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EMISSION SPECTROSCOPY EVIDENCE FOR THE EXISTENCE OF ROTAMERS IN SOLUTIONS OF *trans*-DIARYLETHYLENES AND RELATED COMPOUNDS*

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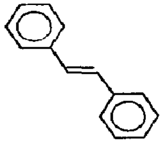
Summary

A large variety of *trans*-1,2-diarylethylenes and 2,6-distyryl naphthalenes exhibit a pronounced variation in their emission spectra with the wavelength of excitation. (The aryl group can be phenyl, substituted phenyl, naphthyl, pyridyl, quinolyl, phenanthryl or anthryl.) The most reasonable working hypothesis seems to be that in solution these compounds exist as mixtures of two or three almost isoenergetic rotational conformers involving the quasi-single bonds. The conformers have slightly different absorption and emission spectra. Compounds in which such conformers cannot be postulated or are expected to be far from isoenergetic do not exhibit the phenomena. In some cases the modifications also differ in their emission decay times and emission yields and can be distinguished by time-resolved emission spectroscopy. We are not aware of the application of other physical methods to prove the existence of such conformers in these compounds.

1. Discussion

The configuration of 1,2-diarylethylenes is determined by the interplay between free rotation around the quasi-single bonds, giving equal probabilities to any angle α of twist around these bonds, and the tendency towards coplanarity of the whole system, stemming from the delocalized π electron system extending over the central double bond and the aromatic groups. This tendency is modified by steric repulsion, which is rather small in *trans*-stilbene **1** but large in *cis*-stilbene **2** and in *trans*-α,α'-dimethylstilbene **3**.



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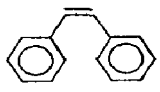

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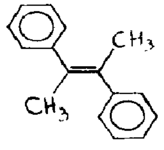

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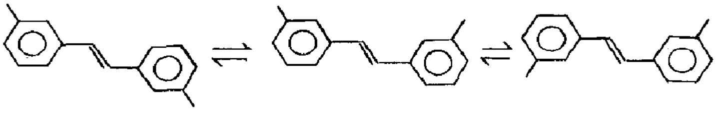
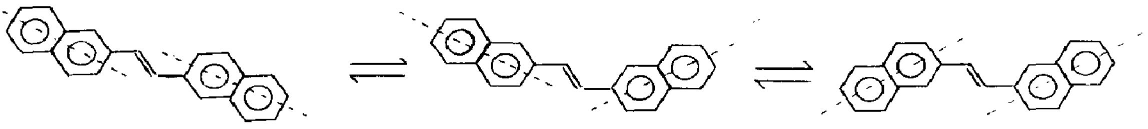
As a result, these and related molecules are expected to possess two potential minima for certain values α_{min} separated by energy barriers at $\alpha = 90°$. For **1** α_{min} is probably not very different from 0°, while for **2** and **3** α_{min} is probably [1] 30° - 50°. When the phenyl rings in **1** and **2** have "marked edges", the configurations in the two potential minima are no longer equivalent, as, for example, in **4** and **5** where three different rotamers **a**, **b** and **c** can be envisaged:

