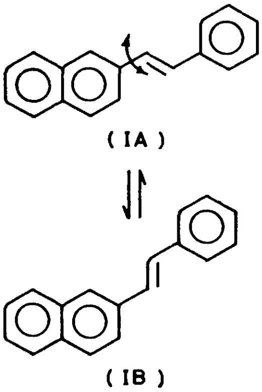
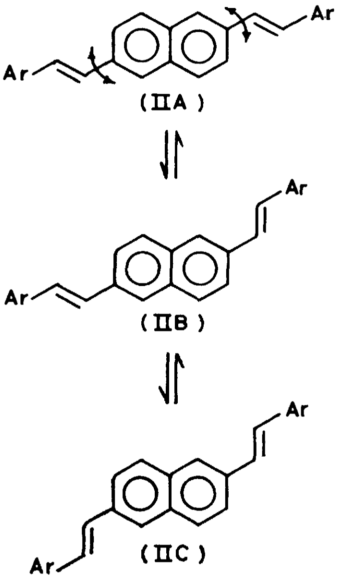
# Conformational Equilibria in 1,2-Diarylethylenes manifested in their Emission in Solution. Part 5.[1] 2,6-Distyrylnaphthalene and Related Compounds

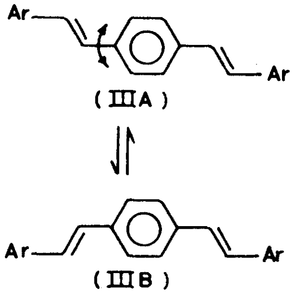
By **Gabriella Fischer** and **Ernst Fischer,*** Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel

The emission spectra of the title compounds vary with the wavelength of the exciting light. These spectra can be described as superpositions, for each compound, of three sets of emission peaks which contribute to the overall spectra to an extent varying with the excitation wavelength. It is suggested that in solutions of each compound three modifications exist in a dynamic equilibrium. They have essentially similar but slightly shifted absorption and emission spectra, so that the fraction of exciting light absorbed by each modification varies with the wavelength of the exciting light. The three modifications are assigned to rotational conformers involving the two quasi-single styryl–naphthyl bonds. In 1,4-distyryl- and 1,5-distyryl-naphthalene, in which only one relatively unhindered conformer can be envisaged, no variation of the emission spectra with the excitation wavelength was observed.

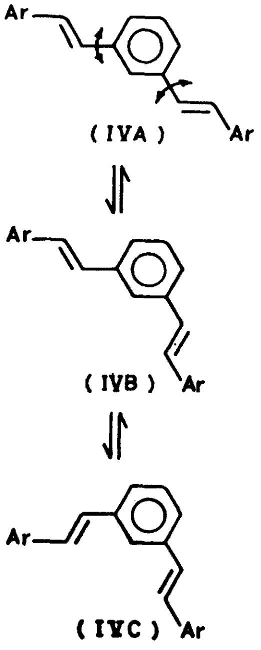
In a series of papers by ourselves [1] and others,[2-4] it was shown that solutions of the *trans*-isomers of several 1,2-diarylethylenes exhibit anomalies in their emission spectra, and in a few cases also in their emission decay rates and quantum yields. The most prominent observation was the variation of the emission spectra with the wavelength of excitation. Moreover, time-resolved emission spectroscopic studies of 1,2-di-(2-

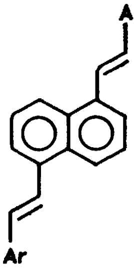






(1) Ar = Ph
(2) Ar = 4-$MeOC_6H_4$
(3) Ar = 2-$C_4H_3S$
(4) Ar = 1-$C_{10}H_7$
(5) Ar = 2-$C_{10}H_7$
(6) Ar = 4-$Pr^iC_6H_4$





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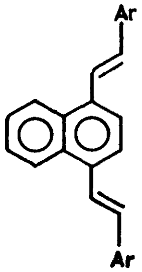


( VI )

naphthyl)ethylene have shown[3] that the emission spectra vary sharply with the time elapsed between excitation and measurement. These anomalies were ascribed to the existence of dynamic equilibria among two or three rotational conformers in solution, as illustrated for 1-phenyl-2-(2-naphthyl)ethylene (I). The basic idea was that the sharply structured absorption spectra of the different conformers are slightly shifted against each other, so that at any but the longest excitation wavelengths light is absorbed by all two or three conformers, but to an extent varying with the wavelength. Similar effects may be expected in related systems, as long as two or more well defined and almost isoenergetic conformers can be postulated, separated by energy barriers due to the loss of resonance energy as the angle of twist around the quasi-single bonds approaches 90°. These barriers have to be sufficiently high to allow the existence of discrete conformers, on the time scale of the method used to characterize these conformers (*cf.* Part 2[1c] for a detailed discussion). The postulated conformers do not have to be coplanar, *i.e.* the equilibrium angle of twist around the quasi-single bonds may differ somewhat from zero, because of the slight steric interference of the protons. If the energy difference is substantial, the contribution of the energetically higher conformer will be too small for detection.

