Absorption and Emission Anomalies in Solutions of *trans*-Azastilbenes and Related Compounds possibly caused by Association

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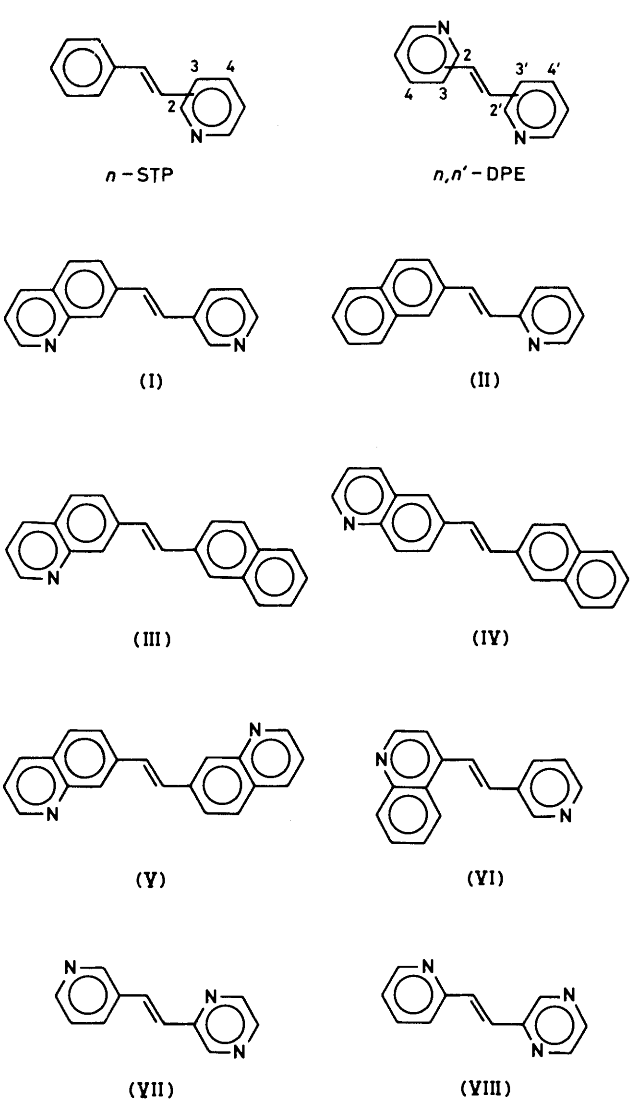
Absorption and emission anomalies have been investigated for *trans*-styrylpyridines, dipyridylethylenes, and some other aza-analogues of stilbene-like molecules in aliphatic hydrocarbon solvents at low temperatures. Fluorescence spectra, quantum yields, and lifetimes have been measured at different excitation and emission wavelengths. On cooling, the structured fluorescence spectrum of the monomer is gradually replaced by a new broad red-shifted band which becomes prominent when irradiation is carried out at the red tail of the absorption spectrum. Its intensity decay is multi-exponential and the measured lifetimes depend on both λ_{ex} and λ_{em}, reflecting a continuum of new species of longer lifetime than the monomeric compounds. The extent of these anomalies depends on solvent, concentration, temperature, rate of cooling, and structure of the olefin. The emission spectra of the crystalline azastilbenes differ from the broad-band emission which is tentatively assigned to association products with a more or less narrow size distribution.

In an earlier publication one of us reported[1] that when solutions of *trans*-1,2-diarylethylenes (in which at least one aryl is pyridyl or quinolyl) in aliphatic hydrocarbon solvents are cooled to below *ca.* 190 K, the regular, sharply structured fluorescence spectrum is gradually and partially replaced by a new broad red-shifted band. Less pronounced changes were observed in the absorption spectra. The solvents used, 2-methylpentane (2-MP), 3-methylpentane (3-MP), methylcyclohexane (MCH), or their mixtures, are known as ' poor ' solvents. No similar phenomena were encountered with solutions in ' good ' solvents, *e.g.* toluene (T) or its mixture with MCH. It was therefore suggested that these observations reflect some sort of association. Similar findings were recently reported[2,3] by us for some azastilbenes.