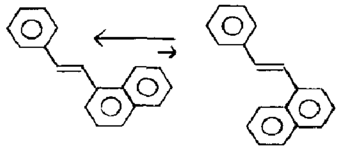


4b **4a** **4c**



5b **5a** **5c**

The same consideration holds for the corresponding *cis* isomers. The steric repulsions, if any, are identical in the three rotamers of **4** and not far from identical in **5**, so that we may expect a dynamic equilibrium between these almost isoenergetic rotamers in solution. In order to prove the existence of such equilibria between discrete rotamers, methods must be employed which are able to distinguish between the rotamers and which, moreover, are inherently fast on the time scale of the rate of interconversion of the rotamers. If the barriers are 5 - 10 kcal mol^{-1}, nuclear magnetic resonance (NMR) methods may or may not be fast enough at room temperature, but methods depending on electronic excitation are certain to be adequate from this point of view. Furthermore, even if the postulated rotamers differ slightly from each other in their spectral absorption properties, it is difficult to unravel the superimposed spectra without additional information. Only methods depending on properties of the electronically excited states have the great advantage of putting an additional parameter at our disposal: the wavelength λ_{ex} of excitation. This is because slight differences in optical absorption spectra make selective photoexcitation possible, since at any absorbed λ_{ex} the proportion of light absorbed by each rotamer will be different. When the absorption spectra of the rotamers are shifted relative to each other, excitation at the long wavelength tail of the absorption may hit one conformer predominantly even if its contribution to the overall equilibrium is small. In the *cis* isomers it has been shown by Jacobs and Havinga [2] with hexatriene derivatives, and by ourselves [3, 4] with *cis*-**5** and related compounds, that photocyclization products derived from the various rotamers are obtained in proportions depending on λ_{ex}. In the *trans* compounds, such as **5**, no similar photoreactions occur but a pronounced variation in the emission properties, in particular the emission spectrum, with λ_{ex} is observed. It is this property, observable with relatively simple equipment, which has been used most extensively by us and by other researchers for a large variety of compounds. Early and scanty reports by ourselves [5, 6] have been followed by more extensive reports by Shekk *et al.* [7], by ourselves [8 - 13], by Birks *et al.* [14] and by Ghiggino [15]. With very few exceptions, the compounds for which almost isoenergetic rotamers, *i.e.* with similar steric interactions, can be postulated exhibit this variation in the emission spectrum with λ_{ex}, while compounds such as **6** and **7**



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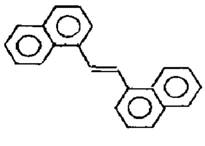

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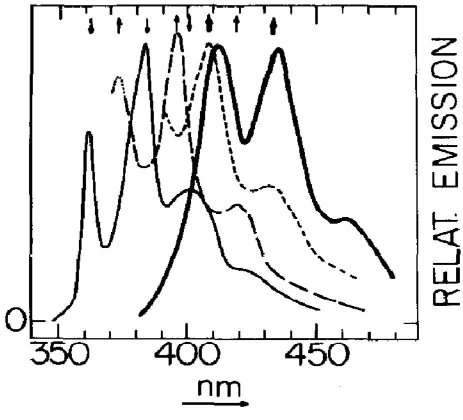
in which no such isoenergetic rotamers can be envisaged do not exhibit the variation. Some examples are shown in Figs. 1 and 2 [11]. The emission spectra obtained at various wavelengths can be described as superpositions of two or three discrete but rather similar spectra characterized by sets of peaks similar to those denoted by arrows in Figs. 1 and 2, shifted slightly relative to each other and contributing in various extents to the overall spectrum. (In these figures the short wavelength peaks are partly overshadowed by stray exciting light and therefore are not shown.) In favourable cases, *e.g.* **5**, *varying* λ_{ex} in steps of 1 - 2 nm already results in pronounced changes in the emission spectra [8].

We have mentioned that the rotamers should be almost isoenergetic. In reality there will be small energy differences between them and therefore some temperature dependence of the equilibrium between them may be expected, as long as it is established. Thus for **5** in fluid solution we observe three modifications at room temperature but only two modifications at −100 °C and below. However, if the compound is embedded in polyethylene, three modifications are still observed [13] at −100 °C (see Fig. 1). We believe that in this medium the



