

SPECTROSCOPY, PHOTOPHYSICS AND PHOTOCHEMISTRY OF 1,3-DIKETOBORONATES

IV: LUMINESCENCE SPECTROSCOPIC INVESTIGATIONS OF 2-NAPHTHYL-SUBSTITUTED 1,3-DIKETOBORONATES

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Summary

Aryl-substituted 1,3-diketoboronates exhibit high fluorescence quantum yields. In the case of 2-naphthyl-substituted 1,3-diketoboronates, excitation-wavelength-dependent luminescence spectra and luminescence-wavelength-dependent excitation spectra were recorded. In polar solvents the compounds exhibit large Stokes shifts and the fluorescence lifetimes depend on the excitation and fluorescence wavelengths. The multiple fluorescence behaviour is interpreted by assuming the existence of excited non-equilibrated rotamers with different photophysical properties and high dipole moments in the excited state. The relaxation of polar solvents around these high polar species contributes to the broadening of the fluorescence bands and to the fluorescence-wavelength dependence of the lifetimes caused by the fluorescence of incompletely solvent-relaxed species.

1. Introduction

The 1,3-diketoboronates (for general formula, see Fig. 1) exhibit interesting photophysical and photochemical properties [1 - 5]. The compounds

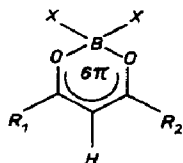


Fig. 1. General formula for the 1,3-diketoboronates studied.

have intense long wavelength UV-visible absorption bands and high fluorescence quantum yields. The electron-acceptor groups $-\text{OBX}_2\text{O}-$ induce high electron affinities in the molecules, resulting in considerable dipole moment changes on electronic excitation [4].

We have recently reported on the fluorescence behaviour of the 2-naphthyl-substituted 1,3-diketoboronates (2-NDBK) [1, 5]. In more highly polar solvents the fluorescence bands are strongly red shifted and the corresponding bandwidths are drastically enlarged. Initial measurements of the fluorescence decay resulted in different decay times within the broad fluorescence bands. These effects occur only in the presence of at least one 2-naphthalene ring in the molecule [1]. For further elucidation of the deactivation processes, the solvent, temperature and wavelength dependence of the fluorescence, fluorescence excitation and phosphorescence spectra have been studied. Moreover, we have investigated the fluorescence decay times at different fluorescence wavelengths by means of a single-photon counting apparatus for the compounds listed in Table 1.

TABLE 1

Compounds studied (*cf.* Fig. 1)

<i>Compound</i>	R_1	R_2	X_2
1	Phenyl	Phenyl	(Acetyl) ₂
2	4-Methoxyphenyl	4-Methoxyphenyl	(Acetyl) ₂
3	Methyl	2-Naphthyl	(Acetyl) ₂
4	Phenyl	2-Naphthyl	(Acetyl) ₂
5	4-Methoxyphenyl	2-Naphthyl	(Acetyl) ₂
6	2-Naphthyl	2-Naphthyl	(Acetyl) ₂
7	Phenyl	Phenyl	Oxalyl
8	Methyl	2-Naphthyl	Oxalyl
9	Phenyl	2-Naphthyl	Oxalyl
10	2-Naphthyl	2-Naphthyl	Oxalyl
11	Methyl	9-Anthranyl	Oxalyl
12	Phenyl	Phenyl	F ₂
13	2-Naphthyl	2-Naphthyl	F ₂

2. Experimental details

The preparations of the compounds studied will be described in a subsequent paper [6]. The IR, mass spectroscopic and nuclear magnetic resonance spectroscopic characterization will also be reported shortly [7]. CCl_4 , CH_3CN and $\text{C}_3\text{H}_7\text{CN}$ were distilled first over P_2O_5 under N_2 gas and second over anhydrous K_2CO_3 . The fluorescence measurements were performed using an FICA 55 (ARL) correcting spectrofluorometer-phosphorometer with a low temperature accessory. The fluorescence quantum yields were determined relative to Rhodamine B ($\phi_F = 0.70$) and quinine

sulphate ($\phi_F = 0.54$) as standards. The absorbance measurements were carried out on a Cary 17 spectrophotometer (Varian) and an M 40 spectrophotometer (VEB Carl Zeiss, Jena). The fluorescence decay kinetics were measured by means of the single-photon counting technique [8] and an LIF 200 (AdW, D.D.R.) boxcar system was used. The deconvolution of the fluorescence signals from the excitation pulse was performed using standard techniques (*cf.* ref. 9).

3. Results

3.1. Absorption, fluorescence and phosphorescence spectra

Figure 2 shows the normalized fluorescence and fluorescence excitation spectra of CCl_4 and CH_3CN solutions of selected compounds.