We report now in more detail the relevant behaviour of the three isomeric styrylpyridines (STP) and the three isomeric symmetric dipyridylethylenes (DPE), including emission anomalies such as wavelength-dependent emission and excitation spectra, slow and multi-exponential decay, variable quantum yields, *etc.* We also show that these phenomena are fairly general with the nitrogen-heterocyclic analogues of stilbene, phenyl(naphthyl)ethylenes and dinaphthylethylenes. Finally, we demonstrate the effect of solvent, temperature, concentration, rate of cooling, and structure of the solute on the extent of these anomalies.



Scheme.

Experimental

Compounds and Solvents.—The STPs and DPEs have been described.[3-5] Compounds (I)—(V) were kindly supplied by Professor R. H. Martin, as reported.[1] Compounds (VI)—(VIII) were synthesized as previously reported.[6] Solvents were all spectroquality and dried by passing through columns of active basic alumina. This also served to remove aromatic impurities from the aliphatic hydrocarbons MCH, 2- and 3-methylpentane, and isopentane. Solutions in polyethylene were prepared by immersing pieces of film in an MCH solution of the compound overnight, followed by washing with 3-MP and drying.

Spectrophotometry. Emission Quantum Yields.—Absorption spectra were measured by a Cary 14 (Rehovot) or a Cary 17 (Perugia and Göttingen) spectrophotometer equipped with a cryostat. Emission spectra were taken on Perkin-Elmer

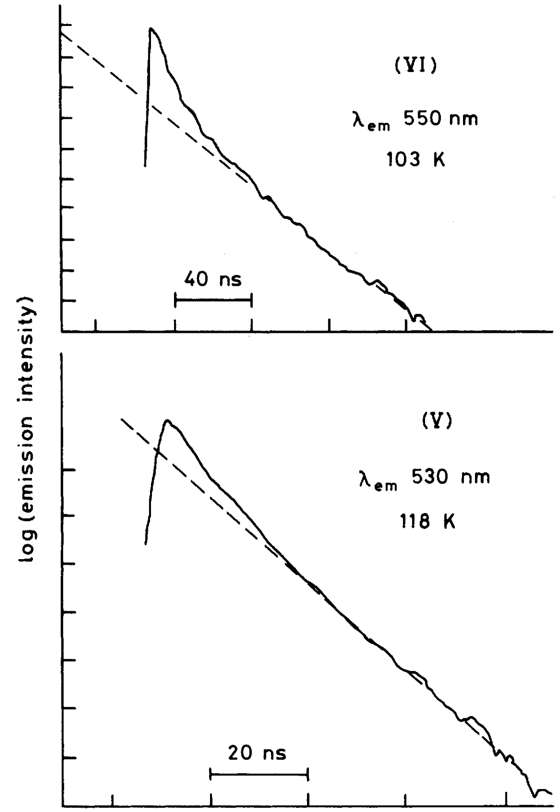


Figure 1. Emission decay profiles: log (emission intensity) *versus* time for compounds (V) and (VI) under the conditions indicated. Excitation with an N_2 laser at 337 nm, experiments performed in Göttingen (see text)