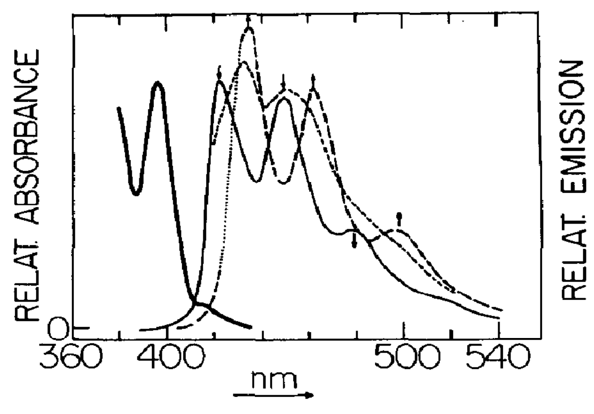


Fig. 1. Uncorrected emission spectra of compound **5** at −100 °C: (in an unstretched polyethylene film) ——, λ_{ex} = 350 nm; — — —, λ_{ex} = 366 nm; - - -, λ_{ex} = 380 nm; ——, polycrystalline material.

Fig. 2. Uncorrected emission spectra of 3An-Th (see text) in toluene at −75 °C: ——, λ_{ex} = 370 nm; — — —, λ_{ex} = 430 nm; - - -, λ_{ex} = 415 nm. The three spectra represent the two almost pure modifications and a mixture of the modifications (concentrations, about 4×10^{-6} M).

high microviscosity and low temperature combine to freeze in the equilibrium for some higher temperature on cooling to −100 °C.

The well-known sharpening of absorption and emission spectra on cooling makes photoexcitation at low temperatures much more selective and also allows a better separation of the emission peaks. Thus most of our spectroscopy was carried out at low temperatures, but this is by no means essential.

The *trans* diarylethylenes Ar–CH=CH–Ar′ in which the presence of two or three modifications is certain according to our emission measurements are as follows: Ph-2N; sub-Ph-2N; 1N-2N; 2N-2N; 2N-3Phe; 3Phe-3Phe; 3Phe-4BP; 2N-4BP; 3Phe-4BP; 3An-Ph; 3An-sub-Ph; 3An-Th; 3An-2N; Qu-Ph; Qu-2N; Qu-Qu; Qu-3Py; 6BF-Ph; 6BT-Ph. We have used the abridged notation Ar-Ar′ and the following radical abbreviations: Ph, phenyl; 1N, 1-naphthyl; 2N, 2-naphthyl; 3Phe, 3-phenanthryl; BP, 2-benzo[c]phenanthryl; 3An, 3-anthryl; Th, 2-thienyl; Qu, 6-quinolyl or 7-quinolyl; 3Py, 3-pyridyl; sub-Ph, various substituted phenyls; 6BF, 6-benzo[b]furanyl; 6BT, 6-benzo[b]thienyl. Thus compound 5 is denoted 2N-2N.

The emission spectra in our laboratory were measured [8 - 13] with a Perkin–Elmer MPF-44 instrument equipped with our usual cryostat, using 2 nm excitation slits and 2 - 4 nm emission slits. Still narrower excitation slits did not improve the results substantially.

The extent of the wavelength shift between the several modifications is in the range 5 - 20 nm, varying with the compound and increasing at longer wavelengths. At 400 nm, 10 nm is roughly equivalent to 600 $\mathrm{cm^{-1}}$ or 0.23 kcal $\mathrm{mol^{-1}}$. This is thus the change in the energy difference between the ground and excited states when going from one modification to the neighbouring modification. Whether this change is due to a change in the energy of the ground state, the excited state or both is still a matter for speculation. We need calculations of the expected spectral difference between the postulated rotamers.

It is obviously of interest to shift the equilibrium between the various modifications in favour of one of them. In view of the small energy differences between them (otherwise only one form would exist in solution anyway), external factors are expected to suffice to bring about such a shift. Crystal forces do indeed cause a shift; *e.g.* **5** was found [16] to crystallize as **5b**, the most extended configuration. Indeed, the emission from crystalline **5** is virtually independent of λ_{ex}, apart from phenomena ascribable to surface factors [13] (Fig. 1). However, the large shift in absorption and emission spectra to long wavelengths observed for many diarylethylenes [6] makes a direct comparison with solution spectra impossible. Incorporation into unstretched and stretched polyethylene films, as described above, does not lead to preferential stabilization of one modification [13]. Cooling shifts the equilibria to some extent, as long as they are established, but usually the state at some intermediate temperature is frozen in. The shapes of the various molecular modifications are clearly not sufficiently different to cause preferential incorporation in stretched films or liquid crystals. The only successful method was found by chance: on cooling solutions of the sparsely soluble 3Phe-3Phe in a methylcyclohexane–methylpentane mixture to −120 °C, excitation at one wavelength first gave rise to a mixed emission spectrum; further slow cooling to −140 °C resulted in the gradual transition to an almost pure spectrum of the long wavelength modification. Nothing similar happened in the "good" solvent mixture toluene–methylcyclohexane. We believe the explanation to be a sort of association, perhaps better called cluster formation, in which one modification is preferred.