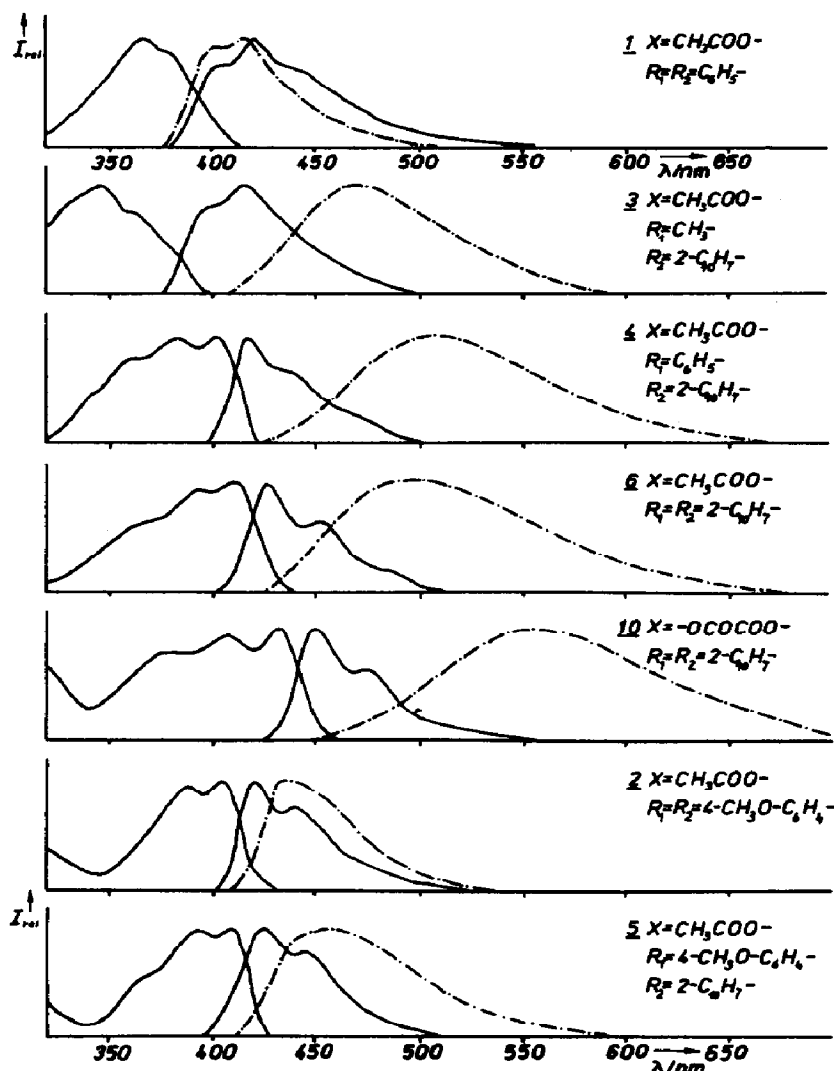


Fig. 2. Normalized fluorescence and fluorescence excitation spectra of selected 1,3-diketoboronates (293 K): —, CCl_4 solution; - - -, CH_3CN solution.

TABLE 2
Luminescence properties of compounds under study

Compound	CCl ₄ solution (293 K)				CH ₃ CN solution (293 K)				2-MTHF solution (77 K)				Remark		
	$\lambda_{\text{abs}}^{\text{00}}$	$\lambda_{\text{f}}^{\text{00}}$	ϕ_{f}	$\tau_{\text{f}}^{\text{0}}$	$\tau_{\text{f}}^{\text{n}}$	$\tau_{\text{f}}^{\text{SB}}$	$\lambda_{\text{abs}}^{\text{00}}$	$\lambda_{\text{f}}^{\text{max}}$	ϕ_{f}	$\tau_{\text{f}}^{\text{0}}$	$\lambda_{\text{abs}}^{\text{00}}$	λ_{exc}		$\lambda_{\text{f}}^{\text{00}}$	$\lambda_{\text{p}}^{\text{00}}$
1	382s	402s	0.9	2.1	2.3	2.10	377s	400(s, 00)	0.8	1.5	394	373	398	476	a, b
2	405	420	1.0	2.1	2.1	2.10	410	435(00)	0.7	2.1	421	395	425	—	b, c
3	380s	400s	0.1 ₆	1.6	10.0	3.51 ^d	380s	470	0.1 ₃	13.6	385	365	403	525	e
4	400	419	0.5 ₈	1.1	2.2	2.40	400	510	0.5 ₂	9.4	419	330	405	523	e
5	413	425	0.8 ₀	1.2	1.5	1.90	411	457	0.6 ₀	3.0	427	425	432	541	e
6	415	488	0.6 ₁	1.1	1.8	2.20	420	505	0.5 ₆	5.5	430	417	441	546	e
7	384	496	0.5 ₀	1.1	2.2	4.42 ^d	384	403	0.4 ₁	1.4	396	435	415	—	c
8	400s	422	0.0 ₆	5.1	85	(20) ^d	400s	510	0.03	18.8	423	420	462	549	e
9	435s	451	0.4 ₈	1.6	3.3	3.44 ^d	435	555	0.4 ₀	5.4	423	435	556	553	f
10	438	451	0.8 ₀	1.8	2.2	3.22 ^d	435	550	0.3 ₀	4.6	455	420	465	553	f
11	494	514	0.1 ₀	1.2	12	7.41 ^d	494	527	0.02	2.1	390	450	467	565	
12	375s	389	0.1 ₅	0.22	1.5	1.80 ^d	376	398	0.8	0.35	390	371	395	489	b
13	412	428	0.9	1.1	1.2	2.27	419	510	0.7	5.6	435	400	452	548	f
												430	451	551	

