Viscosity-induced Emission Anomalies in 1,2-Diarylethylenes and in Distyryl-benzenes and -naphthalenes

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trans-Stilbenes and a variety of compounds related to *trans*-1-styrylnaphthalene exhibit normal fluorescence behaviour in fluid solutions. At high viscosities ($>10^5$ cP) of the medium, anomalous phenomena start to appear: the spectra change their shape and vary with the excitation wavelength, particularly with excitation in the red tail of the absorption spectrum. The extent of these anomalies increases with the viscosity and with the size of the aryl group. Another anomaly, observed in 1,2-di-(9-anthryl)ethylenes, is a viscosity-controlled, very pronounced enhancement of fluorescence yields. Our working hypothesis is based on the restriction, at high viscosities, of the rate of torsional relaxation, so that emission is mainly from molecules still having the geometry of the absorbing state. Irradiation at very low energies excites selectively those ground-state molecules having a geometry similar to that of the relaxed excited state. In the dianthrylethylenes, the rate of non-radiative decay processes $S_1 \rightarrow S_0$ associated with torsional relaxation is reduced at high viscosities, causing the observed strong enhancement of fluorescence yields, in addition to the variation of spectral shape with the temperature and the excitation wavelength.

In a number of publications from our and other laboratories, certain emission-spectroscopic anomalies were described for fluid solutions of a variety of 1,2-diarylethylenes, all of which were essentially related to 2-styrylnaphthalene (**I**).[1,2] The working hypothesis put forward to explain these anomalies (the most prominent one being a variation of emission spectra with excitation wavelength λ_{exc}) was the existence in solution of an equilibrium mixture of two or three rotational conformers, *e.g.* (**Ia** and **b**) (see Scheme), separated by an energy barrier of 5—10 kcal mol^{-1} due to resonance stabilization of the coplanar configurations *versus* those twisted by 90° around the quasi-single bonds. Since the extent of non-bonded interactions in the two conformations (**Ia** and **b**) is roughly the same, the two species may be expected as a first approximation to be isoenergetic, and therefore to exist in not very different proportions.

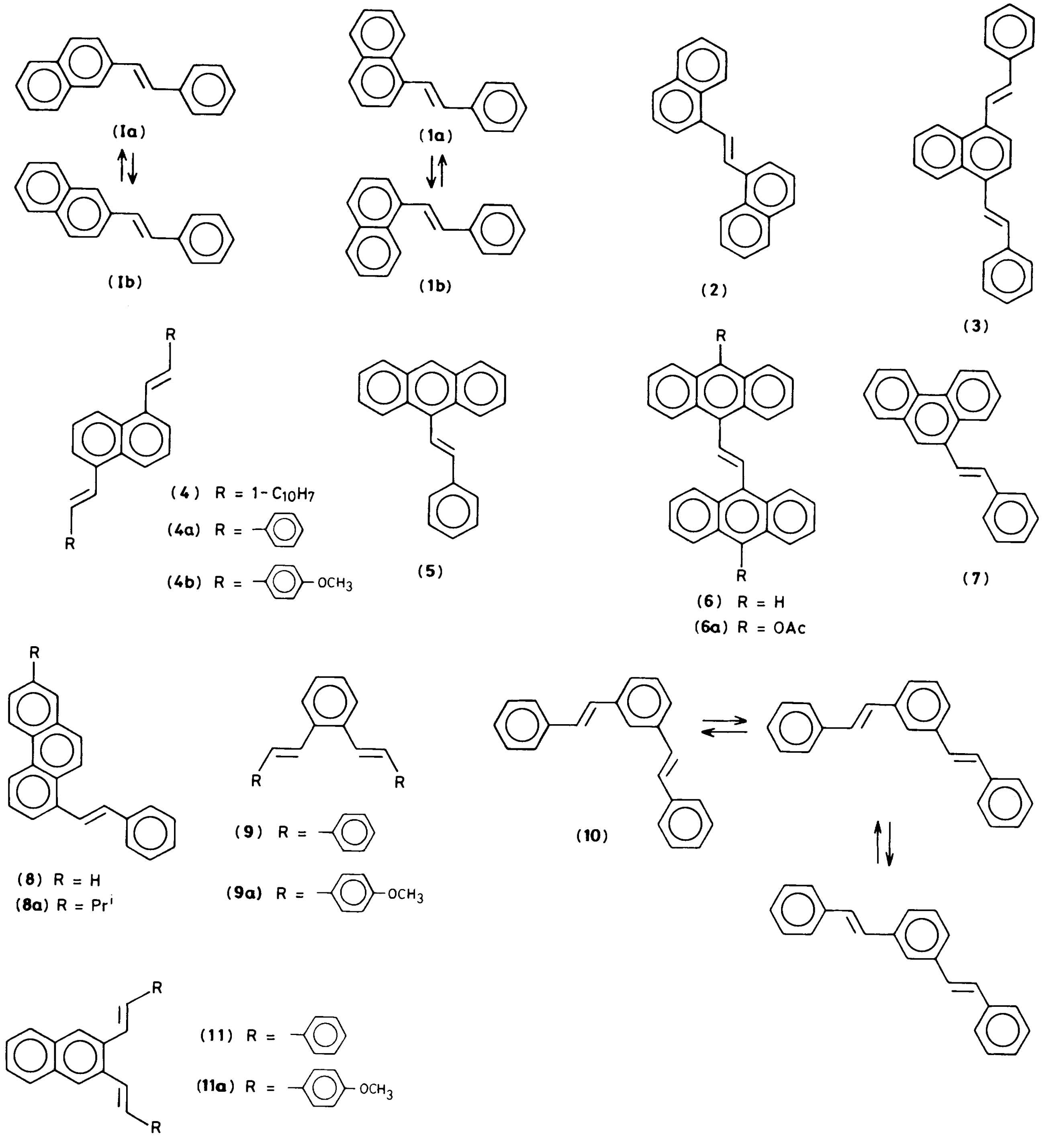
This no longer holds for 1-styrylnaphthalene (**1**) and related compounds, where the (hypothetical) coplanar conformation (**1a**) is less overcrowded than (**1b**). Indeed, all our results have so far indicated that these compounds do not manifest any emission anomalies of the type observed with (**I**) and related compounds. These negative results have been interpreted as further confirmation of the basic concepts, namely the absence of interconversion (**1a**)$\rightleftharpoons$(**1b**) in the excited state, and the existence, in 2-naphthylethylenes and related compounds, of roughly isoenergetic ground-state rotamers separated by sufficiently high energy barriers.[1-3]