Similar ideas may be applied to the title compounds (II) and their derivatives. The three conformers (IIA—C) differ from each other regarding both the position of the two quasi-double bonds relatively to each other and their position relatively to the naphthalene. Conformers (IIA—C) may be almost coplanar, and in any case do not differ from each other substantially as far as steric interference is concerned. These compounds seemed therefore to be excellent candidates for the existence and detection of ground-state conformers. The present paper deals with six compounds belonging to type (II), and two belonging to types (V) and (VI). In a forthcoming paper we hope to describe compounds (III), (IV), and related ones. In the absence of other than steric factors, compounds (V) and (VI) are expected to exist only as the conformers depicted, while two isoenergetic conformers can be postulated for (III) and three for (IV).

## RESULTS AND DISCUSSION

The emission spectra of compounds (1)—(6) were found to vary with the wavelength of excitation, in particular when exciting at the long wavelength edge of the absorption. These variations were easily observable at room temperature but more clearcut results were obtained at reduced temperatures. This is so because the absorption and emission spectra undergo the usual sharpening on cooling, thus enhancing the chances for selective excitation of each species, as well as improving the separation of the spectra of the various modifications. The results are summarized in the Table, and illustrated for three compounds in the Figure, where wavelengths of excitation were chosen at which the emission spectra represent what we believe to be the almost pure three modifications characterized by three sets of peaks shifted against one another by 3—12 nm. These sets are denoted by a, b, and c in the order of increasing wavelength. At other excitation wavelengths a superposition of two modifications is observed, as shown by the curve for 400 nm in Figure 1A. In most cases the ratio between the intensities of the shortest emission band and the neighbouring one is larger in the b and c modifications.

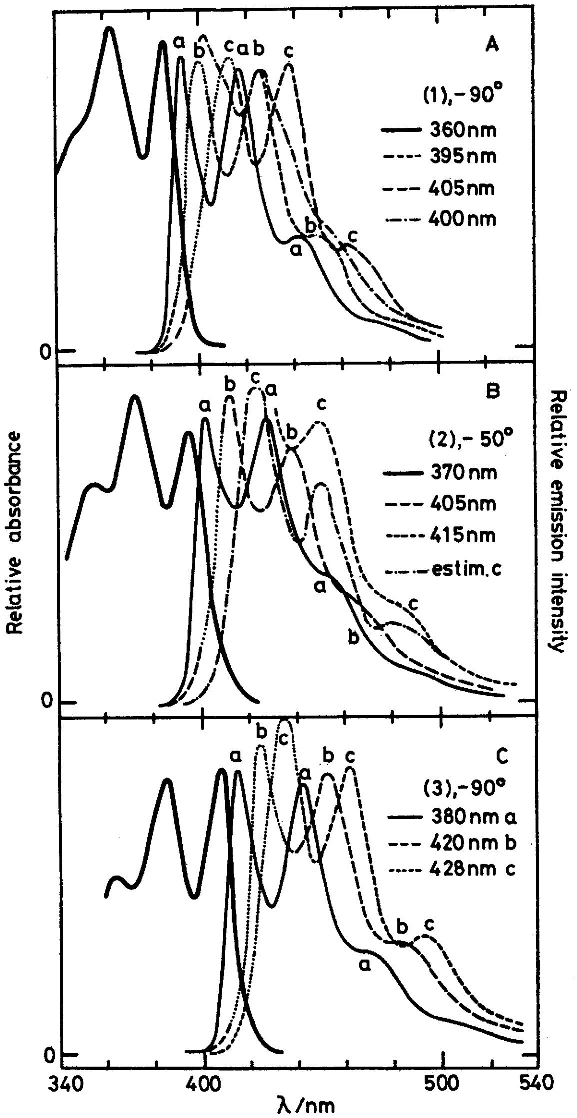
Positions, in nm, of the three sets of emission peaks in each compound. Solutions in toluene at $-90$ °C, unless stated otherwise

| Compound | | | | |
|---|---|---|---|---|
| (1) | a | 393 | 418 | 441 |
| | b | 401 | 426 | 449 |
| | c | 413 | 438 | 463 |
| (2) $-50°$ | a | 403 | 427 | |
| | b | 412 | 438 | |
| | c | (422) | 450 | |
| (3) | a | 414 | 441 | 470 |
| | b | 423 | 451 | (480) |
| | c | (434) | 459 | (487) |
| (4) $-50°$ | a | 417 | 443 | |
| | b | (423) | (447) | |
| | c | 428 | 453 | |
| (5) $+25°$ | a | (417) | (437) | |
| | b | (419.5) | (440.5) | |
| | c | (422) | (443.5) | |
| *o*-Dichlorobenzene | | | | |
| (6) | a | 398 | 421 | (445) |
| | b | 406 | 430 | (456) |
| | c | 416 | 441 | (475) |

