SPECTROSCOPIC RESOLUTION OF ROTATIONAL CONFORMERS IN *trans*-DIARYLETHYLENES: TIME-RESOLVED FLUORESCENCE STUDIES[†]

ANNE C. MATTHEWS, RICHARD SAKUROVS and KENNETH P. GHIGGINO

Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052 (Australia)

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Summary

Steady state and time-resolved fluorescence techniques have been used to investigate the presence of ground state conformers in solutions of *trans*-diarylethylenes. For a number of compounds where such conformers can be proposed, the fluorescence spectra depend on the excitation wavelength and the fluorescence decay kinetics can only be described by multiexponential decay functions. Quenching experiments and temperature dependence studies have provided some insight into the number and properties of the species present in solution. The results are consistent with the identification of two or three distinct rotational conformers on the time scale of electronic excitation, and the possible excited state relaxation pathways of these conformational species are discussed.

1. Introduction

The photochemical behaviour of stilbene and related diarylethylene derivatives has been extensively studied using both theoretical and experimental techniques. Of particular interest has been the mechanism of *trans–cis* photoisomerization which is relevant for understanding the overall photochemistry of this important class of molecules. Previous studies have variously attributed *trans–cis* isomerization in stilbenes to occur via the singlet state and/or the triplet excited state following light absorption [1 - 4]. However, the very short fluorescence lifetimes characteristic of many *trans*-diarylethylenes have limited the direct observation of excited state dynamics.

Recent spectroscopic evidence [5 - 10] has suggested that certain *trans*-diarylethylenes may exist in solution as an equilibrium mixture consisting of

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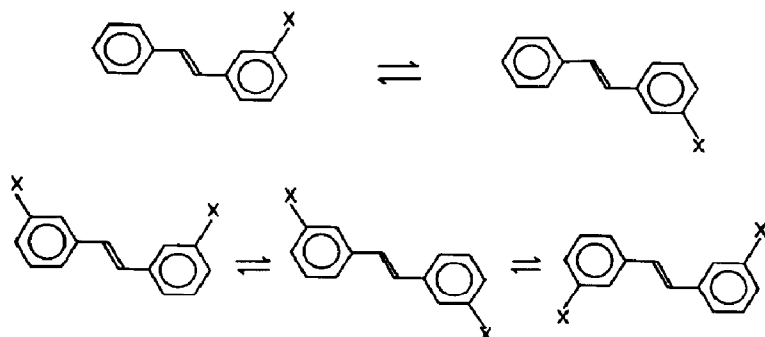[†]Paper presented in part at the 28th IUPAC Congress, Vancouver, 1981.

Fig. 1. Possible conformers of *trans*-diarylethylenes.

two or three distinct coplanar rotational conformers (Fig. 1). The tendency towards coplanarity of these structures arises as a result of the delocalization of the π electron system over the whole molecule. For such conformers to exist, the curve of potential energy of the molecule *versus* the angle of twist around the quasi-single bonds should possess shallow, and almost isoenergetic, minima at twist angles of about 0° and 180° which stabilize an approximately coplanar geometry. In addition the potential minima must be separated by a sufficiently high energy barrier to allow the existence of discrete conformers on the time scale of the detection method.

In a previous note [8] we reported the time-resolved fluorescence behaviour of *trans*-1,2-di-(2-naphthyl)ethylene which supported the existence of at least two discrete conformers of this molecule on the time scale of electronic excitation. It was suggested in this work that the different fluorescence lifetimes observed for each conformational species might be related to the photochemical behaviour of each conformer.

In the present work we have undertaken a detailed time-resolved fluorescence study of a number of *trans*-diarylethylenes. The experimental results further support the existence of distinct ground state conformers in certain derivatives and provide an insight into the excited state relaxation pathways of these conformational species.

2. Experimental details

2.1. Materials

The *trans* isomers of 4,4'-dimethylstilbene (4-DMS), 3,3'-dimethylstilbene (3-DMS), 1,2-di(2-naphthyl)ethylene (DNE), 1-phenyl-2-(2-naphthyl)ethylene (PNE), 1,2-di(3-phenanthryl)ethylene (DPE) and