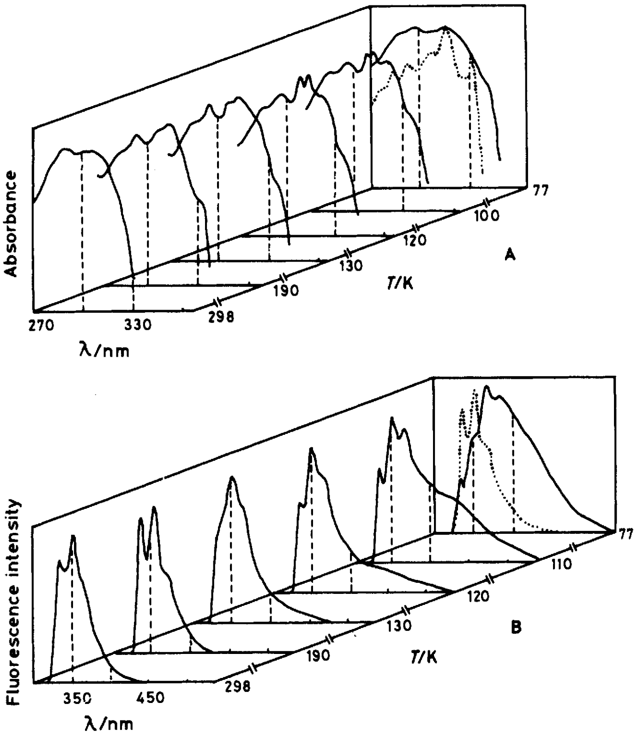


Figure 2. Absorption (A) and fluorescence (B) spectra (λ_{ex} 298 nm) of 3-STP (2 × 10^{-6}M) in 3-MP as a function of temperature. The dotted absorption and emission spectra at 77 K refer to fast cooling

MPF-44 spectrophotofluorimeters equipped with a ' corrected spectra ' accessory. In the ' slow cooling ' mode, samples were contained in regular 10 × 10 mm cross section cells cooled in a cryostat. In the ' fast cooling ' mode samples in thin quartz tubes (i.d. 4 mm) were immersed in liquid nitrogen. Fluorescence quantum yields were determined as previously described.[3]

Emission Decay Time Measurements.—Two types of measurement were carried out. The first consisted of single-shot measurements involving excitation with a pulse nitrogen laser (Lambda Physik) and a locally built detection system linked to a computer. No deconvolution methods were employed. These measurements were carried out at the M.P.I.f.Biophysik. Chemie, Göttingen. The slopes of the log (emission intensity) *versus* time curves give a rough indication of the decay times, provided these are longer than 3—4 ns. The curves also indicate deviations from mono-exponential decay. Excitation was only at 337 nm. By means of this method a rapid survey of all compounds available could be carried out, using in each case several emission wavelengths at various temperatures, in ' good ' and ' poor ' solvents. Figure 1 illustrates the decay behaviour of compounds (V) and (VI) measured by this method.

The second method employed was based on the single-photon counting technique. The data accumulated in the multi-channel analyser were fed into a Z80-based Cromemco Z-2D microcomputer and then processed by using a single- or double-exponential deconvolution program employing a non-linear least-squares fitting procedure.[7] This more complex procedure naturally restricted the number of measurements. Most samples were measured in capillary tubes immersed in liquid nitrogen (' fast cooling ').

Results

General.—All the anomalies to be described are observed when 10^{-6}—10^{-4}M solutions in the ' poor ' solvents cited above are cooled to below at least 190 K. Solutions in ' good ' solvents exhibit regular behaviour. This means that, in the latter solvents, no broad red-shifted fluorescence band or long component in the fluorescence decay is observed. The absorption and emission spectra show the usual sharpening of the peaks on cooling, accompanied by moderate shifts in position, and the fluorescence decay kinetics follow an essentially mono-exponential trend (τ 1—3 ns). The slight dependence of the spectra on λ_{ex} and deviations from mono-exponentiality are attributed to the presence of conformational isomers in solution.[2–5]

The behaviour of the compounds investigated in ' poor ' solvents displays the following anomalies.

Absorption Spectra.—In many cases, illustrated by 3-STP in Figure 2A and by the compounds described earlier,[1] the absorption spectra, when compared with solutions in T-MCH or in diethyl ether–isopentane–ethanol (5 : 5 : 2), get less structured and extend to longer wavelengths on cooling. With several compounds, the differences between the low-temperature spectra in ' good ' and ' poor ' solvents are very pronounced. This is illustrated in Figure 3 for 3,3′-DPE. In most cases excitation in the red tail of the absorption causes preferential appearance of the broad-band emission (b.b.e.).

