263. Conformational Equilibria in *trans*-1,2-Diarylethylenes Manifested in their Emission in Solution

Part VI

Heterocyclic Analogues, their Triplets and Exciplexes

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Dedicated to Prof. *A.E. Siegrist*, Basel

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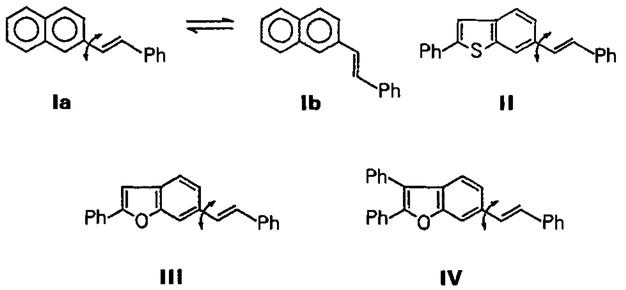
Summary

Solutions of heterocyclic analogues of 2-styrylnaphthalene (2-St-N), with benzo[*b*]thiophene and benzo[*b*]furan groups replacing the 2-naphthyl group, exhibit emission anomalies similar to those reported for 2-St-N, the most prominent one being a variation of the emission spectra with the excitation wavelength. The exciplexes formed when emission is quenched by *N,N*-dimethylaniline (DMA) show a smaller variation of their emission maxima. Ground-state rotamers may be responsible for the anomalies. The lifetimes of regular fluorescence in toluene are ≤ 2 ns, and our equipment did not allow to determine whether or not the decay is mono-exponential. Exciplex lifetimes in toluene are 20–30 ns. The triplets ($\lambda^{T}_{max} = 500$–520 nm) are characterized by short lifetimes (180–190 ns) and appear to have substantial contributions from twisted configurations.

Introduction. – By now it seems to be well-established that in solutions of many 1,2-diarylethylenes for which several more or less coplanar iso-energetic conformations can be postulated, ground-state equilibria involving such conformations are indeed established [1] [2]. This is exemplified by trans-2-styrylnaphthalene (2-St-N, **I**), in the *Scheme*. Moreover, in recent papers [2] [3] it has been shown that the emission spectra of the exciplexes of several 1,2-diarylethylenes with *N,N*-dimethylaniline (DMA) and other amines also vary with the excitation wavelength.

To find further support for the generality of the underlying concepts, we have investigated a few analogous compounds in which the 2-naphthyl group of **I** is replaced by benzo[*b*]thiophene and benzo[*b*]furan groups, as in compounds **II**–**IV**. These and several other related compounds were made available to us by Prof. *A.E. Siegrist*, Basel. We could indeed show that all these compounds, exemplified by **II**–**IV**, exhibit the expected emission-spectroscopic anomalies. In addition, transient absorption-

Scheme



spectral measurements employing nanosecond laser flash photolysis and pulse-radiolysis gave spectral and kinetic data concerning the short-lived triplets of these heterocyclic diarylethylenes.

Results. – a) *Emission Spectra.* These are shown in *Fig. 1* and *2*, for solutions in toluene at −50°C; at the low temperature, the spectral resolution is improved. Excitation wavelengths in these *Figures* were deliberately chosen to yield widely differing emission spectra. Attention is drawn to the short-wavelength portions of the emission spectra, outside the region were scattered exciting light makes measurements impossible.

The emission spectra are obviously superpositions of (at least) two separate spectra contributing to various extents to the overall spectrum. The short wavelength edge of the emission clearly disappears upon excitation at long wavelengths. For **III** *(Fig. 2, top)*, a third spectrum arises when exciting at and beyond 340 nm. At short wavelengths of excitation, one clearly observes superimposed spectra, while at intermediate