$\lambda_{\text{abs}}^{\text{00}}$, 0-0 transition of absorption spectra; $\lambda_{\text{f}}^{\text{00}}$, 0-0 transition of fluorescence (phosphorescence) spectra; $\tau_{\text{f}}^{\text{0}}$ (ns), fluorescence decay time (no spectral resolution of the fluorescence bands); $\tau_{\text{f}}^{\text{n}}$ = $\tau_{\text{f}}^{\text{0}}/\phi_{\text{f}}$ = $1/k_{\text{f}}^{\text{n}}$; λ_{exc} (nm), excitation wavelength; s, shoulder.

^aWeak phosphorescence.

^bNo wavelength dependence of excitation and luminescence detectable.

^cNo phosphorescence detected.

^dSolvent, CH₂Cl₂.

^eClear wavelength dependence.

^fSmall wavelength dependence.

Since the fluorescence excitation spectra are only slightly affected by the polarity of the solvent, compounds 7 - 11 are nearly insoluble in saturated hydrocarbons and the fluorescence quantum yields are not very different in methylcyclohexane and CCl_4 solution (*cf.* Table 2), CCl_4 was generally used as the solvent. The absorption and fluorescence spectra in CCl_4 display mirror symmetry. The vibronic structure of the fluorescence bands of the 2-NDKB vanishes in CH_3CN . Figure 3 shows the fluorescence spectra of compound 6 dissolved (a) in a series of aliphatic alcohols and (b) in CCl_4 - CH_3CN mixtures of increasing CH_3CN concentration. The polarity-induced solvent shifts of the fluorescence bands of the 2-NDKB allow the change in the dipole moment between the S_0 state and the S_1 state to be calculated as $(50 - 80) \times 10^{-30} \text{ C m}$ [4].

In polar solvents at room temperature the fluorescence and fluorescence excitation spectra exhibit a weak dependence on the excitation and fluorescence wavelength (*cf.* Fig. 4, *e.g.* compound 6). The long wavelength regions of the fluorescence bands have a lower intensity in the case of long wavelength edge excitation and the fluorescence maxima are shifted by a few nanometres to shorter wavelengths. Thus the shape of the fluorescence excitation spectra is dependent on the fluorescence wavelength.

When butyronitrile is used as the solvent, decreasing the temperature at first produces a small red shift of the fluorescence maximum (*cf.* Fig. 5). At the freezing point of the solvent a drastic hypsochromic shift of the fluorescence band is observed and vibronic structure appears as in the case of non-polar solvents. The spectral changes of all 2-NDKB, both in