Emission Spectra.—The appearance of the b.b.e., shifted towards the red relative to the regular emission, is the most

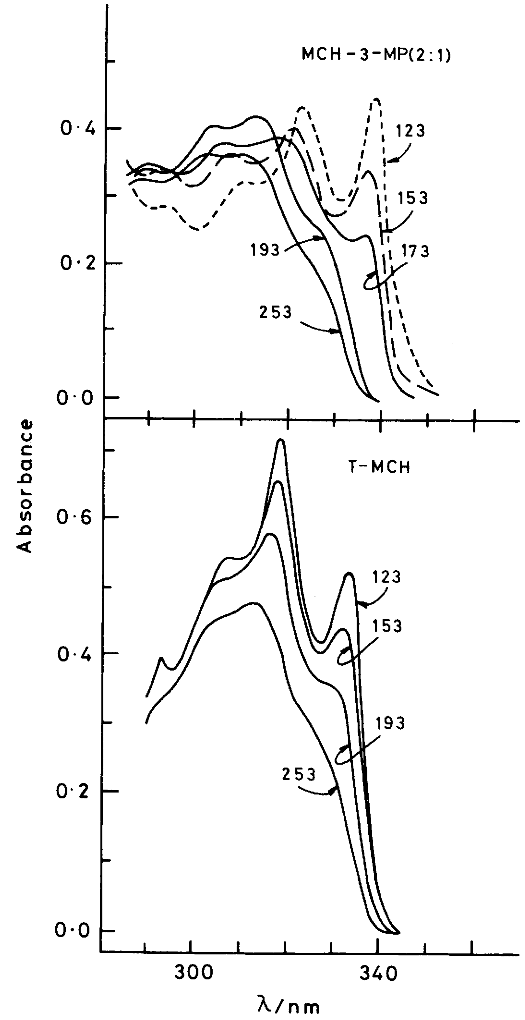


Figure 3. Absorption spectra of 3,3′-DPE in the solvents and at the temperatures indicated

Table 1. Approximate positions (peak and range) of broad-band emission spectra of various compounds, in ' poor ' solvents, measured at the temperatures indicated

Compound	Peak (nm)	Range (nm)	*T*/K
2-STP	380	350—500	77
3-STP	380	350—500	77
4-STP	390	350—500	77
2,2′-DPE	400	350—550	123
3,3′-DPE	420	350—550	153
4,4′-DPE	420	350—550	153
2,3′-DPE	435	350—490	123
(I) [a]	480	400—600	153
(II)	450—500	400—600	113
(III)	458—485	400—600	123
(IV) [a]	450	370—550	123
(V) [a]	500	430—630	153
(VI)	470	400—610	123
(VII)	480	370—580	113

[a] Described in ref. 1.

Table 2. Temperature dependence of φ_F and τ_F for STPs in 3-MP

T/K	2-STP	3-STP		4-STP
	φ_F	φ_F	τ_F [a]/ns	φ_F
296	0.000 62	0.064		0.0015
270	0.0010	0.119		0.0018
250	0.0015	0.182		0.0020
230	0.0017	0.215		0.0022
210	0.0024	0.265	1.1	0.0027
190	0.0044	0.280		0.0029
170	0.0082	0.233	1.2	0.0044
150	0.017	0.141		0.0067
130	0.024	0.111	1.8	0.035
100	0.060	0.083	2.8 (1.8, 10.5)	0.083
85	0.063	0.079		0.099
77	0.065	0.078	2.8 (1.8, 11.2)	0.10

[a] The bi-exponential treatment leads to the separate values for τ_1 and τ_2 shown in parentheses only in the last two cases.

pronounced anomaly, as illustrated in Figure 2B (see also Figures 5—7). This emission is superimposed on the regular emission, with the ratio between the two varying with the excitation wavelength (Figure 5B), the solvent composition, the rate of cooling (Figures 2B and 6), the concentration (Figure 5), the compound, and possibly other factors, as detailed above. Quantitative reproducibility of the results is consequently poor, but not unexpected, as will be shown in the Discussion section. However, the *extent* of the anomalies in the absorption and the emission spectra run parallel: solutions exhibiting only a small contribution of the b.b.e. show only slight deviations of the absorption spectra from the normal ones. Table 1 lists the approximate positions of the b.b.e. in all the compounds investigated.