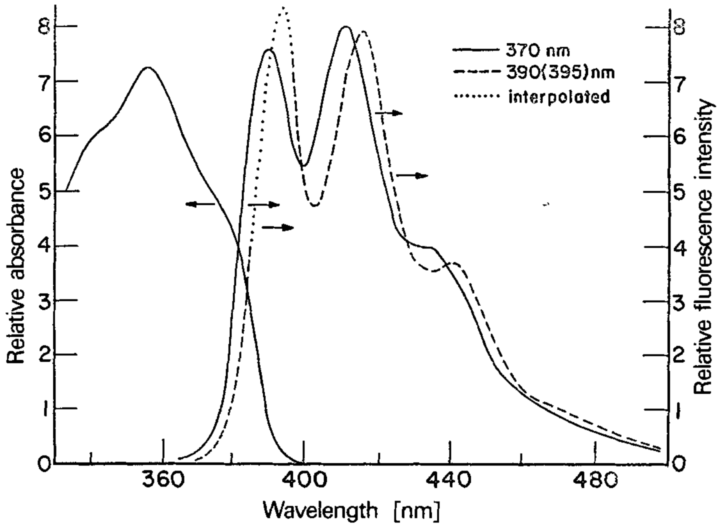


Fig. 1. *Uncorrected emission spectra of* **II** *in toluene at* −50°C *excited at the indicated wavelengths.* The dotted line show the estimated part of the curve in the spectral region obstructed by the scattered exciting light. Concentration: *ca.* 5×10^{-5} M. The solid curve on the left side denotes the absorption spectra.

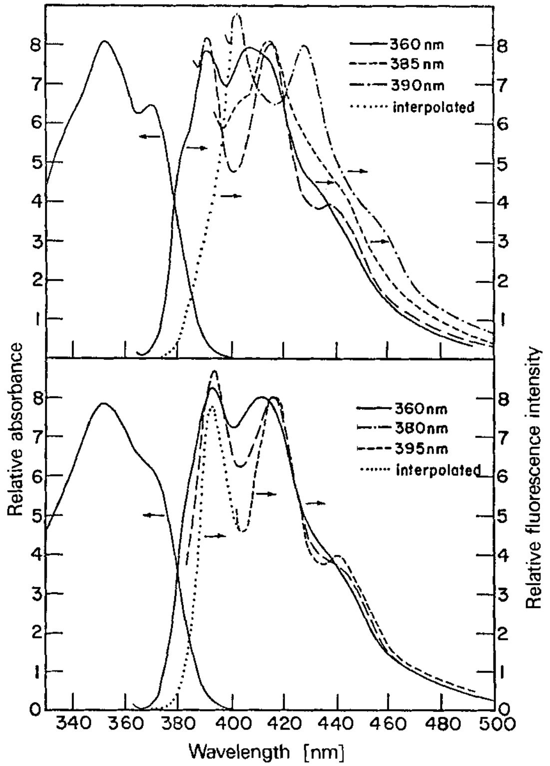


Fig. 2. *Uncorrected emission spectra of* **III** (top) *and* **IV** (bottom) *in toluene at −50°C with λ_{exc}'s shown.* Dotted lines indicate the estimated portions of the spectra in the region obscured by the scattered exciting light. Solid curves on the left side denote absorption spectra. Concentrations used: *ca.* 5×10^{-5} M.

Table 1. *Emission Peaks of the Two Sets of Emission Spectra Estimated from* Fig. 1 *and* 2. Solutions in toluene at −50°C.

Compound	Peaks [nm]		
II	(389)	410	431
	393	416	440
III	(382)	404	(432)
	390	414	439
IV	(382)	405	
	393	416	441

and long wavelengths (except for **III**), emission spectra are better resolved. In *Table 1*, we have tried to make a rough estimate of the position of the first two sets of emission peaks. We did not consider it justified to accurately analyze the spectra obtained at short excitation wavelengths, since we intended only to show the existence of a wavelength dependence, essentially similar to that observed with the homocyclic analogues [1] [2].

b) *Decay Curves.* Within the capabilities of our deconvolution procedures, these were mono-exponential. A typical curve is given in *Fig. 3* where τ_F is 1.3 ± 0.1 ns for **IV**

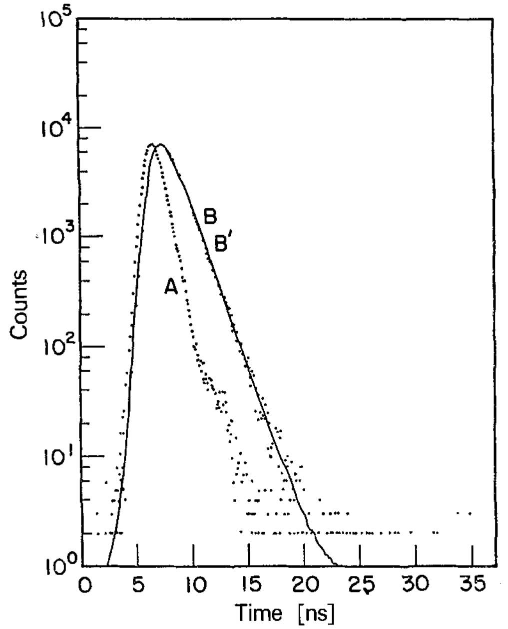


Fig. 3. *Emission decay profile of* **IV** *in toluene at room temperature* (λ_{ex} = 370 nm and λ_{mon} = 415 nm). The dotted line denotes the excitation profile (lamp). The full line denotes the curve convoluted with τ_F = 1.3 ns.