We now report that practically all those diarylethylenes related to (**1**) which are at our disposal, as well as related distyryl-benzenes and -naphthalenes, exhibit pronounced emission anomalies when their solutions are sufficiently viscous. The extent of these anomalies increases with the viscosity and with the size of the aryl group, and is most pronounced in 1,2-di-(9-anthryl)ethylenes (**6**). The effects are strictly viscosity controlled, and can be observed at a variety of temperature–solvent combinations having roughly similar viscosities. The main anomaly is again the variation of emission spectra with excitation wavelength, once the solutions are viscous enough. The anomalies are more evident when the excitation is performed at the red tail of the absorption band. In 1,2-di-(9-anthryl)ethylene the quantum yield of fluorescence is extremely enhanced at high viscosities, in addition to the main anomaly of variation of spectral shape with the temperature and excitation wavelength.

Experimental

Compounds and Solvents.—Most of these were generously put at our disposal by Professor A. E. Siegrist, Basel,[4] and used without further purification. 1-Styrylnaphthalene (**1**), 1,2-di-(1-naphthyl)ethylene (**2**), 9-styrylanthracene (**5**), and 9-styrylphenanthrene (**7**) were synthesized according to the literature and had the correct m.p.s. 1-Styrylphenanthrene (**8**) was a gift from Professor W. M. Laarhoven, Nijmegen. Compounds (**1**), (**5**), (**7**), and (**8**), studied in Perugia, had been synthesized for previous investigations there[2b] and put at our disposal by Professor G. Galiazzo, Padova. The 1,2-di-(9-anthryl)ethylenes (**6**), studied in Rehovot, were kindly provided by Professor H. D. Becker, Goteborg, who first showed the effect of viscosity in the emission spectrum of these compounds.[5] Solvents were spectrograde and dried by passing through columns of active basic alumina, except propylene glycol, which was 'fluorimetric grade' and used as such.

Spectrophotometry.—Absorption spectra were measured with Cary 2200 (Rehovot) or Cary 17 (Perugia) spectrophotometers equipped with a cryostat. Emission spectra were recorded on MPF-44 spectrophotofluorimeters without (Rehovot) or with (Perugia) a 'corrected spectra' accessory. In the 'slow cooling' mode, samples were contained in cells made of 10 × 10 mm cross-section Suprasil tubing (Heraeus) cooled in a cryostat. In the 'fast cooling' mode, the samples, in 4 mm i.d. Suprasil tubes, were immersed in liquid nitrogen, in the phosphorescence accessory. Solutions were flushed with argon throughout. The emission spectra were taken at varying sensitivity to give identical peak heights in order to make comparison of spectra easier.



Scheme.

Emission Decay Time Measurements (*Perugia*).—Fluorescence lifetimes (mean deviation of three independent experiments about 5%) were measured with a home-assembled fluorometer (Laben electronics; Applied Photophysics source and monochromators) based on the single-photon time-correlation technique. The data accumulated in the multichannel analyser were fed into a 68000-based Cromemco CS1D2E microcomputer and then processed by using a single- or double-exponential deconvolution program employing a non-linear, least-squares fitting procedure. The low-temperature measurements were carried out in the 'fast cooling' mode.