Emission Quantum Yields.—The fluorescence quantum yield (φ_F) values of the three STPs were measured in the ' poor ' solvent 3-MP as a function of temperature. The data presented in Table 2 have two interesting aspects. First, the φ_F values of all three compounds at 77 K are rather similar, *ca.* 0.1, but much smaller than those observed on fast cooling [4] and those reported in EPA (a good solvent) after either fast or slow cooling.[3] Secondly, the values for 3-STP pass through a maximum at *ca.* 190 K, *i.e.* at low temperatures where the emission anomalies start appearing (see Figure 2B). In ' good ' solvents φ_F increases monotonically on cooling. In view of the overlapping regular and anomalous absorption and emission spectra, it is obviously difficult even to estimate the φ_F of the new species, but it is clearly much smaller than unity.

The effects observed on spectra and φ_F are accompanied by interesting behaviour of the fluorescence lifetime, τ (see next paragraph), which is also shown in Table 2 for 3-STP. The τ value, too short to be measured at room temperature, becomes observable below 210 K. On decreasing the temperature further, τ increases but the decay is no longer mono-exponential.

Emission Decay Kinetics.—The results of the survey carried out by the single-shot measurements (see Experimental section) are listed in Table 3. They indicate that (i) the decay of the species responsible for the b.b.e. is much longer than that of the regular emission (at shorter λ_{em}), and (ii) the decay is not mono-exponential, the slope of the logarithmic decay curve decreasing continuously with time that has elapsed after excitation. For all compounds the decay times measured at short emission wavelengths or with solutions in T-MCH (no b.b.e.!) were below 3 ns .The contribution of regular emission to the decay curves beyond, say, the first 10 ns after excitation, should therefore be negligible, in particular at long λ_{em} where the bulk of the emission is due to the new species (*cf.* Figures 5 and 6).

Table 3. Emission decay times τ_F (in ns), calculated from the slope of the experimental ' log (emission intensity) *versus* time ' curves at various emission wavelengths λ_{em} (nm) and at several time intervals, t.i. (ns) after excitation. Solutions in MCH–2-MP (2 : 1) at 113 ± 5 K unless stated otherwise, and flushed with argon (slow cooling)

Compound	λ_{em}	T.i.	τ_F	Compound	λ_{em}	T.i.	τ_F
2,2′-DPE	370,		<3	(I)	540	8—20	14
	400,					30—70	20
	450					50—130	37
(93 K)	500	10—20	4.5		590	10—30	25
		20—60	20			70—170	60
	550	10—30	6	(II)	480		<3
		30—70	15				
3,3′-DPE	455	10—20	10		550	10—30	22
		20—60	13			50—130	36
	505	10—20	10	(IV)	490	8—25	12
		20—60	15			60—140	47
4,4′-DPE	370		<3		560	10—30	18
						50—150	51
(93 K)	450	30—50	23	(VII)	500	5—15	4
						20—60	22
	500	10—90	22		550	20—60	40
	550	20—60	17	(V)	380		<3
					530	10—20	13
						20—40	18
						40—90	26
				(VI)	480	15—50	15
						60—120	48
				(103 K)	550	30—80	34
						80—160	55
					600	20—60	
						60—160	70

Table 4. Fluorescence decay parameters for some azastilbenes in 3-MP at 77 K after fast cooling

Compound	λ_{ex}/ nm	λ_{em}/ nm	τ_1/ ns	τ_2/ ns	A_1/A_2	χ^2
3-STP [a]	356	400	2.6	9.9	8.0	2.1
	356	425	2.9	11.3	6.4	1.5
4-STP	315	380	0.8	8.8	42.7	2.8
	336	400	1.5	10.8	23.0	1.0
3,3′-DPE	315	375	2.7	20.2	6.1	1.5
	336	400	4.5	26.0	2.5	1.6
	336	450	10.0	39.0	0.9	1.2
	336	500	8.3	41.0	1.0	1.2
4,4′-DPE	315	380	3.1	17.2	4.3	1.7
	315	400	4.3	22.6	2.7	1.4
	315	480	5.8	30.0	1.5	1.2
(IV)	336	450	2.5	14.1	5.5	1.8
	336	500	4.7	26.4	4.4	1.8
	336	550	4.7	30.1	3.2	1.1

[a] Slow cooling.