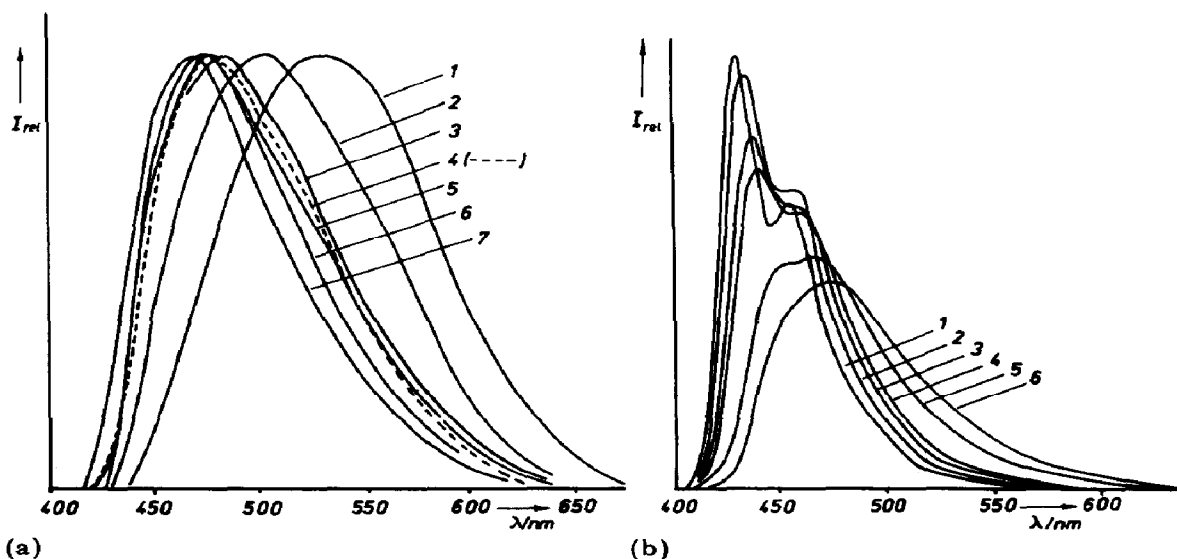


Fig. 3. Normalized fluorescence spectra of compound 6 (a) in aliphatic alcohols (curve 1, ethylene glycol; curve 2, ethanol; curve 3, hexanol; curve 4, heptanol; curve 5, *n*-propanol; curve 6, butanol; curve 7, decanol) and (b) in CCl_4 with increasing CH_3CN concentration (curve 1, $[\text{CH}_3\text{CN}]$ (mol l^{-1}) = 0; curve 2, $[\text{CH}_3\text{CN}]$ = 0.191; curve 3, $[\text{CH}_3\text{CN}]$ = 0.476; curve 4, $[\text{CH}_3\text{CN}]$ = 0.762; curve 5, $[\text{CH}_3\text{CN}]$ = 1.524; curve 6, $[\text{CH}_3\text{CN}]$ = 9.527); spectra have been corrected.

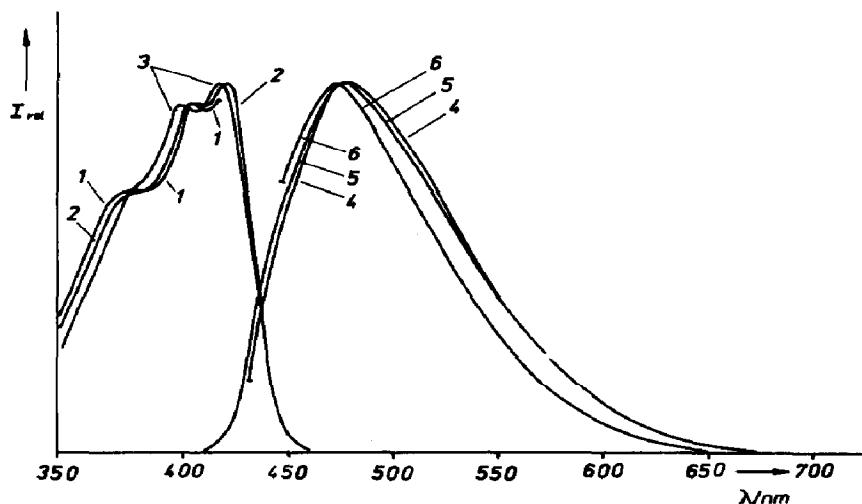


Fig. 4. Excitation and fluorescence wavelength dependence of fluorescence and fluorescence excitation spectra of compound 6 in butyronitrile solution (293 K; slit width, 2.5 nm): curve 1, $\lambda_f = 440$ nm; curve 2, $\lambda_f = 472$ nm; curve 3, $\lambda_f = 540$ nm; curve 4, $\lambda_{exc} = 390$ nm; curve 5, $\lambda_{exc} = 420$ nm; curve 6, $\lambda_{exc} = 436$ nm.