Results

General.—With most compounds, the emission behaviour of 10^{-6}—10^{-5}M solutions in methylcyclohexane–2-methylpentane (MCH–2MP) (2:1) was compared with that of similar solutions in decalin (D). This technique has been applied extensively by one of us[6a] (E.F.) to the emission of sterically hindered stilbene derivatives, in order to distinguish between the effects of viscosity and of temperature, in chemically similar solvents. This is illustrated by Table 1, which shows that similar viscosities are attained in the two solvent systems at temperatures differing by 50—70°; true 'viscosity effects' would

Table 1. Approximate viscosity η (cP), of MCH–2MP, D, and PG at various temperatures

Temp. (°C)	−51	−64	−70	−80	−95	−106	−113	−127	−138	−144	−160	−173	−182
log η, MCH–2MP									1.8	2.1	3.6	6.5	9.5
log η, D		1.7	1.9	2.4	3.4	4.5	5.4	7.7	9.8	11			
log η, PG	5	6.4	7	8.2	10.2	12							

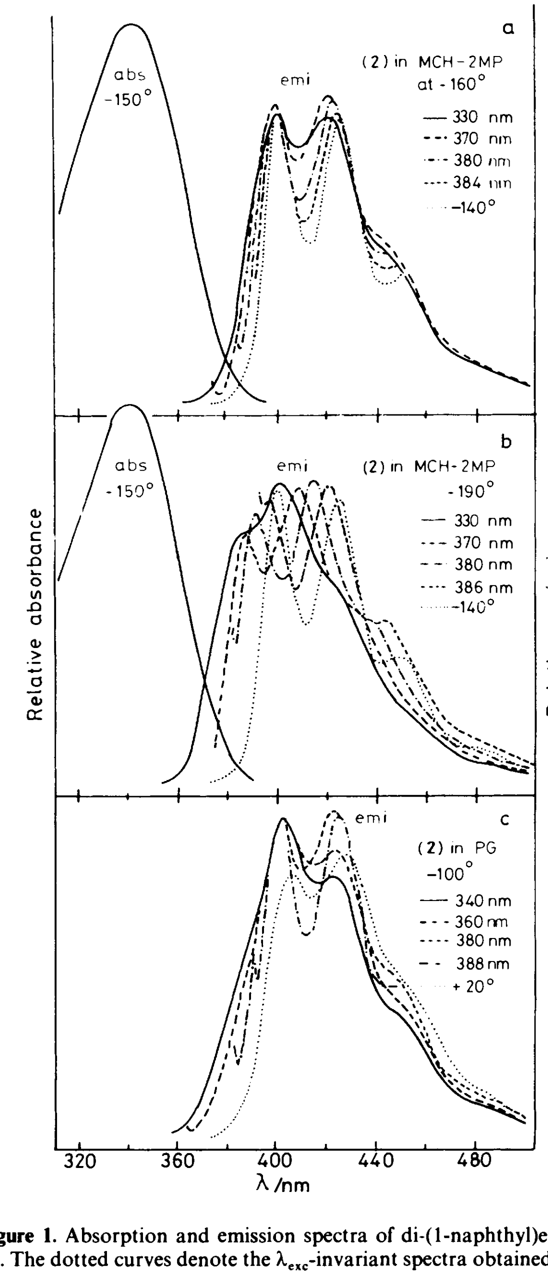


Figure 1. Absorption and emission spectra of di-(1-naphthyl)ethylene (**2**). The dotted curves denote the λ_{exc}-invariant spectra obtained at low viscosities

therefore be expected in each of the two solvent systems at temperatures of roughly equal viscosity. This was indeed the case with several compounds. Propylene glycol (PG) was also used as a solvent. In view of its very much higher viscosity,[6b] the emission anomalies to be described later are expected and observed at still higher temperatures than in decalin.

Viscosity.—As shown earlier,[6a,b] viscosity measurements, in particular at high viscosities and in mixtures forming glasses at low temperatures, exhibit rather bad reproducibility. Viscosities reported in the literature often vary by as much as an order of magnitude. Moreover, what one actually measures are *macro*viscosities, which may run roughly parallel to the *micro*viscosity experienced by the solute, but are not necessarily identical. This is certainly true when comparing chemically different solvents, like decalin and propylene glycol, but may hold to some extent even when comparing decalin with methylcyclohexane–isohexane mixtures. In addition, cooling as such often sharpens absorption and emission spectra. All this has to be taken into account when comparing emission anomalies observed in two solvent systems of roughly equal macroviscosity and widely different temperatures.

Emission Anomalies controlled by Viscosity.—(a) *Variation of emission spectra with the excitation wavelength,* λ_{exc}. This is mainly observed when exciting in the red tail of the absorption, at high viscosities of the solvent, above a more or less defined minimal viscosity, achieved in each solvent by cooling to appropriate temperatures. At higher temperatures, *i.e.* lower viscosities, no such variation is observed. This is illustrated in Figures 1 and 2, where the dotted emission spectra are independent of the excitation wavelength, while the others vary with it, to an extent increasing at lower temperatures. Compound (**2**) is a particularly good example, with very pronounced effects at −190° in MCH–2MP and smaller ones at −160°. In decalin solutions (not shown), a slight effect is already observed at −100° while at −120° and below the situation is rather similar to that observed in MCH–2MP at −190° (Figure 1b). In the much more viscous PG (Figure 1c) the variation of the emission spectrum with the wavelength of excitation λ_{exc} at and below −60° is similar to that in MCH–2MP at −160° (Figure 1a).

