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PHOTOCHEMICAL PRODUCTION OF NON-EQUILIBRIUM CONFORMER CONCENTRATIONS IN GLASSY SOLUTIONS OF DIARYLETHYLENES AT 77 K

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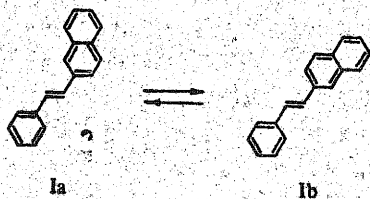
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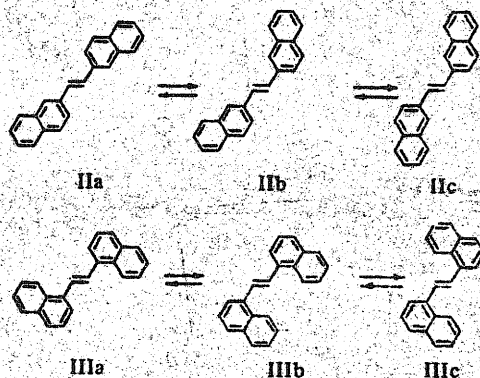
Absorption and fluorescence spectra of glassy solutions of some trans-stilbene-like molecules were found to differ remarkably provided trans-diarylethylenes were obtained photochemically at 77 K in situ. The phenomenon has been rationalized as being due to the production of non-equilibrium concentrations of conformers (rotamers) in view of the restrictions imposed by the solid matrix.

1. Introduction

The effects on photophysical properties of conformational (rotational) isomerism in molecules of diarylethylenes have been demonstrated in our earlier publications [1-4]. The spectroscopic consequences of dynamic conformational equilibria between two or three nearly isoenergetic conformers (rotamers, *S*-isomers) in diarylethylene solutions have been confirmed, specified, and discovered for a number of related compounds with a flexible molecular structure, both by luminescent [5-10] and photochemical [11,12] methods. Most detailed information has been accumulated for the compound Ph-2N, I [5,7-9,12].



For this compound, photophysical properties of conformers Ia and Ib were separated [5,9], and equilibrium ratios of conformer concentrations were established within a wide temperature range [9]. Similar, though somewhat less extensive, information can also be found in the literature [1-13] for naphthylethylenes II (2N-2N) and III (1N-1N), which are shown below in three possible conformations.



The situation prior to this study may be characterized by the facts that (i) no experimental evidence has been provided so far for the existence of the third conformer of compound II, which was tentatively explained under the assumption of identical photophysical properties for a pair of conformers [5]; (ii) subsequent measurements [5] have not confirmed earlier observations [1,2] of the dependence of the fluorescence spectra of III on the wavelength of excitation, which could be rationalized either by almost identical photophysical properties of all three conformers of III, or by the absence from solution of these conformers in view of the steric hindrance involved [5].

In the present paper, we shall provide new spectroscopic data for compounds I-III, which will be rationalized within the framework of conformational

isomerism manifested in the emission spectra of the compounds studied.

2. Experimental

The experiments were carried out in frozen ethanol solution at 77 K. Cis isomers of 1-phenyl-2-(2-naphthyl)ethylene (I, Ph-2N), 1,2-di-(2-naphthyl)ethylene (II, 2N-2N) and 1,2-di-(1-naphthyl)ethylene (III, 1N-1N) were synthesized and purified as reported elsewhere [13], extreme care being taken to exclude impurities which could be responsible for part of the emission. Concentrations were 10^{-4} – 10^{-3} M. Emission and absorption spectra were measured in quartz cells of 2 mm optical pathlength with a standard grating spectrofluorimeter (SDL-1) and spectrophotometer (Unicam SP-800), respectively. All spectra are uncorrected.