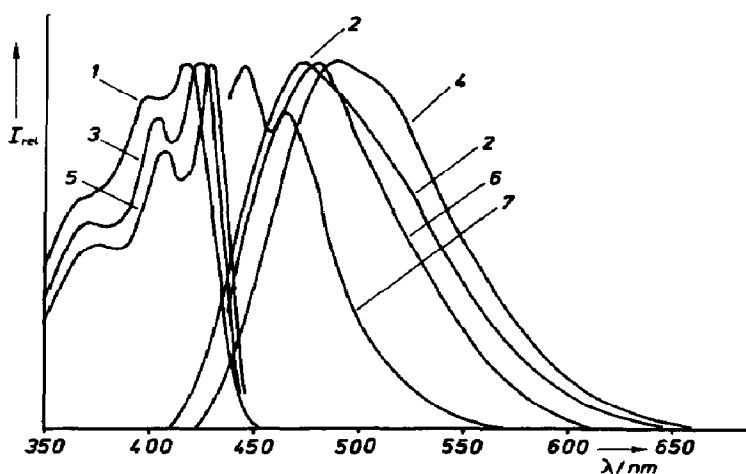


Fig. 5. Temperature dependence of fluorescence spectra of compound 6 in butyronitrile solution: curve 1, 273 K, $\lambda_f = 475$ nm; curve 2, 273 K, $\lambda_{exc} = 420$ nm; curve 3, 228 K, $\lambda_f = 490$ nm; curve 4, 228 K, $\lambda_{exc} = 428$ nm; curve 5, 208 K, $\lambda_f = 473$ nm; curve 6, 208 K, $\lambda_{exc} = 428$ nm; curve 7, 183 K, $\lambda_{exc} = 428$ nm.

2-methyltetrahydrofuran (2-MTHF) and in diethyl ether–isopentane–ethanol (2:2:5) (EPA), are analogous to the example shown in Fig. 5. The wavelength dependence of the fluorescence and fluorescence excitation spectra is more pronounced with the solid solutions (*cf.* Fig. 6).

At 77 K some compounds (*cf.* Table 2) phosphoresce with decay times of the order of seconds. In the case of 2-NDKB in butyronitrile, 1-propanol and 2-MTHF the S_0 – S_1 phosphorescence excitation spectra and

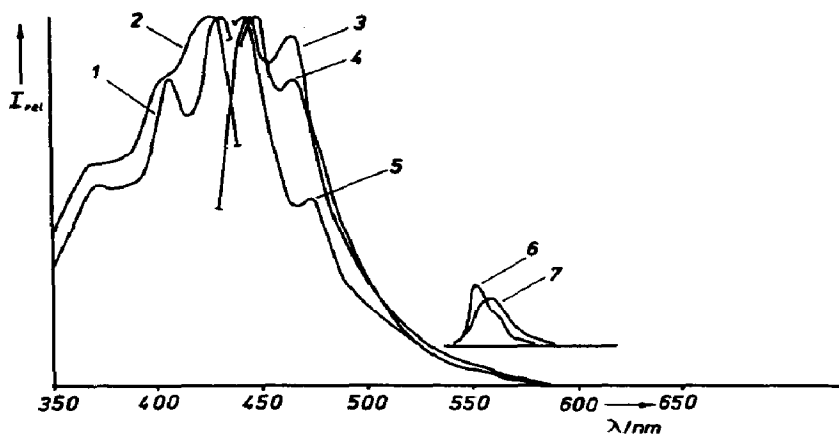


Fig. 6. Wavelength dependence of fluorescence excitation and luminescence spectra of a solid solution of compound 6 in butyronitrile (173 K): curve 1, $\lambda_f = 440$ nm; curve 2, $\lambda_f = 452$ nm; curve 3, $\lambda_{exc} = 400$ nm; curve 4, $\lambda_{exc} = 411$ nm; curve 5, $\lambda_{exc} = 440$ nm; curve 6, $\lambda_{exc} = 423$ nm (77 K, with chopper); curve 7, $\lambda_{exc} = 440$ nm.

