–	/
7a	E	32,790	16.0	28,570	< 0.001	–	/
	B	32,260	/	–	/	–	/
8a	E	33,330	17.0	20,245	< 0.001	–	/
	B	31,745	/	22,730	< 0.001	–	/

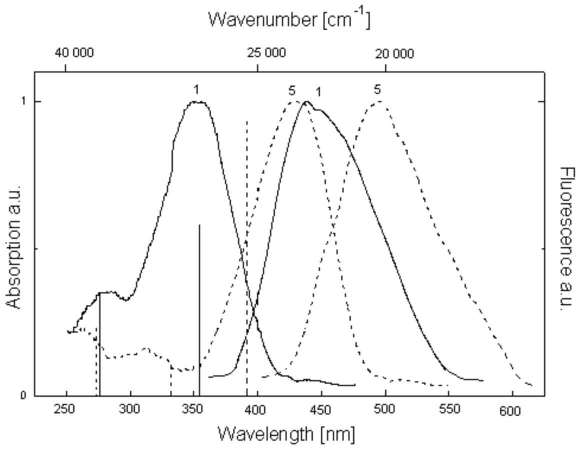

Fig. 1. Absorption and fluorescence spectra of the compounds **1** (X = H) and **5** (X = $N(CH_3)_2$) in ethanol at 300 K. The vertical lines denote the computed energies of the $\pi\pi^*$ transitions and the corresponding oscillator strengths.

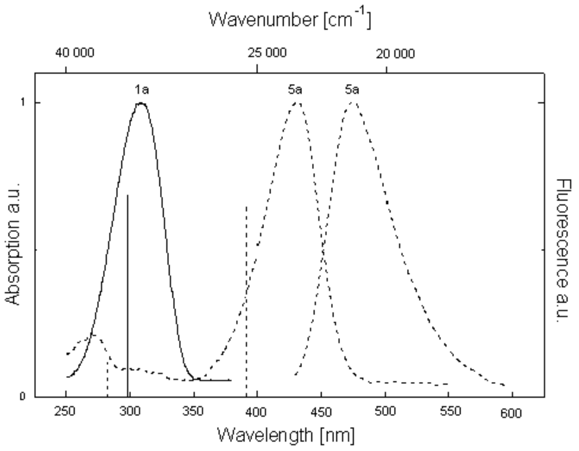

Fig. 1a. Absorption and fluorescence spectra of the compounds **1a** (X = H) and **5a** (X = $N(CH_3)_2$) in ethanol at 300 K.

Frank-Condon transitions of BIA are hypsochromically shifted by about 500 cm^{-1} in comparison to 2-benzothiazoleacetonitrile-α-phenylmethylenes [22]. This agrees with [23] where it is shown that due to replacement of an S-atom with an N-atom in a delocalized system a blue shift of the absorption maximum is observed. The substitution of the benzoimidazole fragment (BIA) with a CN-group (DCE) leads to a hypsochromic shift of the longest wavelength absorption band up to 6300 cm^{-1} in the case of X = NO_2 (compounds **7** and **7a**), because of the shortened π-conjugated system. The energy of the absorption maxima of all compounds shifts bathochromically with increasing electron-donating and electron-withdrawing ability of the substitute X, thus indicating the presence of conjugation through the systems. In the case of the compounds **5** and **5a**, introducing of $N(CH_3)_2$ at the *p*-position in the phenyl ring leads to a new absorption band bathochromically, shifted by about 5400 cm^{-1} and 9000 cm^{-1}, respectively, against the longest wavelength absorption band of **1** (X = H) (Figure 1) and **1a** (X = H) (Figure 1a). In the literature [24] such an effect concerning similar compounds is attributed to a charge transfer transition determined by the presence of the strongest electron-donating substitute $N(CH_3)_2$

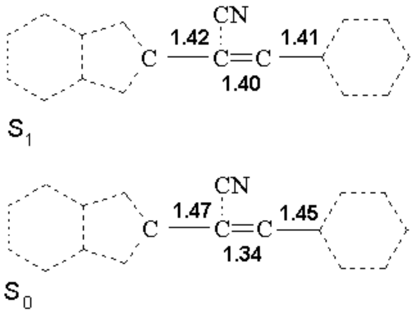

Fig. 2. Calculated bond lengths in the allyl chain of compound **1** in the S_0 and S_1 ($\pi\pi^*$) state.

and the electron-withdrawing CN-group. The results of quantum-chemical calculations support the assumption that the new absorption band of **5** and **5a** is due to an additional transition; the calculated orbitals indicate a conjugation of the donor and acceptor moieties, which lay in the planes at about 33° and make possible [25] the CT processes.