in toluene at room temperature. The result did not vary significantly with the wavelengths of excitation or emission. It should however be noted that a biexponential decay consisting of two components with short lifetimes, say, 1 and 1.5 ns, may remain indistinguishable from a mono-exponential decay in our measurements. For **II** and **III** the respective decay times are 1.1 and 1.2 ns.

c) *Quenching with DMA and Exciplex Emission.* As shown earlier [3], aliphatic and aromatic amines serve as charge-transfer quenchers of singlets of homocyclic 1,2-dia-

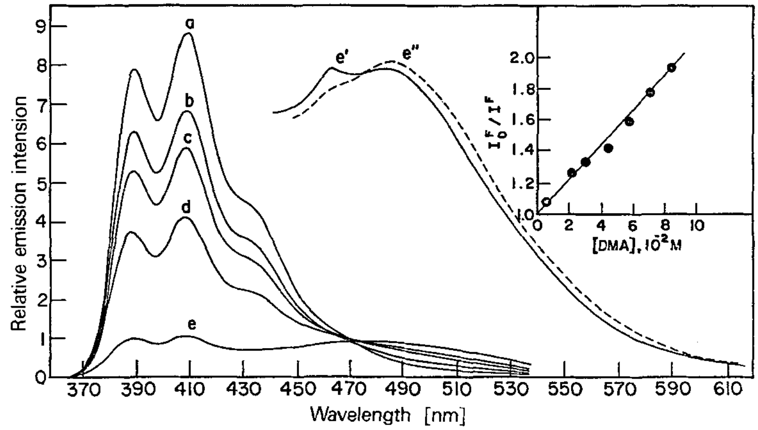


Fig. 4. *Emission spectra of a* 1.5×10^{-5} M *solution of* **III** *in toluene at room temperature before and after 'titration' with DMA.* DMA concentrations were: *a*, 0; *b*, 2.2×10^{-2}; *c*, 4.4×10^{-2}; *d*, 8.4×10^{-2}, and *e,e',e''*, 3.5×10^{-1} M. Curves *e'* and *e''* were recorded at ×10 higher sensitivity. λ_{exc} = 340 nm for all curves except *e''*, which was obtained at 390 nm excitation. Inset: *Stern-Volmer* plot based on these results (λ_{mon} = 409 nm).

Table 2. *Quenching Constants* (K_{SV}) *of* **II–IV** *with DMA in Toluene at Room Temperature* (calculated from *Stern-Volmer* plots $I_0^F/I^F = 1 + K_{SV}$ [DMA], where I denotes emission intensity)

Compound	λ_{ex} (nm)	λ_{mon} (nm)	K_{SV} [M^{-1}][a]
II	340	409	10.8
	390	413	11.6
III	340	403	6.5
	390	412	5.5
	400	412	5.3
	340	413	6.0
IV	340	407	6.6
	390	414	5.1
	400	418	4.9

[a] *ca.* ±15%.

Table 3. *Data Concerning Exciplex Emission Spectra and Decay.* Solutions in toluene at room temperature. [DMA] = 0.35–0.43 M.

Compound	λ_{max}^{ex} [nm][a]	τ^{ex} [ns][b]
II	485	22 (27)
III	460	26 (31)
IV	460	35 (34)

[a] Excited at 340 nm. As seen in *Fig. 4*, the exciplex emission is shifted to longer wavelengths at long excitation wavelength in the case of **II**.