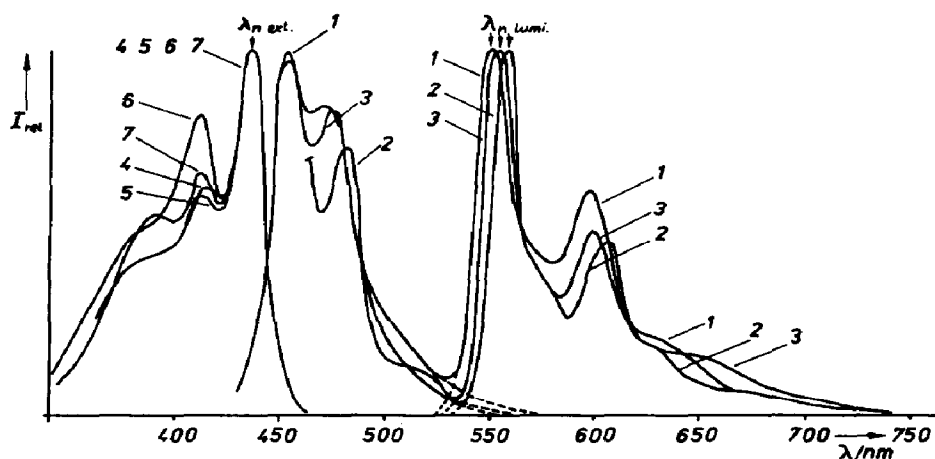


Fig. 7. Wavelength dependence of normalized (at λ_n) luminescence excitation and luminescence spectra of compound 13 in 2-MTHF solution (measurements using the chopper of the FICA 55; fluorescence is suppressed by a factor of 100): curve 1, $\lambda_{exc} = 400$ nm; curve 2, $\lambda_{exc} = 430$ nm; curve 3, $\lambda_{exc} = 445$ nm; curve 4, $\lambda_f = 460$ nm; curve 5, $\lambda_f = 480$ nm; curve 6, $\lambda_p = 550$ nm; curve 7, $\lambda_p = 605$ nm.

the phosphorescence spectra are dependent on the phosphorescence and excitation wavelength respectively (*cf.* Fig. 7, *e.g.* compound 13). For the fluoro-substituted compound 13 the wavelength dependence of the luminescence spectra is also caused by the presence of the naphthalene rings. The effect is not markedly influenced by the different substituents X (*cf.* Fig. 1), as indicated by comparing Fig. 7 (compound 13) with Fig. 6 (compound 6).

3.2. Solvent, temperature and wavelength dependence of the nanosecond fluorescence decay

No dependence of the fluorescence lifetimes on either the excitation wavelength or the fluorescence wavelength was found for any of the compounds in CCl_4 . The experimental k_f ($k_f = \phi_F/\tau_F^0$) are generally in good agreement with the k_f^{SB} calculated by means of the Strickler–Berg equation [10] (*cf.* Table 2). Adding CH_3CN to CCl_4 solutions leads to an increase in the fluorescence lifetime in the short wavelength range (*cf.* Table 3) and to a decrease in the fluorescence intensity in this spectral range (*cf.* Fig. 3(b)).

In polar solvents the fluorescence lifetimes increase slightly with increasing fluorescence wavelength (*cf.* Table 4). Moreover, a weak dependence on the excitation wavelength is observed, and the fluorescence decay is mono-exponential within the limit of experimental errors. Above 5 ns there is no wavelength range within the fluorescence band in which an increase in fluorescence could be found. Decreasing the temperature results in increasing fluorescence lifetimes both in the short and the long wavelength range of the fluorescence spectra (*cf.* Table 4). At the freezing point of the solutions the τ_f decrease and are strongly influenced by the excitation wavelength.

TABLE 3

Fluorescence decay times at different fluorescence wavelengths of compound 6 in CCl_4 - CH_3CN solvent mixtures ($\lambda_{\text{exc}} = 405 \text{ nm}$)

$[\text{CH}_3\text{CN}]$ (vol.%)	$\tau_f^0(440)$ (ns)	$\tau_f^0(550)$ (ns)
0	1.1	1.1
5	1.9	2.3
20	3.0	3.5
40	3.5	4.2
60	4.7	4.7
80	4.7	5.3

4. Discussion

The results presented for the 2-NDKB series can be best understood as resulting from multiple fluorescence of excited species with high dipole moments. Processes which can lead to dual or multiple emission are reviewed in refs. 11-13 and include the following possibilities: (i) equilibria between non-ionic and ionic species, *e.g.* establishment of prototropic equilibria [14, 15]; (ii) intramolecular excimer or exciplex formation between non-conjugated moieties of aromatic molecules [16, 17]; (iii) intramolecular charge transfer with a full charge transfer in the excited state (TICT) [12, 18]; (iv) formation of exciplexes with solvent molecules [19]; (v) formation

TABLE 4

Wavelength and temperature dependence of fluorescence decay times of selected 2-naphthyl-substituted 1,3-diketoboronates in polar solvents

Compound	Solvent	T (K)	λ_{exc} (nm)	λ_f (nm)	τ_f^0 (ns)
3	CH ₃ CN	293	333	420	13.0
			333	470	13.6
			333	550	14.2
4	CH ₃ CN	293	405	450	8.9
			405	550	9.1
5	CH ₃ CN	293	405	440	3.7
			405	540	4.1
			436	440	3.2
			436	540	4.0
6	CH ₃ CN	293	333	450	5.4
			333	580	5.9
			405	450	5.3
			405	580	5.9
	C ₃ H ₇ CN	77	365	475	2.0
			405	475	2.4
			436	475	2.6
10	C ₃ H ₇ CN	293	405	440	6.1
			405	530	6.6
		233	405	530	8.1
			77	405	530
13	CH ₃ CN	293	405	450	5.9
			405	570	6.7
			436	450	5.7
			436	570	6.2

of isoenergetic, non-equilibrated rotamers with different photophysical properties, *e.g.* in the case of 2-naphthyl-substituted stilbenes [13] or 3-pyridylstilbenes [20]; (vi) existence of solvent reorientation effects [21 - 23], *e.g.* fluorescence from partly relaxed species.