The main features of the results described in Figures 1a—c and 2a, b are as follows. In fluid solutions the emission spectra are sharp and independent of λ_{exc}. As the viscosity increases (by cooling), the emission spectrum excited at short wavelengths generally broadens towards the left, while excitation at longer wavelengths results in spectra which get progressively sharper and shifted to the red, with more pronounced minima and maxima, approaching in some cases the λ_{exc}-invariant spectrum at low viscosity (dotted curves). The shortest λ_{exc} in each Figure denotes *that* λ_{exc} beyond which the emission spectrum starts changing. Thus for (**2**) in Figure 1b, excitation at 330 nm and shorter wavelengths results in emission curve '330' (full curve). As seen when comparing Figures 1a and b, the extent of this λ_{exc} dependence increases with the viscosity. In some cases this variation with λ_{exc} could be described as being due to a superposition of two sets of spectra, contributing to various extents to the overall spectrum. In the case described in Figure 1b this is not possible, and we doubt if such a procedure is justified in any of the cases described. This is in contrast with the 'rotamer behaviour' described earlier,[1,2] which is already observed at very low viscosities. Such 'rotamer behaviour' is illustrated by compound (**10**), in which we anticipated[7] and now observed a variation of emission with λ_{exc} even in fluid

Table 2. Compounds in which the 'viscosity effect' was observed. Solvents: MCH–2MP, D, or PG. Type of behaviour as illustrated in Figures 1 and 2 or expressed in estimated red shift of peaks when exciting at long wavelengths

Compound	Solvents	Temp. range (°C)	Described in, or similar to Figure	Estimated red shift (nm)
Stilbene[a]	MCH–2MP	−180 to −190	*Cf.* text	2
	D	−140 to −150	(370 nm peak rises)	2
	PG	−60 to −90		2
3,3′-Dimethylstilbene	MCH–2MP		As stilbene	
	D			
	PG			
(**1**)	MCH–2MP	−170 to −180	2a	5—7
	D	−120 to −150[a]	2a	
(**2**)	MCH–2MP	−160 to −180	1a, b	15—20(!)
	D	−110 to −150	1a, b	
	PG	−10 to −90	1c	
(**3**)	MCH–2MP	−150 to −180	2b	8—12
	D	−120 to −150	2b	
	PG	−50 to −90		
(**4**)	MCH–2MP	−150 to −180	2c	
	D	−100 to −150	2c	
	PG	−50 to −90		slight effect
(**4a**)	MCH–2MP	−140 to −180	2b	10—14
	D	−110 to −150	2b	
	PG	−50 to −90	2b	
(**5**)	MCH–2MP	−160 to −180		4—6
	D	−140 to −160		None
(**7**)	MCH–2MP	−160 to −180	2b	5—7
	D	−120 to −150		3—5
(**8**)	MCH–2MP	−160 to −180	2a	6—8
	D	−120 to −150		
	PG	−60 to −90		
(**8a**)	MCH–2MP	−170 to −180	2a	6—8
	D	−120 to −150		
	PG	−50 to −90		
(**9**), (**9a**)	MCH–2MP	−170 to −190	2a	
(**11**)	MCH–2MP	−160 to −180	2b	4—5
	PG	−50 to −90		none

[a] Similar effects were observed in methyltetrahydrofuran at −180 °C (not −150 °C) and in MCH–toluene (1:1) at −160 °C (not −120 °C).

media, ascribable to the existence of the equilibrium among the ground-state rotamers depicted in the formulae.

The extent of the above viscosity effect increases with the size of the aryl group. Thus in stilbene proper the effect manifests itself only in a red shift of 1—2 nm and slight sharpening when exciting highly viscous solutions beyond 330 nm. The effect is larger with 1-styrylnaphthalene (**1**), and still more spectacular with the dinaphthyl compounds (**2**) and (**4**) (Figures 1b, 2c). Among the cases not involving compounds related to 1-styrylnaphthalene (**1**) we mention, besides stilbene and 3,3′-dimethylstilbene, 1,2-distyrylbenzene (**9**), 2,3-distyrylnaphthalene (**11**), and 9-styrylanthracene (**5**). Table 2 summarizes this type of viscosity effect as observed in all the relevant compounds available to us.

One should recall that even for 4-styrylpyridine where, similarly to stilbene, a single species is expected to exist in fluid solution, at least two slightly different spectra have been observed[8] in a rigid matrix at different λ_{exc}. This could be ascribed to the phenomenon here described, though a matrix effect stabilizing specific conformations cannot be excluded.[8–10]

The anomalies observed in the emission spectra were also evidenced by the excitation spectra recorded at different λ_{em}. In fact, Figure 3 shows, together with the described dependence of emission spectra on λ_{exc}, a corresponding red-shift of the excitation spectra when λ_{em} moves towards the red tail of the fluorescence spectra. Figure 3 shows also that the absorption spectrum changes with the temperature, probably because of a change in the distribution of conformations at high viscosities, favouring the rotamers of lower energy.