All solutions were in toluene, because several of the compounds tend to precipitate on cooling solutions in methylcyclohexane. Compound (2) could be measured only at a rather low concentration even in toluene, while compound (5) could be studied only in *o*-dichlorobenzene at room temperature. In compounds (4) and (5), the spectral definition of the three modifications was poor because the spectral shift between the various modifications was small. In most compounds the emission spectra were almost invariant with the wavelength of excitation at shorter wavelengths than those illustrated; this may indicate that a large fraction of the molecules exists in the a-modification (Figure).

As before,[1c] we attempted to estimate the contribution of the various conformers from the emission spectra observed when exciting in a very broad band of light, by using the maximal excitation slit width (20 nm). However, in the range 340—400 nm, excitation of compounds (1)—(3) with 2 nm and with 20-nm slits yielded almost identical emission spectra, probably representing a conformer mixture very rich in the a-modification. This again indicates a high contribution of this modification to the equilibrium mixture.

In Parts 1 and 3 we reported that the modifications of (I) and related compounds differ also in their fluorescence lifetimes $\tau_F$. This gave rise to preferential quenching by



Uncorrected emission spectra and partial absorption spectra of *trans*-2,6-distyrylnaphthalene and derivatives in the solvents and at the temperatures indicated. Excitation wavelengths as given in the description of the curves. Dotted lines denote interpolated parts of the emission curves, in those wavelength regions inaccessible because of scattered exciting light

oxygen, causing a shift of the shape of the emission spectra in favour of the shorter-lived modification.[1d] Since at present the facilities for extensive measurements of emission decay curves are not available to us, we only checked the effect of oxygen on the emission spectrum of (1). None was found, indicating that there are no large differences in the $\tau_F$ values of the three modifications.

Excitation spectra were measured with compounds (1)—(3), at the middle emission peak of each of the three modifications [*e.g.* for (1) at 418, 426, and 438 nm]. As expected from the emission spectra, the excitation spectra were observed to vary with the emission wavelength in each case.

In solutions of compounds (V) and (VI) (aryl = phenyl) no variation of the emission spectra with the excitation wavelength was observed, in accord with the expectations expressed in the Introduction. Obviously the two other rotamers which can be postulated for each of these compounds are much more hindered, and therefore have a higher energy content, because of the deviation from coplanarity, than the modifications depicted. Consequently their contribution to the conformer equilibrium is negligible.

As in the cases described before,[1-4] no assignment of the three postulated conformers (IIA—C) to each of the three observed modifications can be made. Indeed, the assumption of these conformers is still only a reasonable but unproven explanation of the mounting volume of similar observations. It is to be hoped that $^{13}$C n.m.r. measurements, or possibly other physical methods, will eventually provide more direct evidence. The same holds for eventual calculations of the expected differences among the absorption and emission spectra of the postulated conformers.

As mentioned earlier,[1c,d] we believe that no changes in the rotamer equilibrium (IIA) $\rightleftarrows$ (IIB) $\rightleftarrows$ (IIC) take place in the excited state hyperface prior to emission. This was based on (a) the observations of the decay curves, in particular in cases where the postulated conformers have different emission decay times, and (b) the fact that rotation around the bonds which are quasi-single in the ground state is much more hindered in the excited state, where these bonds are quasi-double. We conclude that the major reason for the observed phenomena is the existence of a rotamer equilibrium (possibly frozen-in at low temperatures) in the electronic ground state of these compounds. For more details see the Discussion in Parts 1 and 2.

## EXPERIMENTAL

Emission spectra were measured on a Perkin-Elmer–Hitachi MPF-44 instrument. Excitation and emission slits were 2 nm throughout. Absorption spectra were measured on a Cary 14 spectrophotometer. Both instruments were fitted with our usual cooling arrangement,[5] based on controlled passage of liquid air through a copper block surrounding the spectrophotometric quartz cell inside a quartz Dewar. All emission spectra are uncorrected. Excitation was at right angles. For further details see ref. 1*c*. Fluorescent-grade toluene served as the solvent. Concentrations were 1—4 × $10^{-6}$M. Solutions were flushed at −20 °C with argon containing $<$5 p.p.m. oxygen and then kept under a slight pressure of argon during measurements.

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