We interpret the luminescence behaviour of the 2-NDKB by the existence of different ground state rotamers with high dipole moments in the excited state, with the inclusion of solvent relaxation effects around these species.

The ring-opening reaction of the six-membered ring, as discussed for the ground state of *N*-boron chelates [24], seems to be impossible because of the differences in the Stokes shifts between the 2-NDKB and the other compounds in Table 1. Also, molecular orbital (MO) calculations [25] exclude the existence of such species. Since the ring-opening process is a requirement for the formation of intramolecular excimers or exciplexes between the aryl substituents, this process is impossible too.

In a first hypothesis [5] some of us supposed the existence of TICT states because of the many similarities to the fluorescence behaviour of *N*-aryl-carbazoles [26]. However, the luminescence properties of the 9-anthranlyl-substituted compound 11 and of the 2-naphthyl-substituted compound 14 (*cf.* Fig. 8) give no indication of TICT. Compound 11 does

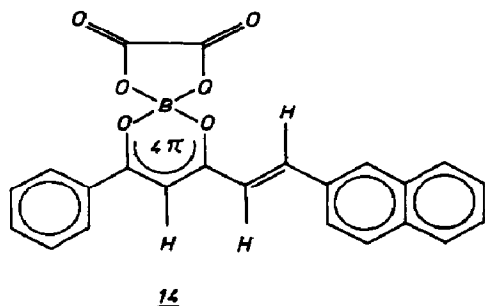


Fig. 8. The 2-naphthyl-substituted compound 14.

not show multiple fluorescence behaviour and has only a small Stokes shift in CH_3CN even though a full charge transfer is expected for this compound. However, compound 14 exhibits fluorescence properties similar to those of 2-NDKB [4]. Nevertheless, a TICT state is impossible for compound 14 as the potential donor and acceptor moieties are linked by a double bond. Also, MO calculations give no indications of TICT states [25]. Therefore we have to exclude processes which lead to TICT states for all 1,3-diketoboronates.

The fluorescence of exciplexes between 2-NDKB and polar solvents (*e.g.* CH_3CN) can also be excluded because of the growth of the lifetimes, in both the short and the long wavelength regions of the fluorescence bands, in CCl_4 solutions of increasing CH_3CN concentration. Usually, exciplex formation causes a decrease in the lifetimes in the short wavelength range [27].

To best understand the spectral behaviour of the 2-NDKB compounds reported, the existence of ground state rotamers about the quasi-single bonds as pictured in Fig. 9 must be assumed. In previous papers [1, 2] we have shown, and it will be presented more precisely in ref. 4, that BO_2X_2 groups induce a polarization of the π electron system of the 1,3-diketoboronates. Therefore polar structures (*cf.* Fig. 10) with different participations in the S_0 and S_1 states [25] will be established. The rotamers do not equilibrate in the excited state (non-equilibration of excited rotamers principle, *cf.* ref. 13) and the different spectral and photophysical properties of the simultaneously present rotamers lead to multiple fluorescence behaviour.

The most important indication for the existence of the 2-NDKB rotamers consists in the dependence $I_f = f(\lambda_{\text{exc}})$ and $I_{\text{exc}} = f(\lambda_f)$. The hypsochromic shift of the fluorescence bands at room temperature in polar solvents in the case of red edge excitation has the same origin. In many other cases the red edge excitation induced the red shift of the fluorescence spectra (edge-excited red shift effect [22]). Obviously, the rotamers have such

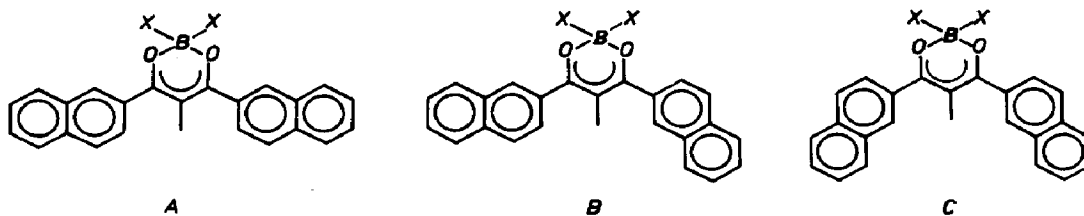


Fig. 9. Ground state rotamers about quasi-single bonds.