The results obtained by the single-photon counting technique are given in Table 4. The two lifetimes shown, as obtained by the bi-exponential deconvolution program, follow equation (1). The ratio of the pre-exponential factors and the

$$i(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} \qquad (1)$$

χ^2 values, giving the goodness of the fit, are also reported in Table 4. In all cases, the τ values are seen to vary with λ_{em}, as do the relative contributions of the two decay modes to the overall decay. This indicates, within the limitations of the method, that we are not dealing with just one new specific species, in addition to the monomeric one, but rather with a continuum of new species characterized by a continuum of τ values, which are long in comparison with the τ of the regular emission. This hypothesis is confirmed by the behaviour observed with 4,4′-DPE at a concentration when the emission spectrum indicates practically complete conversion into

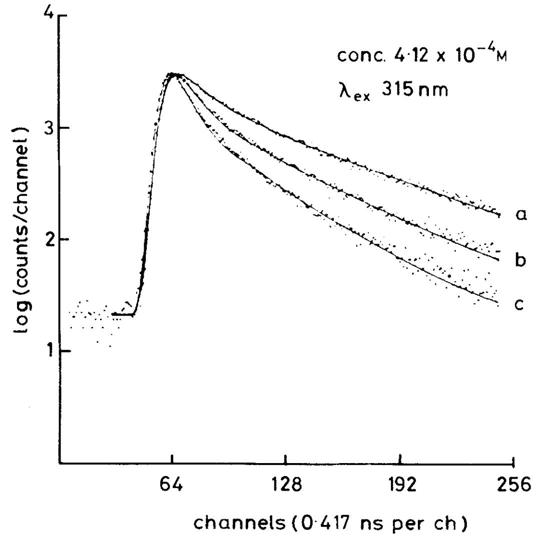


Figure 4. Fluorescence decay of 4,4′-DPE in 3-MP at 77 K after fast cooling observed at different λ_{em} (a, b, c at λ_{em} = 480, 400, and 380 nm, respectively) (full lines show the fit of the bi-exponential convolution procedure)

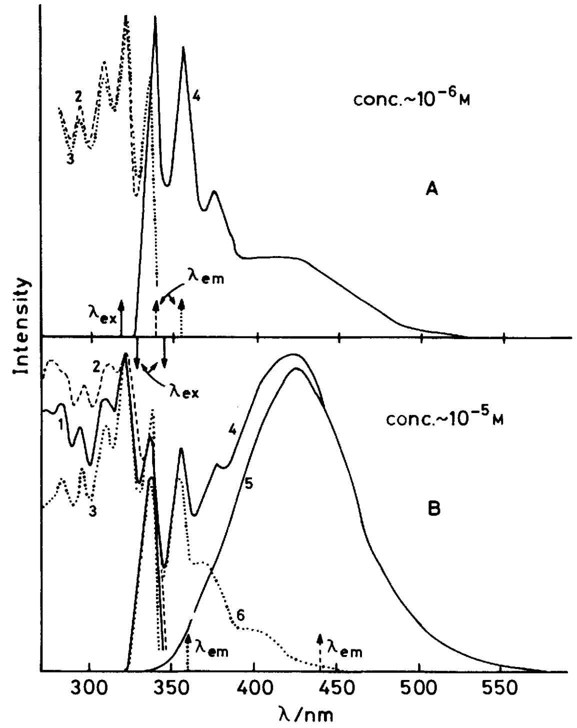


Figure 5. Absorption (1), excitation (2, 3 at two λ_{em}) and emission (4, 5 at two λ_{ex}, 6 calculated) spectra of 3,3′-DPE in 3-MP at 77 K at different concentrations after fast cooling