(b) *Temperature- and viscosity-induced changes in the shape of the emission spectrum at one* λ_{exc}. This is illustrated for (**5**) in Figure 4a, where all curves were taken at roughly the same sensitivity. In MCH–2MP, cooling from −20 to −120° causes little change, but from *ca.* −150° down, the spectrum narrows (*cf.* at −180°). In decalin the maximum narrowing is already achieved at −150°. On top of this, one finds some variation with λ_{exc} at −180° in MCH–2MP, and at −150° in D. Thus both effects are again viscosity controlled.

(c) *Viscosity-controlled emission quantum yields.* Compound (**6**) and its diacetoxy derivative (**6a**) display an exceptional combination of three effects: the one described in (a) above, *i.e.* a very pronounced variation of emission spectra with λ_{exc} in highly viscous media (Figure 4b); one similar to (b), *i.e.* a severe narrowing of the emission band towards shorter wavelengths at high viscosities, illustrated to some extent in Figure 4c; and a new effect, namely an extreme enhancement of emission yields with the viscosity of the medium. Table 3 shows this by comparing relative emission intensities at various temperatures in one solvent, and in solvents of different viscosities at one temperature. Figure 4c also illustrates an interesting hysteresis effect. When slowly cooling a solution in decalin, the emission spectrum at −80° is broad and its intensity low. When continuing to cool to −150° and reheating to −80°, the spectrum retains both its narrow shape as at lower temperature, and its high intensity during many hours. On further heating to −60°, the original (cooling) emission spectrum is restored within *ca.* 30 min. Temperature measurements inside and outside the sample cell showed that temperature equilibration

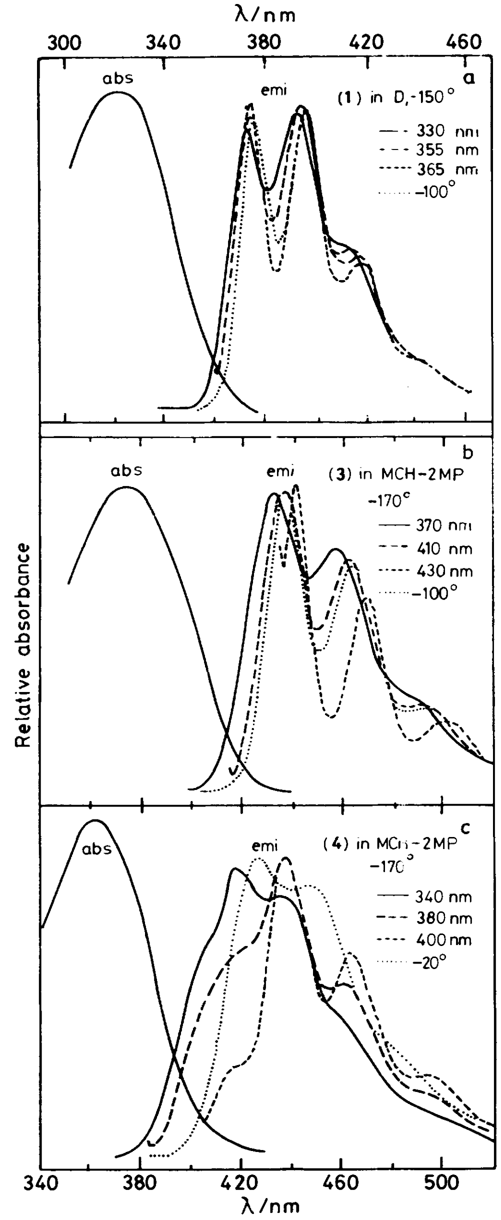


Figure 2. Absorption and emission spectra of three typical compounds. The dotted curves denote λ_{exc}-invariant spectra obtained at low viscosities

between the thermostat and the contents of the cell takes place within *ca.* 20 min for decalin (−80°). On this time scale the two spectra in Figure 4c are both completely stable.

Effect of Rate of Cooling.—Apart from the hysteresis effect described above, the various effects were found to be unaffected by the rate of cooling. Very fast cooling by immersion of 4 mm i.d. tubes in liquid nitrogen gave similar results to those found when the same temperature was reached in 30 min. The spectra observed at any particular temperature were independent of the way this temperature was attained.