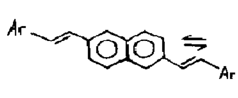
A rough estimate of the contribution of the two modifications to the mixture is possible by exciting over a broad range of wavelengths, *i.e.* with very wide slits. By comparing the observed emission spectrum with those of the two individual species and assuming equal absorbances and fluorescence quantum yields for both rotamers (but see later) we may compare the observed spectra with those of the pure species. For Ph-2N and 2N-2N such estimates led to estimated contributions of 10% - 30% by the long wavelength component. In many other cases the contribution was found to be much smaller, and the long wavelength component could be detected only because at the long wavelength tail of the absorption spectrum this rotamer absorbs very much more strongly than the other rotamer. This was even more obvious for the third longest wavelength rotamer, when it was observed at all. It should be remembered that room temperature equilibrium constants [rotamer **a**]/[rotamer **b**] of 2, 5, 10 and 100 are roughly equivalent to free-energy differences between **a** and **b** of 0.4 kcal mol^{-1}, 1.0 kcal mol^{-1}, 1.4 kcal mol^{-1} and 2.4 kcal mol^{-1} respectively. Energy differences of the order of 1 kcal mol^{-1} are probably feasible in view of the known partial bond localization in naphthalene, phenanthrene and anthracene, which makes the aromatic bond lengths non-identical and therefore causes differences in the extent of the deviation from coplanarity.

Recently an attempt has been made by Muszkat and Wismontski [17] to correlate the different spectra observed with the three rotamers postulated for 2N-2N and the two rotamers for Ph-2N. The method is based on the highly resolved "quasi-line" emission spectra obtained with some aromatic compounds in the so-called Spolskii *n*-hexane polycrystalline matrixes at 4 - 20 K. If we make the common assumption that planarity furthers incorporation in such matrixes, the more planar of the postulated rotamers should be incorporated preferentially and yield quasi-line spectra. Experimentally, superpositions of two distinct spectra were observed, with only one of them exhibiting the typical quasi-line structure. From its relative spectral position this spectrum could be assigned to the "short wavelength" species. However, if we take into account the actual bond lengths [16] in the naphthyls of **5**, the most planar rotamers of Ph-2N-**5** and 2N-2N-**5** are expected to be the **b** type. Subject to the correctness of the above basic assumption regarding Spolskii matrixes, the modifications of Ph-2N and of 2N-2N emitting at shorter wavelengths may therefore be assigned the extended configuration **b** in which the horizontal axis of the naphthyl rings is roughly parallel to the ethylenic double bond.

Finally, in cases where different rotamers can be envisaged but none of the spectral evidence described above is found, the reason may well be too slight a difference between the spectral properties of the rotamers. Here, also, high resolution experiments or possibly ^{13}C NMR measurements may detect these rotamers after all. An example may be 3,3′-dimethylstilbene **4** where no clear-cut spectral evidence has been obtained and ^{1}H NMR of the methyl protons did not help [9].