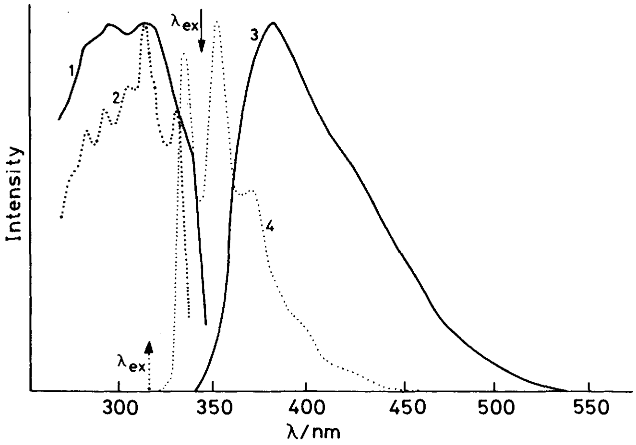


Figure 6. Absorption (1, 2) and fluorescence (3, 4) spectra of 3-STP in 3-MP at 77 K (—— after slow cooling, concentrations 2 × 10^{-6}M; · · · · after fast cooling, concentrations 2.12 × 10^{-5}M)

the new species. Nevertheless, the decay is not mono-exponential and depends on λ_{em} (see Figure 4 and Table 3).

Factors influencing the Emission Anomalies.—(a) *Solvents*. As described in the Introduction, the anomalies shown in the preceding paragraph are peculiar to solutions in aliphatic hydrocarbon solvents, which serve as ' poor ' solvents. Decalin acts as a ' good ' solvent, as do toluene and its mixture with MCH. In these solvents no b.b.e. was observed.

(b) *Concentration*. Higher concentrations favour the appearance of b.b.e. Figure 5 illustrates this for 3,3′-DPE in 3-MP (fast cooling). At 10^{-6}M (Figure 5A) the regular emission prevails, while at 10^{-5}M (Figure 5B) the b.b.e. predominates and the excitation spectra at two λ_{em} differ from each other and from the absorption spectrum. By exciting at the threshold of the absorption, at 345 nm, the almost pure b.b.e. spectrum is obtained (curve 5 in Figure 5B). By subtracting it from the emission excited at 330 nm (curve 4), one obtains spectrum 6, which is identical with the regular emission spectrum.

(c) *Viscosity*. No aliphatic hydrocarbons which form highly viscous glasses at *ca*. 190 K were available. We therefore used polyethylene, which is known to be rather similar to the lower aliphatic hydrocarbons as a solvent, but much more viscous. Compounds were embedded in 0.1 mm polyethylene sheet. Despite the much higher concentration in these films, only regular emission was observed down to 120 K with 3,3′-, 4,4′-DPE and with (III).

(d) *Rate of cooling*. As reported,[3] the appearance of the b.b.e. is aided by slow cooling. This is illustrated in Figure 6 for 3-STP in 3-MP at 77 K. For the dotted spectra, cooling was achieved by immersion in liquid nitrogen (' fast cooling '), while the full-line spectra were recorded after slow cooling (*ca*. 3 h from room temperature to 77 K). The latter spectra clearly show a much larger contribution of the anomalous emission. 2-STP and 2,2′-DPE show almost no anomalous emission when their solutions are cooled rapidly, while on slow cooling considerable b.b.e. is observed. Conversely, if a solution is warmed quickly from, say, 120 to 170 K, the b.b.e. gradually decreases with time. The formation and the disappearance of the new species are therefore relatively slow processes.

(e) *Structure of the compound*. The presence of the heteroatom seems to be essential for the appearance of the new species. Moreover, the position of the nitrogen is important: the tendency to form the new species increases in the order 2-STP, 3-STP, and 4-STP and 2,2′-DPE, 3,3′-DPE, and 4,4′-DPE. The latter exhibits the b.b.e. even after fast cooling and at low concentrations, while 2,2′-DPE does not (Figure 7). Among the STPs, only 4-STP has a slow decay, on fast cooling, with τ_F *ca*. 10 ns. The short-lived component has τ_F *ca*. 1 ns and is assigned to the regular emission (see Table 4).