In benzene the Franck-Condon absorption transition shifts batochromically by about 700 cm^{-1} (Tables 1 and 1a) in comparison to ethanol. This indicates negative solvatochromism, which is rationalized as arising from a more polar ground state than the excited state [26].

3.2. Fluorescence

The investigated compounds have weak (Q_fl at about 10^{-2} – 10^{-3}) or no fluorescence in solution at room temperature (Tables 1 and 1a). The only exception is compound **8** (X = CN) which has a fluorescence quantum yield in ethanol ($Q_\text{fl} = 0.21$) by two orders higher than Q_fl of the other compounds.

The maxima of Franck-Condon fluorescence transitions of the compounds are in the region 22,700 – 19,600 cm^{-1} (Tables 1 and 1a) with the exception of compound **7** (X = NO_2). It has a maximum at 17,540 cm^{-1} and a very broad fluorescence band (FWHM = 17,000 cm^{-1}). As ascribed in the literature [20], this effect can be attributed to the presence of the NO_2-group. The fluorescence spectra are independent of the excitation wavelength and the corrected excitation spectra are identical to the absorption spectra in all solvents used.

There is no evidence for a specific influence of the proton-donating ability of the solvents upon the low fluorescence quantum yield caused by forming of intramolecular hydrogen bonds in excited state [27] of all compounds investigated.

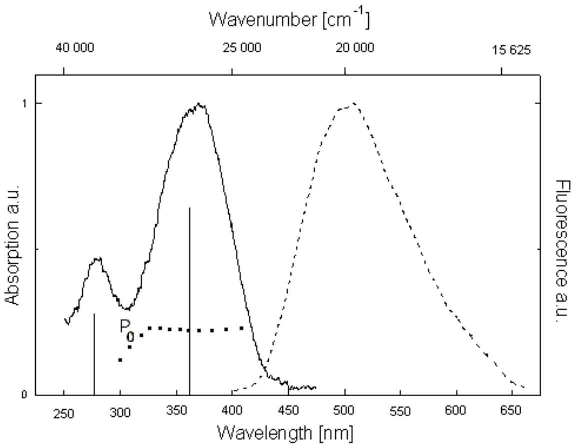

Fig. 3. Absorption and fluorescence spectra of compound **8** (X = CN) in ethanol at 300 K. Vertical lines indicate the calculated electron transitions, P_0: polarization degree in frozen ethanol matrix at 77 K.

Bearing in mind the structure of the investigated 2-benzoimidazoleacetonitrile-α-phenylmethylenes – two heavy fragments connected by an allyl chain, the most probable explanation of the low Q_fl at room temperature is intramolecular out-of-plane motions in the fluorescence excited state, which is also in line with some literature data [28]. This hypothesis is supported by results in the frozen matrix at 77 K, where the fluorescence quantum yield of BIA in all solvents used increases by more than two orders of magnitude, for compound **8** Q_fl increases twice – Table 1. In frozen solutions at 77 K the Franck-Condon fluorescence transitions are hypsochromically shifted (Table 1) against the corresponding maxima at room temperature similarly to literature data [29].

The hypothesis of quenching of the emission by intramolecular motions in the case of BIA is supported also by quantum-chemical calculations. The data in Fig. 2 show that upon excitation to the S_1 ($\pi\pi^*$) state the bond length of the central double bond in **1** increases, while that of the neighbouring single bonds decreases similarly as in [30, 31], and this leads to a considerable smoothing of the bond alternation. The energy-minimized conformation of molecule **1** shows a torsional angle of 28° between the planes of the phenylene and benzimidazole part in the S_1($\pi\pi^*$) state. This is in line with the high fluorescence ability of the com-

Table 2. Absorption (ν_{abs}) and fluorescence (ν_{fl}) Frank-Condon transitions and fluorescence quantum yield (Q_{fl}) of compounds **5** and **8** in different solvents at 300 K

No	Solvent	**5** ν_{abs}	**5** ν_{fl}	**5** Q_{fl}	**8** ν_{abs}	**8** ν_{fl}	**8** Q_{fl}
1	Benzene	22,990	20,200	0.004	26,315	20,410	0.10
2	Chlorbenzene	22,730	20,410	0.002	26,315	20,200	0.22
3	Diethylether	23,700	20,245	< 0.001	26,670	20,500	0.30
4	Chloroform	22,780	20,160	< 0.001	26,315	20,000	0.14
5	Methylenchlorid	22,780	20,120	0.001	27,030	20,200	0.18
6	1-Butanol	23,810	20,580	< 0.001	27,030	20,200	0.35
7	1-Propanol	23,310	20,580	< 0.001	27,030	20,160	0.25
8	Acetone	23,420	20,325	< 0.001	27,030	20,000	0.26
9	Ethanol	23,255	20,000	< 0.001	27,030	19,685	0.21
10	Acetonitrile	23,420	19,920	< 0.001	27,780	19,840	0.20
11	Methanol	23,255	20,000	< 0.001	27,780	19,800	0.12