Emission measurements were taken at right angles upon excitation by filtered irradiation of wavelength $\lambda = 313$ nm from a 250 W Hg arc lamp, and/or $\lambda = 337$ nm irradiation from a nitrogen laser. The cis–trans photoisomerization was initiated by filtered irradiation at $\lambda = 240$ – 390 nm with a total intensity of 10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ from the Hg lamp; the conversion rate was monitored from the trans-isomer fluorescence intensity in liquid solution [13]. Fluorescence decay curves were measured as described previously [4].

3. Results and discussion

Upon 5 min irradiation of freshly prepared frozen solutions of cis-diarylethylenes at $\lambda = 240$ – 390 nm (absorption spectra 1 in fig. 1), these were converted into corresponding trans molecules (absorption spectra 2 in fig. 1) due to photochemical cis–trans isomerization in the glassy matrix.

The absorption and fluorescence spectra (2 and 2', respectively) of photochemically produced trans molecules at 77 K were found to be essentially different from the absorption and fluorescence spectra (3 and 3', respectively) observed from samples prepared in the "usual" way, i.e. by dissolving the corresponding trans compounds in ethanol and subsequently cooling to 77 K. Control experiments showed that the "unusual" spectra 2 and 2' take their "usual" appearance 3 and 3'

when photochemically prepared solid solutions are subjected to warming to room temperature and then cooling again to 77 K.

It may therefore be concluded that trans-diarylethylenes may be present in solution at least in two different forms. One, henceforth referred to a "equilibrium", is attained upon "usual" preparation of glassy solutions, while the second, called "non-equilibrium", results from the photochemical cis–trans isomerization in a solid matrix at low temperature. The effects observed are discussed below for each compound.

Ph-2N, I (fig. 1a). The fluorescence spectrum of trans-I has been shown [5,9] to be comprised of superpositions of two distinct spectra, vibrationally well resolved at -185°C . These were assigned to conformers Ia and Ib: the "long- λ " conformer with fluorescence decay time $\tau_1 \approx 4$ ns, and the "short- λ " conformer with $\tau_2 \approx 23$ ns [5,9]. The contribution of each of these to the overall spectrum is dependent upon the excitation wavelength, λ_{ex} [5,9], and on the temperature [9]. An almost pure "long- λ " spectrum (with τ_1) is excited at $\lambda_{\text{ex}} = 360$ nm [5,9]. Since the energy barrier between conformers Ia and Ib has a value of ≈ 140 cm^{-1} [9], the equilibrium Ia \rightleftharpoons Ib is shifted toward the "short- λ " conformation (with τ_2) at low temperature: $C_1/C_2 = 0.07$ at 77 K and 0.48 at room temperature [9].

The direction of changes upon going from the "non-equilibrium" to the "equilibrium" spectrum may be determined from the change in the $\lambda = 355$ nm peak, which is assigned [5] to the "short- λ " conformer (with τ_2), and in the $\lambda = 430$ nm peak belonging to the "long- λ " conformer (with τ_1) (cf. fig. 2b in ref. [5]). As seen from fig. 1a, on going from the spectrum 2' to the spectrum 3', the intensity of the $\lambda = 355$ nm peak is increased, while that of the $\lambda = 430$ nm is decreased. Therefore, upon repeated freezing the equilibrium is shifted in the direction

"long- λ " configuration (τ_1)

→ "short- λ " configuration (τ_2),

i.e. the ratio C_1/C_2 is decreased. This conclusion is supported by decay-time measurements for "equilibrium" and "non-equilibrium" fluorescence, observed at $\lambda_{\text{em}} = 430$ nm (fig. 2). The fraction of long-lived "short- λ " conformers is clearly seen to be enhanced