Fluorescence Lifetimes.—The appearance of emission anomalies at high viscosities could, in principle, be accompanied by changes in the profile of the fluorescence decay with both temperature and λ_{exc}, due to changes in lifetime and to

Table 3. Approximate relative emission intensities I^F_{rel} of (**6a**) in MCH-2MP, in MCH-toluene (1:1), and in D, at several temperatures. The following emissions were too weak for a reasonable estimate: MCH-2MP at −100°, toluene at −90°

T/°C	Solvent	I^F_{rel}
−120	MCH-2MP	3
−150	MCH-2MP	50
−180	MCH-2MP	150
−20	D	1
−60	D	2.7
−80	D	10
−100	D	40
−120	D	150
−150	D	500
−100	MCH-T	1
−120	MCH-T	100
−150	MCH-T	400

Table 4. Fluorescence lifetimes of 1-styrylnaphthalene and some structurally related compounds in inert solvents at room temperature (λ_{exc} 335 nm; λ_{em} 400—440 nm)

Compound	Solvent	τ_F/ns	χ^2
1-Styrylnaphthalene (**1**)	n-Hexane	1.8	1.12
1-Styrylphenanthrene (**8**)	n-Hexane	9.8	1.10
9-Styrylphenanthrene (**7**)	n-Hexane	5.2	1.09
9-Styrylanthracene (**5**)	MCH	3.6	1.11
1,1-Dinaphthylethylene (**2**)	MCH	2.2	1.01

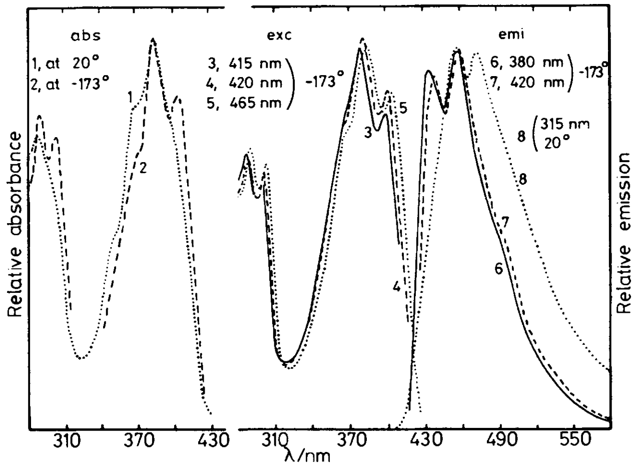


Figure 3. Absorption (1,2), excitation (3—5), and emission (6—8) spectra of 9-styrylanthracene (**5**) in 3-methylpentane at temperatures and λ_{em} (or λ_{exc}) indicated

polyexponential decay. The emission decay was studied under two extreme conditions: in a fluid solution at room temperature and in a rigid matrix at 77 K.

The results obtained at room temperature (Table 4) show that the decay is monoexponential, as expected for 1-styrylnaphthalene (**1**) and related compounds whose conformational equilibrium is largely in favour of the less crowded species.[1-3] In some cases, the dependence of the emission decay on λ_{exc} was checked but the lifetime turned out to be independent of the wavelength used [*e.g.*, for 9-styrylanthracene (**5**) in n-hexane, at λ_{em} 500 nm and λ_{exc} = 335, 375, and 400 nm, the lifetime is 3.66, 3.62, and 3.55 ns, respectively].

Table 5 lists lifetimes τ_F calculated from the decay profiles observed at 77 K with compounds (**2**) and (**5**) at various λ_{exc} and