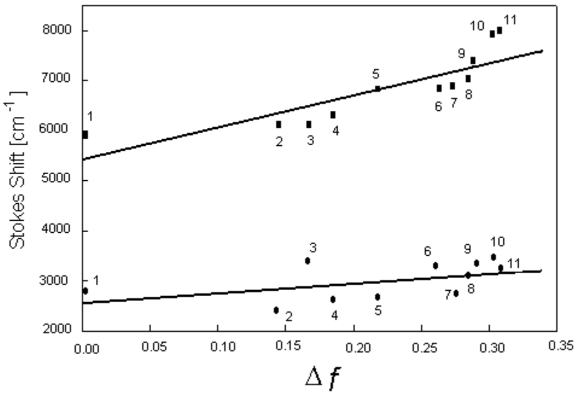

Fig. 4. Dependence of the Δf constant of the solvents on the Stokes shift of compounds **5** (●) and **8** (■). The numbering denotes the solvents listed in the Table 2.

pounds at 77 K, as it is seen from the data in Table 1. But at the same time increasing of the double bond length in the $S_1(\pi\pi^*)$ state intensifies the probability of the non-radiating processes due to intramolecular libration along it, and this explains the low fluorescence quantum yield of BIA at room temperature.

Although the difference between the two presented structures is only the benzoimidazole fragment, freezing the solutions of DCE at 77 K does not lead to the appearance of either fluorescence or phosphorescence at 77 K even in the presence of C_2H_5J. These peculiarities in the luminescence ability of 1-aryl-2,2-dicyanoethenes are not yet understood.

The polarization degree P_0 computed from the polarized fluorescence excitation spectra of **8** remains constant (about 0.35) over the whole longest wavelength absorption band (33,300–23,800 cm^{-1}) (Figure 3), the angle between the absorption and the emission transition moments calculated in [32] is $\beta = \pm 31 + \pi$.

As is seen in Fig. 4, the Stokes shift of the compounds **5** and **8** becomes larger with increasing solvent polarity. According to Lippert's model [33], the difference of the dipole moments in the ground and excited state is 3.1 D and 6.2 D for the compounds **5** and **8**, respectively. The good match with the theoretical values, which are 2.8 D and 7.2 D, is worth mentioning.

The natural lifetimes τ of the fluorescence $S_1(\pi\pi^*)$ state and the amplitudes of the studied compounds **2** (X = CH_3), **6** (X = Cl), **7** (X = NO_2) and **8** (X = CN) are presented in Table 1. The fluorescence decay curves of all investigated compounds are biexponential both in ethanol solutions at 300 K and in the frozen matrix at 77 K. The amplitude of each lifetime is given in percent, where the sum of the amplitudes of the two components is scaled to 100%.

At 77 K the fluorescence lifetimes of all investigated compounds are resembling – one short component of about 2 ns with a very high amplitude (about 95%) and a second component with a longer lifetime of about 10 ns.

In the case of compound **8**, which has a high luminescence quantum yield both at 300 K ($Q_{\text{fl}} = 0.21$) and 77 K ($Q_{\text{fl}} = 0.93$), the values of the two lifetime components and the ratio between their amplitudes is at room temperature the same as at 77 K, and this indicates that most probably the deactivation mechanism in solution and in the frozen matrix is similar. In the compounds **2**, **6** and **7**, however, which have a weak fluorescence at 300 K, the ratio between the amplitudes of short and long lifetimes at room temperature is the same as at 77 K, but the magnitude of shorter lifetime component diminishes by one order and becomes about 0.22 ns (Table 1). The fluorescence lifetime data reveal that low fluorescence quantum yields are characterized also by a short component in the fluorescence decay curve.

4. Conclusions

The experimental results of the steady state photophysical characteristics of 2-benzoimidazoleacetonitrile-α-phenylmethylenes in solution at 300 K as well as in frozen matrix at 77 K indicate that the low emission in solution at 300 K is due to intramolecular out-of-plane motions of the two heavy groups in the allyl chain. The analysis of the fluorescence lifetime data reveale that the low fluorescence quantum yields in solution at room temperature are characterized also by a shorter component in the fluorescence decay curves.

1-aryl-2,2-dicyanoethenes have no fluorescence both in non-polar and polar solvent at 300 K and freezing of the solutions at 77 K does not lead to the appearance of either fluorescence or phosphorescence even in the presence of C_2H_5J.

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