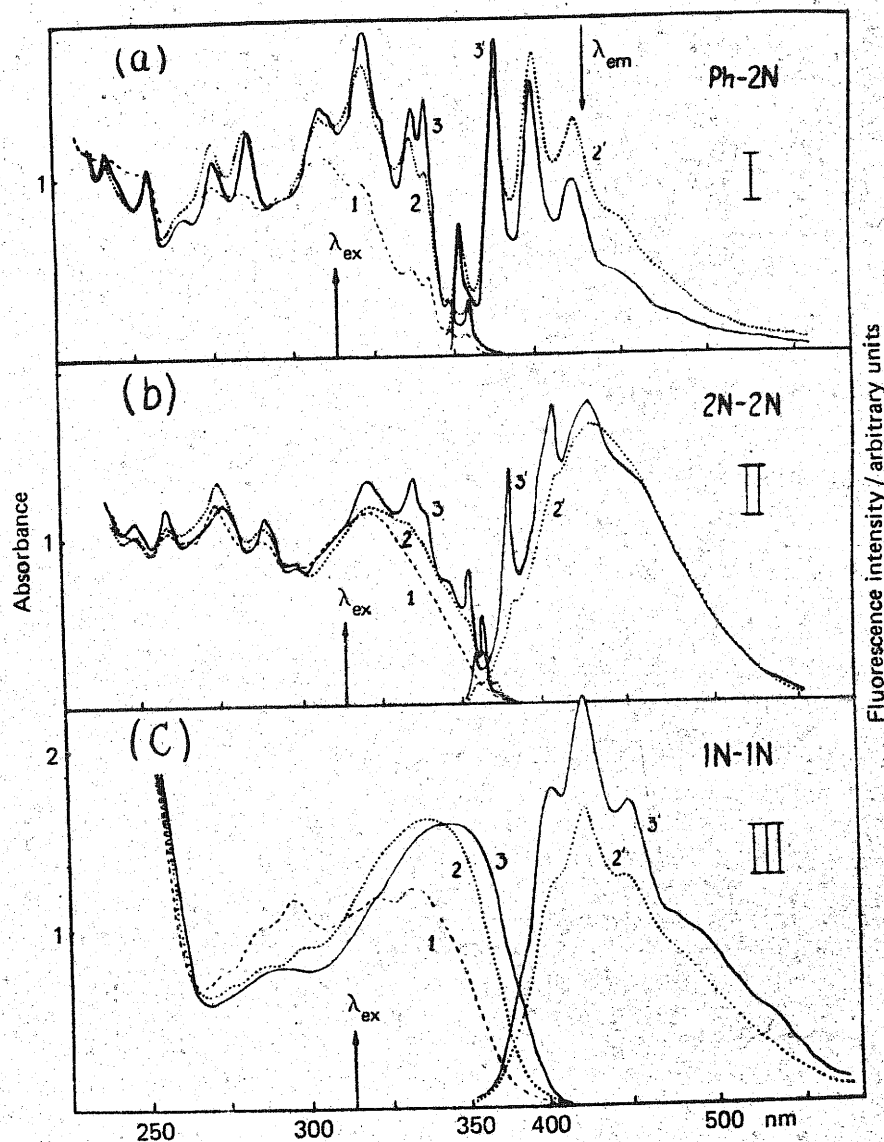


Fig. 1. Spectra 1: Absorption of initially prepared solutions of cis-diarylethylenes in ethanol at 77 K. Spectra 2 and 2': Absorption and fluorescence of photochemically prepared solutions of trans-diarylethylenes in ethanol at 77 K. Spectra 3 and 3': Absorption and fluorescence of solutions of trans-diarylethylenes after repeated freezing to 77 K. No corrections have been made in the fluorescence spectra, and $\lambda_{ex} = 313$ nm.

Upon repeated freezing of a photochemically prepared solution of trans-I in glassy ethanol.

The changes observed in the absorption spectra 2 and 3 also indicate a decrease in the C_1/C_2 ratio, these changes becoming clear when the published [9] separate absorption spectra of "short- λ " and "long- λ " con-

formers of Ph-2N are taken into account.