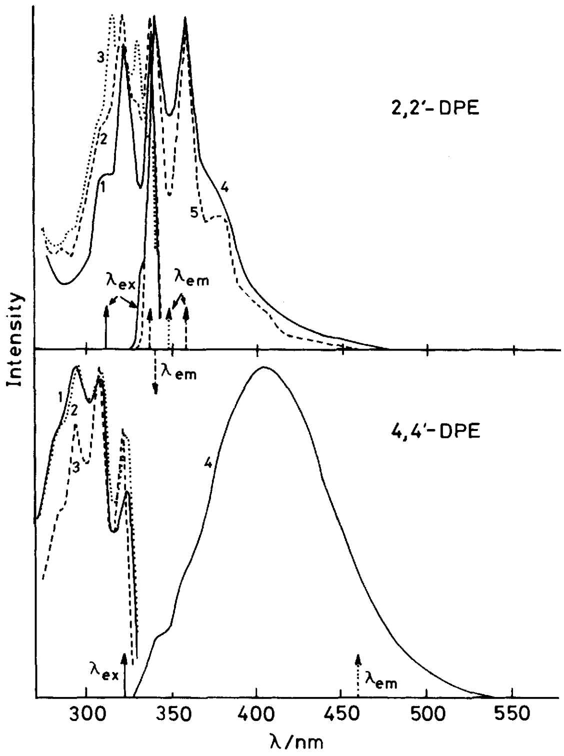


Figure 7. Absorption (1), excitation (2, 3 at two λ_{em}) and emission (4, 5 at two λ_{ex}) spectra of 2,2′- and 4,4′-DPE in 3-MP after fast cooling at 77 K (concentrations are 1.21 × 10^{-5} and 2.09 × 10^{-5}M, respectively)

Discussion

Our results indicate that formation of the new species, characterized by b.b.e. and slow emission decay, is favoured by ' poor ' solvents, low temperatures, high concentrations, and low viscosities. Moreover, it is impeded by fast cooling, and obviously is a slow process, possibly taking minutes or tens of minutes. These findings support our original assignment of these emission anomalies to association products.[1-3] This is also in line with the poor quantitative reproducibility of some of the results and their pronounced dependence on the nature of the solvent used. The question then arises whether these are just microcrystals formed in supersaturated solutions, in an early stage of precipitation. This is supported to some extent by the fact that the emission of the crystalline materials is shifted to the red in many diarylethylenes,[8] including compounds (I)—(VI).[1] However, this seems unlikely for the following reasons. First, the b.b.e. is stable for hours, even at, say, 170 K, where solutions are quite fluid and crystal growth is not impeded. Secondly, the emission spectra of the crystals are not identical with the b.b.e., being particularly different for the crystalline DPEs (peaks at *ca*. 370, 390, and 410 nm for all three symmetrical compounds at 173 K). Thirdly, the lifetimes of the powders, which depend on both excitation and emission wavelengths, as does b.b.e., are noticeably shorter than those measured for b.b.e.

Our working hypothesis is therefore that we are dealing with association products, or clusters, with a more or less narrow distribution of size, which give rise to the observed distribution of emission decay times. Highly viscous media obviously impair diffusion and therefore prevent association. The association products are characterized thus by enhanced absorption in the red tail of the spectrum, a broad emission band to the red of the regular emission, decay times in the range 10—60 ns, and low emission quantum yields.

The anomalies described, observed only for aza-analogues of stilbene, could not be peculiar to these compounds. In fact, the effect of the cooling rate on the fluorescence behaviour of stilbene-analogues shows that φ_F remains sensibly lower (except for concentrations $<10^{-6}$M) if the low temperature is reached slowly.[3] This has been taken as an indirect proof of the formation of non-emitting associates. The fact the b.b.e. is observed only for aza-stilbenes could indicate that only in this case the φ_F of the associates, even if small, reaches well detectable limits.

In earlier publications we have reported low-temperature observations of changes in the absorption spectra of stilbene derivatives and di-(2-naphthyl)ethylene,[9] and in the emission spectrum of stilbene proper,[10] all ascribed to association processes. The changes in emission behaviour reported here are much more pronounced.

At this time we are unable to define the postulated association or aggregation products (oligomers, crystallites, microcrystals) [11] more exactly. However, it is worth mentioning that as far as rotational conformers are concerned, there is a good chance that one of the rotamers is preferred in the aggregates. An example of such behaviour has been described before.[10] For STPs we have suggested [3] that the more planar rotamer predominates in the associate.

Acknowledgements

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