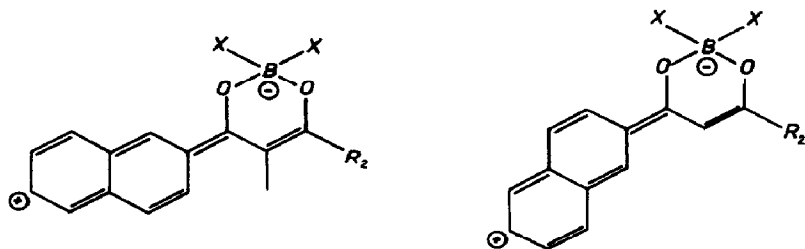


Fig. 10. Polar structures which participate in the S_0 and S_1 states.

different spectral and photophysical properties that they can only be characterized in solvents of high polarity and viscosity. The different wavelength dependences for the properties of the different 2-NDKB compounds (*cf.* Table 2) are probably caused by the varying concentration ratios of the rotamers. This effect will be investigated in a subsequent paper in which the exciplex formation of 2-NBDK with naphthalene is utilized [28].

The dipole moments of the rotamers in the first excited state are also expected to be different. The differences in the calculated S_1 - π -dipole moments of the rotamers B and C in relation to form A (*cf.* Fig. 9) are given by $(\mu_B - \mu_A) \approx 12 \times 10^{-30}$ C m and $(\mu_C - \mu_A) \approx 24 \times 10^{-30}$ C m. These values can be understood with respect to the charge separations. They are larger in rotamers B and C in comparison with the rotamer A. Therefore the large Stokes shift of the 2-NDKB results from the contributions of the rotamers B and C. Additionally, the Stokes-shift differences between the phenyl-substituted and the 2-naphthyl-substituted compounds result from the ionization potential differences between these substituents.

In some cases the 0-0 absorption transitions are situated at shorter wavelengths in CH_3CN than in CCl_4 (*cf.* Table 2). Obviously, the time-averaged torsion angles of the 2-naphthalene rings are reduced in solvents of higher polarity. This effect can be understood by considering that species with more highly planar rings have higher dipole moments and are more stabilized in the solvent shell. The decrease in the torsion angles in polar solvents excludes the possibility of conformational relaxation processes which lead to distinct spectral inhomogeneities, *e.g.* as in the case of biphenyl [29]. The nearly perfect mirror symmetry between the absorption and fluorescence spectra in non-polar solvents also excludes the possibility of major geometric changes in the excited state.

The assumption of the existence of non-equilibrated rotamers in the excited state explains the lifetime differences for different fluorescence wavelengths in solid solutions at low temperatures (*cf.* Table 4) in a satisfying manner.

The solvent relaxation time τ_{0x} around high polar species can be significantly longer than the dielectric relaxation time [21, 22]. Thus, the Stokes shift of polar molecules is time dependent in polar solvents [23]. The increase in the fluorescence wavelength leads us to expect longer fluorescence lifetimes. Thus the dependence of 2-NDKB lifetimes on fluorescence wavelength should be influenced by the ratio τ_{0x}/τ_f at temperatures above the freezing point of the solvent and, of course, at room temperature. For this reason the fluorescence of species with an incompletely relaxed solvent cage contributes to the wavelength dependence of the τ_f and to the broadening of the fluorescence bands in polar solvents. Thus the species in completely relaxed solvent cages show longer fluorescence lifetimes, as in non-polar solvents, owing to the change in the π -electron distribution. Additionally, we have taken into account the lifetime differences of the rotamers with different dipole moments in the S_1 state. This effect should induce a small τ_f dependence on excitation wavelength in polar solvents at room temperature (*cf.* Table 4).

5. Conclusions

The experimental results on the wavelength dependence of the excitation, fluorescence and phosphorescence spectra of the 2-NDKB are interpreted by assuming the existence of ground state rotamers. So far it is impossible to attribute the absorption and fluorescence properties to the individual rotamers. The fluorescence decay is influenced by the solvent relaxation phenomena. Our investigations with time resolution in the picosecond range are discussed in a subsequent paper. These results give further insight into the solvent relaxation processes, *e.g.* it is very likely that the acetato groups rotate in the S_1 state of compounds 3 - 6. For the 2-naphthalene rotamers, the picosecond measurements are new but provide no additional information.

Acknowledgment

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