These data may be explained as follows. Upon irradiation at $\lambda = 240-390$ nm, cis-molecules of I undergo cis-trans photoisomerization, thus giving some distribution between conformers Ia and Ib of the trans molecules of I, which happens to be non-equilibrium

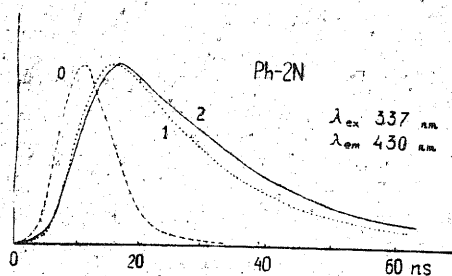


Fig. 2. Fluorescence decay curves for trans-I ($\lambda_{\text{ex}} = 337$ nm, $\lambda_{\text{em}} = 430$ nm) in ethanol at 77 K. 0: Excitation pulse from nitrogen laser, $\lambda_{\text{ex}} = 337$ nm. 1: Photochemically prepared solution. 2: After repeated freezing.

due to the common action of low temperature and microviscosity of the medium. When the solution is thawed, all restrictions are removed, and upon freezing the equilibrium mixture of conformers is attained in solution at 77 K.

2N-2N, II (fig. 1b). The fluorescence spectra of II have also been reported [5] as being a superposition of two well-resolved spectra at -185°C . These are assigned to two of the conformations IIa, IIb and/or IIc: a "long- λ " conformer with $\tau_1 = 7.3$ ns and a "short- λ " conformer with $\tau_2 = 2.2$ ns. Nevertheless, the "non-equilibrium" fluorescence spectrum 2' appears to be almost structureless. For this particular case, we tend to believe that trans molecules are remarkably distorted by the solvent cage. Upon repeated freezing, the spectrum 3', displays distinct structure, which may be regarded as an implication that, in a new solvent cage, trans molecules become more planar. The appearance of a peak at $\lambda = 360$ nm, assigned to the "short- λ " conformer ($\tau_2 = 2.2$ ns), implies that this conformer has a lower energy. From the changes in the absorption spectra 2 and 3, it follows that the "short- λ " conformer of II has a more structured absorption spectrum.

1N-1N, III (fig. 1c). For this compound, a previously reported [1] strong λ_{ex} dependence of the fluorescence spectra was not later confirmed [5]. This inconsistency derived from the presence of non-luminescing impurities in the solutions used in our experiments. The absence of a λ_{ex} dependence may now be accounted for either by small differences between the luminescent properties of conformers IIIa, IIIb and IIIc, or by the entire absence of these con-

formations in view of the steric hindrances involved [5]. However, the data presented in fig. 1c support the conception that these conformations do exist, and that their spectral features can be separated.

Comparison of the absorption spectra 2 and 3 implies that, upon repeated freezing, the absorption spectrum of the solution undergoes a remarkable redshift. To be consistent with the above considerations, this shift may be regarded as being the result if an equilibrium shift towards a "long- λ " conformer of II, which therefore has somewhat lower energy. Comparison of the fluorescence spectra 2' and 3' shows that this is accompanied by an increase in the total fluorescence intensity. Since the optical density at $\lambda_{\text{ex}} = 313$ nm is clearly decreased, it should be concluded that the fluorescence quantum yield for the "long- λ " conformer of III is considerably larger than that for the "short- λ " conformer, although their spectral distributions are almost coincident. These particular features rationalize the absence of a λ_{ex} dependence for solutions of trans-III, but at the same time manifest the occurrence of some equilibrium between conformations of trans-III. However, it should be kept in mind that these conformations may turn out to be non-planar, in contrast to those existing in solutions of trans-I and trans-II.

The effects observed for 1N-1N seem to be similar in nature to those observed [14,15] for trans- and cis-stilbenes. When these molecules were made planar by attaching hydrocarbon bridges between aryl fragments, a sharp increase in the fluorescence quantum yields was observed for the non-flexible planar molecules formed.

4. Conclusions

Upon photochemical preparation of trans-diarylethylenes I-III in glassy solution at 77 K, non-equilibrium concentrations of conformers may be readily obtained. Upon repeated freezing, an equilibrium distribution is established which is manifested in changes in the absorption and emission spectra.

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