[b] ±10%; the data in the parentheses are in benzene at room temperature.

rylethylenes. Since the excitation of our compounds was generally at wavelengths equal to or longer than 340 nm, the absorption of exciting light by DMA did not interfere seriously. *Fig. 4* describes the emission of **II** as a function of DMA concentration. The efficient quenching, and the appearance of a broad-banded exciplex emission peaking at 460–480 nm, is well-documented. Moreover, the exciplex emission spectrum for **II** varies slightly with the excitation wavelength (curves e′ and e″ in *Fig. 4*). The exciplex emission maxima measured for **III** and **IV** in the presence of DMA show practically no wavelength dependence. The quenching constants (K_{SV}) obtained from *Stern-Volmer* equations for various combinations of excitation and emission wavelengths are given in *Table 2*. The observed emission lifetimes of the exciplexes (not deconvoluted for the ~ 8 ns laser pulse at 337.1 nm) were essentially independent of emission wavelengths (440–500 nm) and are presented in *Table 3*, together with the approximate emission maxima.

d) *Spectral and Kinetic Data for Triplets.* Upon direct laser excitation (337.1 nm) of solutions of **II** in benzene or toluene, a short-lived transient species assignable as the triplet is observed in terms of spectral absorption at 400–600 nm (λ_{max} = 510 nm in toluene, see curve C′ in *Fig. 5*). The triplet assignment of the transient is based on its quenchability by oxygen, di(*tert*-butyl)nitroxide radial and ferrocene, the bimolecular rate constants (k_q^T) for the quenching by these typical triplet quenchers being 6.6, 0.85, and 3.6 × 10^9 $M^{-1}s^{-1}$, respectively (in toluene). Non-negligible intersystem crossing in **II** is also indicated by 337.1 nm laser flash photolysis of **II** in the presence of ~ 1 mM β-carotene (in toluene) whereupon growths of the polyene triplet absorption at 530–

550 nm are observed [4] over a time-scale (~ 100 ns) commensurate with the decay of the triplet of **II** ($\tau_T = 180$ ns). Relative to the formation of benzophenone (BP) triplet in benzene ($\Phi_T^{BP} = 1$, $\varepsilon_{max}^{T,BP} = 7.6 \times 10^3$ M^{-1}cm^{-1}) [5], the triplet yield in **II** was measured in toluene using solutions optically matched at the exciting laser wavelength (337.1 nm). Details of this comparative technique are available in [5] [6]. A value of 0.20 ± 0.05 was estimated for Φ_T in toluene using the triplet extinction coefficient data measured pulse-radiolytically by energy transfer from biphenyl (see below).

No transient absorption attributable to a triplet was observed upon direct laser flash photolysis of **III** and **IV** in toluene ($\Phi_T < 0.005$). For these compounds as well as for **II**, triplets were produced by energy transfer from biphenyl triplet generated by pulse radiolysis [7] of toluene solutions containing 0.1M biphenyl and 5–7 mM diarylethylene substrates. The triplet absorption spectra are shown in *Fig. 5*. Comparison of transient absorbance due to the biphenyl triplet at 360 nm ($\varepsilon_{max}^T = 2.7 \times 10^4$ M^{-1}cm^{-1} in benzene) [5] in the absence of a quencher with that due to a diarylethylene triplet produced under nearly complete quenching of the former gave an estimate for the extinction coefficient of the latter. The data concerning triplet lifetimes and absorption spectra of **II**–**IV** are summarized in *Table 4*. It should be noted that as with fluorescence decay profiles, no significant multiexponential behavior was observed in the triplet decay.

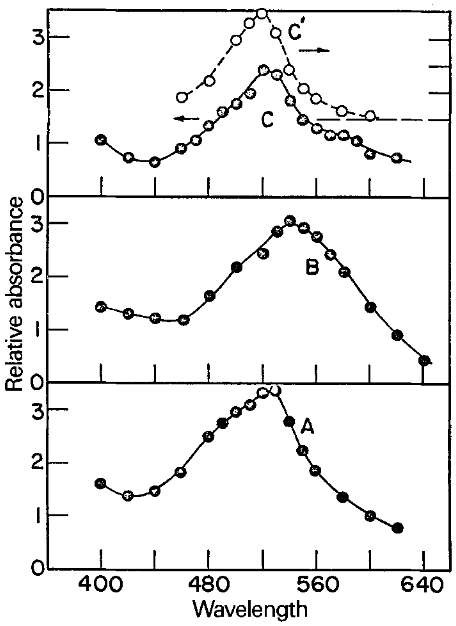


Fig. 5. *Transient absorption spectra of triplets of* **III** (A), **IV** (B) *and* **II** (C) *obtained by pulse radiolysis of toluene solutions* (Ar-flushed) *containing 0.1M biphenyl and* ~ *5* mM **II**–**IV**. The spectrum C' was obtained by 337.1 nm laser flash photolysis of **II** in Ar-saturated toluene.