An intriguing case has been observed by Mazzucato *et al.* [18]. For all three isomeric *trans*-styrylpyridines Ph–CH=CH–Py (Py ≡ 2-pyridyl, 3-pyridyl or 4-pyridyl) they have found a pronounced λ_{ex} dependence of the emission spectra and λ_{em} dependence of the excitation spectra. The solutions were made in ether–isopentane–ethanol (EPA) as well as in alcoholic or aliphatic hydrocarbon glasses at 77 K. A considerable effect was observed even in stilbene itself in EPA, and a slight effect was observed (1 - 2 nm shift) in 3-methylpentane at 77 K. We confirmed these surprising observations [13]. The results with the 4-pyridyl derivative and with stilbene cannot be explained by the existence of rotamers of the type described above, and thus a different reason may apply to these and probably also to the 2 Py and 3 Py results (although on their own the latter could be ascribed to such rotamers). We shall refer to these results later.

The last and rather beautiful illustration of rotamers is provided by the distyrylnaphthalenes **8**, **9** and **10**.



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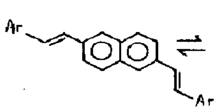

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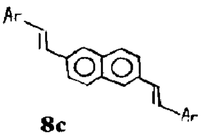

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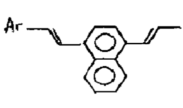

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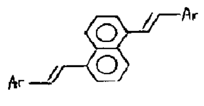

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Applying our previous criteria, **8** is expected to form an equilibrium mixture of three almost isoenergetic rotamers **a**, **b** and **c**, while in **9** and **10** the **a** rotamer is preferred because of its smaller steric interference in the coplanar configuration. Indeed, six derivatives of **8** all showed the effect, while **9** and **10** did not [12]. Figure 3 shows the results obtained with an **8** derivative. We hope to carry out similar measurements with the various analogous distyrylbenzenes and related compounds.

So far we have described the most common emission anomaly ascribed to the existence of rotamers: the variation of the emission spectra with λ_{ex} and of the excitation spectra with λ_{em}. The second anomaly concerns emission decay

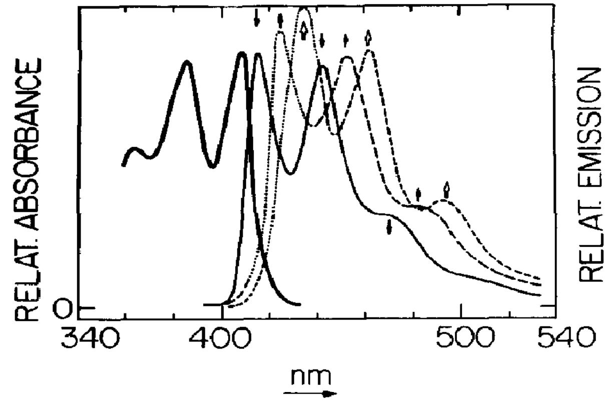

Fig. 3. Uncorrected emission spectra of compound **8** (Ar ≡ Th) in toluene at −90 °C: ——, ↓, λ_{ex} = 380 nm; — — —, ↑, λ_{ex} = 420 nm; - - -, ⇧, λ_{ex} = 428 nm (concentrations, about 5 × 10^{-6} M).

behaviour. Obviously the postulated rotamers *may* differ also in their emission lifetimes τ_F. The first hint in this direction was the variation in the emission quantum yield Q_F with λ_{ex} in Ph-2N where it is almost halved for long λ_{ex} [8]. This means that the corresponding τ_F increases at least to the same extent. The second indication was given by the observed selective quenching of the emission with oxygen. In solutions of Ph-2N, 2N-2N [8] and Ph-3An [11], replacing nitrogen by oxygen in the gas phase resulted in pronounced changes in the shape of the emission spectra, reflecting an enhanced contribution of the long wavelength component and indicating thereby that the short wavelength component is preferentially quenched and therefore longer lived. These results encouraged exact emission decay measurements by Dr. E. Haas in our Institute, with equipment and evaluation methods suited particularly well to superpositions of several decay curves. He has found [8] that indeed the decay of the compounds mentioned above could be expressed only by a biexponential function