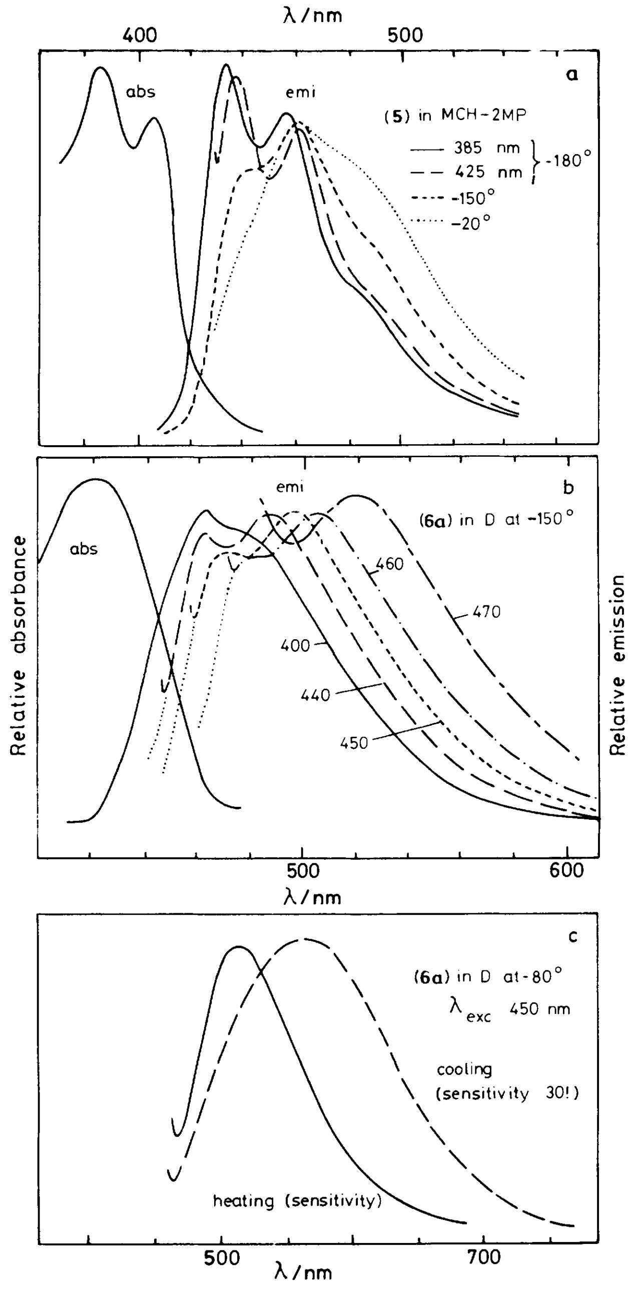


Figure 4. Absorption and emission spectra in the solvents and at the temperatures and λ_{exc} values indicated. (a) (**5**) in MCH–2MP. Variation with temperature and λ_{exc}. At −150° the spectra do not change with λ_{exc}. (b) (**6a**) in D at −150°. Variation of spectra with λ_{exc}. Excitation at wavelengths below 400 nm yields spectra similar to '400'. (c) (**6a**) in D at −80°. Dashed curve, when cooled slowly from RT; full curve, when heated from −150°. Note the sensitivities indicated! The shape of the emission at −100° and −120° is roughly similar to that of the full curve, the one at −60° resembles the dashed curve.

λ_{em}, assuming monoexponential decay. The fit is worse than at room temperature (larger χ^2 values), but if the decay is actually polyexponential, the respective τ_F values must be rather similar, making efficient separation impossible for these rather short τ_F values. The fact that τ_F values at room temperature are larger than at 77 K is surprising. We conclude that the present results do not provide clear-cut evidence for the possibility that the molecular configurations responsible for the variety of emission spectra observed at high viscosities also differ in their decay profiles.

Table 5. Fluorescence lifetime of two typical diarylethylenes in a rigid matrix of methylcyclohexane at 77 K at several excitation and emission wavelengths

Compound	λ_{exc}/nm	λ_{em}/nm	τ_F/ns	χ^2
9-Styrylanthracene (**5**)	335	440	2.70	1.50
	335	480	2.73	1.39
	375	440	2.78	1.35
	375	480	2.76	1.74
	400	440	2.88	1.29
	400	480	2.91	1.17
	405	440	2.83	1.26
	410	440	2.84	1.29
1,1-Dinaphthylethylene (**2**)	335	380	1.79	1.33
	335	400	1.78	1.19
	335	440	1.79	1.003
	375	400	1.85	1.50
	375	440	1.70	1.18

As described above, dianthrylethylene (**6**) exhibited particularly pronounced emission-spectral anomalies, and polyexponential decay profiles could be expected. Indeed, measurements of solutions of (**6**) in decalin at 77 K (λ_{exc} 375 nm, exc. slit 5 nm) resulted in τ_F 3 ns, χ^2 3 for monoexponential treatment and $^1\tau_F$ 2.2, $^2\tau_F$ 7 ns, χ^2 1.05 for biexponential treatment. One should recall that in order to distinguish between bi- and poly-exponential decay, a much more extensive investigation is required. However, the two lifetimes might be due to two different average conformations.[8–10]

Discussion

To some extent the present anomalies in fluorescence behaviour resemble those described earlier. However, it is important to stress the differences, which also reflect a different basis. In compounds like (**I**) or (**10**), two or three almost isoenergetic rotational conformers, separated by substantial energy barriers of 5—8 kcal mol^{-1}, were postulated.[1b] Photoselective excitation was explained as due to small differences in the absorption spectra of the postulated rotamers, causing the relative absorption of light at any particular excitation wavelength λ_{exc} to vary with λ_{exc}. The observed emission spectra could be described by superpositions of two or three distinct spectra, shifted against each other. The λ_{exc} dependence of the fluorescence was not restricted to excitation at the red tail of the absorption spectrum, nor to viscous media. Decay curves could be described by biexponential functions, with the two decay times not changing with the wavelength of excitation or emission. The variation of the fluorescence spectra with λ_{exc} described here *is* most prominent at the low-energy tail of the absorption spectrum, and restricted to highly viscous media. The viscosity-induced changes in the emission spectra cannot be explained as being due to fluorescent entities which existed already in the fluid solutions. It is improbable that unstable rotamers, *e.g.* (**1b**) in compound (**1**), are stabilized when the viscosity of the medium increases. Our working hypothesis partly follows a suggestion made by Nauman *et al.*[9] and by Wild *et al.*[11] for explaining somewhat similar anomalies observed with 2-phenylnaphthalene and biphenyl in 3-methylpentane at 77 K. The basic concept may be valid for many flexible aromatic molecules in which the geometries in the ground and excited states differ considerably (large Stokes shifts!). In the ground state, with a fairly flat energy minimum for a certain combination of torsion angles around the central double bond