Table 4. *Spectral and Kinetic Data for the Triplets of* **II**–**IV** *in Toluene at Room Temperature*

Compound	Φ_T a)	λ_{max}^T (nm) b)	ε_{max}^T (10^3 M^{-1}cm^{-1}) a)	τ_T (ns) c)
II	0.20	520	20	180
III	< 0.005	520	18	190
IV	< 0.005	540	20	190

a) *ca.* ±25%. b) ±5 nm. c) ±20%.

Discussion. – The emission spectra of **II–IV** at room temperature have been reported by *Siegrist & Meyer* [8]. The excitation wavelength dependence of emission spectra observed with these compounds in solutions is reminiscent of the general behavior of diarylethylenes [1] [2] for which isoenergetic rotamers are possible through the rotation of an aryl group about the 'single' bond linking it to the ethylenic moiety. It seems likely that the conformational heterogeneity arising from the rotation of the heterocyclic group in **II–III** is responsible for the observed anomalous emission behaviors. For many diarylethylenes [1] [2], the conformational heterogeneity is also manifested in multiexponential fluorescence lifetimes. Such evidence is lacking in the case of the present systems. It is possible that the rotamers in **II–IV** have short fluorescence lifetimes close to one another; this can also explain the general lack of dependence of K_{SV}'s on the excitation wavelength *(Table 2)*, the rotamers of a given diarylethylene being expected to possess similar charge-transfer characteristics in their excited states.

The lack of intersystem crossing in **III** and **IV** is a photophysical behavior common with many diarylethylenes including stilbene [9a] and naphthylethylenes [9b] [10]. Interestingly, the benzo[*b*]thiophenyl derivative **II** constitutes an exception. The pronounced triplet yield in **II** may be an outcome of two factors, namely, *i*) the existence of low-lying n,π^* states (associated with the lone electron pair on the sulfur atom) which cause facile intersystem crossing between singlet and triplet states of different orbital origin [11], and *ii*) the role of the sulfur atom as a heavy atom in inducing intersystem crossing by a spin-orbit coupling mechanism.

The short lifetimes of the triplets of **II–IV** *(Table 4)* strongly suggest that these are ethylenic in character and that twisted configurations are probably as important for these triplet systems as they are in the case of naphthylethylenes [9b] [10]. The rate constant ($3.6 \times 10^9\ \mathrm{M}^{-1}\mathrm{s}^{-1}$) for the ferrocene quenching of the triplet of **II** enables us to estimate the relative importance of planar and twisted forms for this particular system. Assuming that the planar form is quenched by ferrocene with a diffusion-controlled rate constant ($\sim 8 \times 10^9\ \mathrm{M}^{-1}\mathrm{s}^{-1}$) while the twisted form is not quenched at all, the observed quenching rate indicates that the two forms are nearly equally important (*i.e.*, $K \approx 1$ for planar $\leftrightarrows$ twisted equilibrium).

Experimental. – *Materials.* Compounds II–IV were obtained as generous gifts from Prof. *A.E. Siegrist*, Basel and were used without further purification. *N,N*-Dimethylaniline (*Kodak*) was vacuum-distilled before use. Toluene (*Fluka* or *Eastman*) was of spectral grade. The sources and purification of other reagents are given in previous papers [3] [6] [10].

Measurements. Emission spectra were recorded with Ar-flushed solutions in a *Perkin-Elmer MPF-44* spectrofluorimeter, using 2–3 nm excitation and emission slits. Cells with 1 cm × 1 cm cross section were used in a right-angle configuration. Our usual cooling technique [12] was employed, based on the controlled passage of liquid air through a Cu block surrounding the spectrophotometric cell inside a quartz dewar. Emission decay curves of the unquenched samples were determined (at Notre Dame) in a photon counting set-up [3b] from *Photochemical Research Associates*. Emission decay profiles of the exciplexes were measured in a laser flash apparatus described in earlier publications [3] [10] [13] from the Radiation Laboratory. For exciplex emission measurements as well as for observation of triplet-related transient absorption, nitrogen laser pulses (337.1 nm, ~ 8 ns, 2–3 mJ) from a *UV-400 Molectron* system were used for excitation. The pulse radiolysis experiments were carried out employing 7 MeV electron pulses (5 ns) from Notre Dame *ARCO-LP-7* linear accelerator; further details are available elsewhere [14].

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