$$I = I_0 \left\{ a_1 \exp\left(\frac{t}{\tau_1}\right) + a_2 \exp\left(\frac{t}{\tau_2}\right) \right\}$$

where I is the emission intensity, t is the time and I_0, a_1, a_2, τ_1 and τ_2 are constants. Measurements over a wide range of λ_{ex} and λ_{em} showed that for each compound the values of τ_1 and τ_2, *i.e.* the decay lifetimes, remained reasonably constant, while a_1/a_2, which is proportional to the relative contribution of the two components characterized by τ_1 and τ_2, varies within wide limits. Moreover, no indication for a "growing-in" process during the life of the excited species was found. Similar results with Ph-2N were obtained independently by Mazzucato *et al.* [14]. Later, Ghiggino [15] confirmed our results with Ph-2N and 2N-2N and extended these measurements to Q-2N and 3Phe-3Phe. In Table 1 we summarize some results (this work unless marked otherwise; various aliphatic hydrocarbons were used as solvents).

The behaviour at the longest λ_{ex} proved to be very useful for the correlation between the measurements of emission spectra and decay times: under these conditions we often observed almost pure long wavelength emissions and almost monoexponential decay with τ_1. We may therefore assign τ_1 to the long wavelength spectra. In all cases we found that short wavelength species are associated with long τ and long wavelength species with short τ. These results easily explain the observed preferential quenching of the short wavelength form by oxygen [8] and by other quenchers [15].

In those compounds which have modifications with distinctly different τ_Fs excitation in a broad wavelength range (in which presumably both modifica-

TABLE 1

Compound	*Ph-2N*	*Ph-2N*[a]	*Ph-2N*[b]	*2N-2N*	*2N-2N*[a]	*3Phe-3Phe*[a]	*6Q-2N*[a]	*3An-Ph*
τ_1 (ns)	3.5 ± 0.15	3.1 ± 0.2	5.2	2.2 ± 0.1	1.9 ± 0.04	1.06 ± 0.02	2.5 ± 0.04	7 ± 2
τ_2 (ns)	21 ± 2	23 ± 2.5	27.6	7.3 ± 0.1	8.6 ± 0.7	3.5 ± 0.2	16 ± 2.6	17 ± 4

[a] Ref. 15.
[b] Ref. 14.

tions absorb to the same extent) yields an a_1/a_2 ratio which is identical with the ratio R between the concentrations of the two modifications in solution: $R = (a_1\tau_1/Q_1)/(a_2\tau_2/Q_2) = a_1/a_2$. Values of R estimated [8] in this way are 1.9 for Ph-2N and 2.7 for 2N-2N. These values compare reasonably well with those obtained from the shape of the spectra excited over a broad wavelength range.

Ghiggino [15] has provided a beautiful direct verification of the above phenomena by means of time-resolved emission spectroscopy. He showed that with 2N-2N the emission spectrum measured 30 ns after flash excitation is very similar to that of the short wavelength form described, while the spectrum "immediately" after the flash is clearly a superposition of the short wavelength and the long wavelength spectra. This is of course exactly as expected.

In many cases in which emission spectra were found to vary with λ_{ex}, no biexponential decay or preferential oxygen quenching was observed. A good example is 1N-2N where a monoexponential decay with $\tau_F = 0.95$ ns was found. In such cases the τ_Fs may be too similar for separation by present methods, in particular for $\tau_F < 2$ ns.

2. Some general remarks and conclusions

The basic requirements for the existence of mixtures of rotamers in solutions (or rapidly frozen solutions) of the *trans*-diarylethylenes may be summarized as follows.

(a) The curve of potential energy *versus* angle α of twist around the quasi-single bond(s) must have two or more minima, separated by barriers sufficiently high to force the molecules to spend most of the time in these minima and to make the rate of interconversion slow on the time scale of the measuring method. In relatively unhindered *trans*-diarylethylenes the values of α are not far from 0° or 180°, *i.e.* the almost coplanar configurations are stabilized by delocalized π electrons extending over the whole molecules.