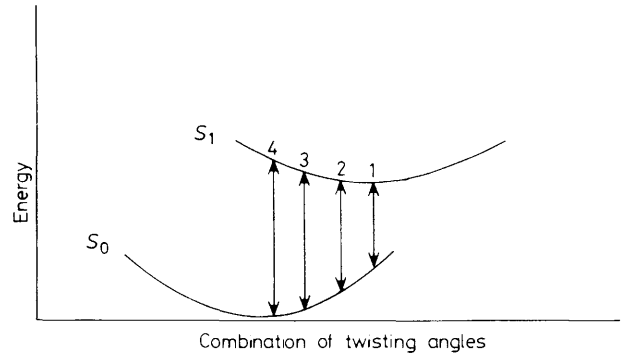


Figure 5. Schematic presentation of variation of energy with a combination of twisting angles of C–C and C=C bonds in the ground and excited states. As the viscosity increases, emission from unrelaxed geometries 2—4 gains in importance

and the two quasi-single bonds, molecules assume a variety of geometries, including those to the right of the minimum (Figure 5). In the excited state, the equilibrium geometry has an energy minimum for a different combination of torsion angles. In fluid solutions, any excitation eventually leads to the relaxed excited state, from which emission takes place. In highly viscous media, this relaxation in the excited state is impeded, and emission will take place from unrelaxed excited states, *i.e.* those which retain the geometries of the absorbing molecules. These will include transitions involving minimal transition energies. When exciting at such low energies, in the red tail of the absorption band, a virtual photoselection will take place of molecules which in the ground state happen to have the geometry of the relaxed excited state. The emission is expected to be similar to that observed in fluid media for all λ_{exc}, because there emission is always from the relaxed state, *i.e.* from the minimum of the energy curve in the excited state. This would explain the observed similarity between the emission spectra in fluid media at all λ_{exc} values and those in highly viscous media at long λ_{exc} values. Excitation at short values in viscous media leads to emission from a variety of unrelaxed geometries in the excited state, and therefore broad and less structured emission spectra. This is obviously a gross oversimplification, but the basic idea of impeded relaxation rates in viscous media seems to provide a qualitative explanation of the facts. This situation is similar to that envisaged by Hochstrasser *et al.*[12] in a shorter time scale after laser excitation of stilbene in fluid solutions at room temperature. The inhomogeneous distribution of S_1 molecules related to the wide range of rotamers in the ground state S_0 arises when the rotation of the aryl group is slow enough to become competitive with radiative deactivation. Regarding the extreme increase in fluorescence yields of 1,2-di-(9-anthryl)ethylene at high viscosities, we assume that, in fluid media, radiationless energy degradation of the excited molecules is very efficient, with very small fluorescence yields. This degradation is probably due to torsional motions, which are impeded at high medium viscosities, causing a parallel decrease of radiationless transitions and an enhancement of emission yields.

The extreme hysteresis effect described in Figure 4c probably reflects a similar hysteresis in microviscosity, peculiar to the (commercial) mixture of *cis*- and *trans*-decalin serving as a solvent. The very pronounced variation of the emission intensity with viscosity makes compound (**6**) a particularly suitable indicator of microviscosity.

Finally, the factors specified in the 'viscosity' paragraph do not allow us to expect more than a semiquantitative correlation between the viscosities of the various solvent systems and the onset of emission anomalies. Such a correlation is indeed observed.

Acknowledgements

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References

1 E. Fischer, (*a*) *J. Mol. Struct.*, 1982, **84**, 219; (*b*) *J. Photochem.*, 1981, **17**, 331. Earlier papers are listed in these publications.
2 (*a*) J. B. Birks, G. Bartocci, G. G. Aloisi, S. Dellonte, and F. Barigelletti, *Chem. Phys.*, 1980, **51**, 113; F. Masetti, G. Bartocci, U. Mazzucato, and G. Galiazzo, *Gazz. Chim. Ital.*, 1982, **112**, 255; (*b*) U. Mazzucato, *Pure Appl. Chem.*, 1982, **54**, 1705.
3 F. Momicchioli, I. Baraldi, and M. C. Bruni, *Chem. Phys.*, 1982, **70**, 161; 1983, **82**, 229; I. Baraldi, F. Momicchioli, and G. Ponterini, *J. Mol. Struct.*, 1984, **110**, 187.
4 A. E. Siegrist, P. Liechti, H. R. Meyer, and K. Weber, *Helv. Chim. Acta*, 1969, **52**, 2521.
5 H. D. Becker, K. Sandros, and L. Hansen, *J. Org. Chem.*, 1981, **46**, 821.
6 (*a*) G. Fischer, G. Seger, K. A. Muszkat, and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1569; (*b*) G. Fischer and E. Fischer, *Mol. Photochem.*, 1977, **8**, 279.
7 G. Fischer and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1264.
8 G. Bartocci and U. Mazzucato, *J. Lumin.*, 1982, **27**, 163.
9 E. Hughes, J. H. Wharton, and R. V. Nauman, *J. Phys. Chem.*, 1971, **75**, 3097.
10 A. N. Fletcher, *J. Phys. Chem.*, 1968, **72**, 2742.
11 K. Gustav, J. Sühnel, and U. P. Wild, *Chem. Phys.*, 1978, **31**, 59, where earlier references are cited.
12 F. E. Doany, B. I. Greene, and R. M. Hochstrasser, *Chem. Phys. Lett.*, 1980, **75**, 206.

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