(b) The 0° and 180° positions should not be identical (in order to be distinguishable), but the energy difference between them should be small, so that the contribution of the more energetic rotamer to the equilibrium should suffice to allow its detection.

(c) To prove the existence of discrete rotamers in a mixture, they must differ in some physical property, *e.g.* absorption and emission spectra, NMR etc.

(d) If the method of detection is based on the creation of electronically excited states, *e.g.* in emission, no (or almost no) interconversion between the rotamers should take place during the time τ_F that the molecules stay in the excited state. This requirement was first described by Jacobs and Havinga [2] as the non-equilibration of excited rotamers (NEER) principle in the context of photocyclizations of hexatriene derivatives.

The correctness of this principle in our cases is shown by the absence of any growing in during the decay measurements and by the actual variation in the shape of the emission spectra with λ_{ex}. No such variation is expected if a new rotamer equilibrium is established in the excited state. The NEER principle is based on the fact that in the excited state the bond order of the quasi-single bonds is greatly enhanced, so that twisting around the quasi-double bond is actually energetically less expensive than twisting around the quasi-single bonds [19]. As mentioned before, a detailed theoretical exploration of the expected properties of these rotamers is badly needed. This also concerns the very large differences in emission decay times and quantum yields of the rotamers in several cases: shorter τ_Fs and smaller Q_Fs of course indicate radiationless deactivation paths which are accordingly much more pronounced in one rotamer than in the other. The question is which paths are involved and what causes these large differences.

With respect to the barriers separating the rotamers, we have already mentioned that these are due to the loss in resonance energy as a twist angle of 90° is approached. This holds for fluid solutions. Highly viscous or rigid media give rise to additional barriers against changes in the twisting angles α from their equilibrium values, and in the extreme case no interconversion between rotamers will take place. This is certainly the case in Spolskii media and in glasses. Moreover, in such glassy or even crystalline media the solute may occupy different sites, possibly stabilizing different configurations even in those diarylethylenes in which a rotation of 180° about the 1-α quasi-single bond leads to identical configurations in fluid solutions. This may explain the observation of the λ_{ex} dependence of the emissions by 4-styrylpyridine and by stilbene described above [18]. In mixed solvents, of which the classical EPA is an extreme example, domains of each component seem to be formed on cooling [20, 21], providing different environments for the solute molecules. This might be the cause of the pronounced variation with λ_{ex} in the shape of the emission spectrum of stilbene observed in glassy EPA at 77 K [18]. It is therefore advisable to perform low temperature work in uniform solvents or at least in mixtures of chemically similar solvents, *e.g.* 1-propanol–2-propanol, methylcyclohexane–isohexane or methyltetrahydrofuran. In a toluene–methylcyclohexane mixture many solutes which are much more soluble in the former than in the latter will behave as if their solvent were toluene. In effect this mixture serves as an aromatic solvent which can be cooled to close to 100 K [21].

Finally, it certainly helped that in most of our cases the fluorescence quantum yields were high and that the absorption spectra were highly structured. It is this structure which makes possible the preferential excitation at suitable wavelengths on which our method of detection is based.

In conclusion, there is extensive emission spectroscopy evidence for the existence of two or three discrete modifications of many *trans*-diarylethylenes in solution. Evidence from other sources is badly needed. The assignment of these modifications to rotational conformers is a plausible working hypothesis in need of support both from calculations and from different physical methods.

The emission anomalies described above reflect one aspect of excited state behaviour ascribed to the existence of several ground state rotamers in the *trans*-diarylethylenes. Obviously this should also show up in the photochemistry of these compounds, *e.g.* intersystem crossing to the triplet states (possibly separate states for each rotamer) and photoisomerization in the singlet excited state. So far the only clear-cut observation seems to be the variation in the quantum yield of *trans* → *cis* photoisomerization with λ_{ex}, complementary to that of Q_F for 2N-Ph and 2N-2N.

Acknowledgment

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