1-(2-naphthyl)-2-(6-quinolyl)ethylene (NQE) were generously donated by Professor E. Fischer, Weizmann Institute of Science, Rehovot, Israel, and were prepared and purified by methods outlined elsewhere [5, 7, 10]. Scintillation grade *trans*-stilbene (Fluka) was used without further purification. The melting points, nuclear magnetic resonance spectra and absorption and emission spectra of the compounds agreed with published data. The structural formulae are shown in Fig. 2. Spectroscopic grade cyclohexane and
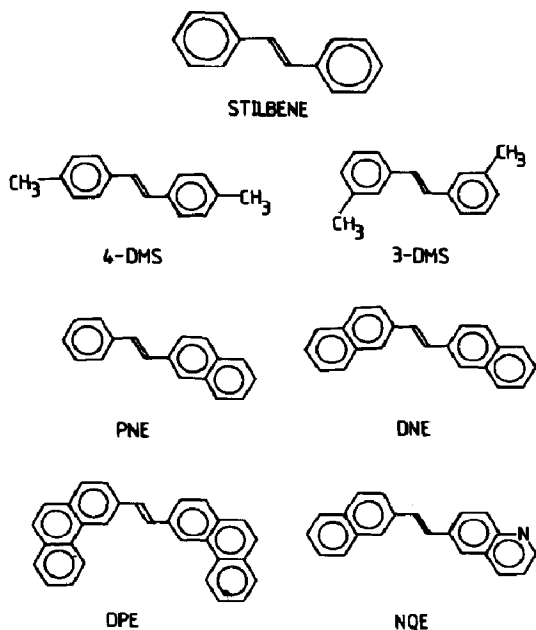

Fig. 2. Structural formulae of the compounds.

methylcyclohexane (BDH) were further purified by passage through a column packed with silica gel (BDH 60 - 120 mesh) to remove any fluorescent impurities. Solutions of the compounds in the solvents at concentrations of 10^{-5} - 10^{-6} mol dm^{-3} (absorbance less than 0.5 at the appropriate excitation wavelength) were degassed by freeze–pump–thaw cycles before use.

2.2. Methods

Steady state fluorescence spectra were recorded on a Perkin–Elmer MPF-44A spectrofluorometer using excitation and emission slit widths of 2 nm and 1 nm respectively. Fluorescence quantum yields were measured relative to *trans*-stilbene in methylcyclohexane at 20 °C for which $\phi_F = 0.047$ [11].

Emission decay data were collected on two instruments. For short fluorescence lifetimes (less than 5 ns) the fourth harmonic of a single pulse

selected from a mode-locked Nd^{3+}–glass laser was used for excitation (λ_{exc} = 265 nm, $\tau \approx 6$ ps), and the fluorescence decay above 400 nm was recorded by a streak camera coupled to an optical multichannel analyser. This pico-second laser streak camera apparatus has been described in detail previously [8]. Fluorescence lifetimes not measured by the laser system were collected on an Applied Photophysics SP2X nanosecond spectrometer using the time-correlated single-photon counting technique. This instrument and the techniques employed have also been described elsewhere [12]. The decay data from both instruments were fed to an on-line Nova 2-10 computer and fitted to single- and double-exponential functions using a non-linear least-squares procedure. The data collected on the photon counting system were analysed by iterative deconvolution and the goodness of fit was established from the inspection of weighted residuals plots and the magnitude of the reduced χ^2 value.

3. Results and discussion

The photophysical properties of the compounds available for study are summarized in Table 1. Stilbene and 4-DMS would not be expected to exhibit separate detectable conformational species as the possible structures which maximize coplanarity are equivalent (see Fig. 1). Indeed the emission spectra of stilbene and 4-DMS did not depend on the excitation wavelength employed and their fluorescence decay could be well described by a single-exponential function which is expected with the existence of a single emitting state. There has been some controversy in the literature concerning the

TABLE 1

Photophysical data for *trans*-diarylethylenes in cyclohexane at 20 °C

Molecule	ϕ_F ($\pm 5\%$)[a]	F[b]	τ_1[b] (ns)	τ_2[b] (ns)
Stilbene	0.046	1.00	0.10 ± 0.01	—
4-DMS	0.20	1.00	0.35 ± 0.02	—
3-DMS	0.08	0.87	0.28 ± 0.01	7.1 ± 0.52
PNE[c]	0.51	0.72	3.1 ± 0.2	23 ± 2.5
DPE[c]	0.73	0.83	1.06 ± 0.02	3.5 ± 0.19
DNE[c]	0.68	0.90	1.92 ± 0.04	8.6 ± 0.7
NQE[c]	0.63	0.87	2.48 ± 0.04	16 ± 2.6

[a]Fluorescence quantum yield with excitation at 265 nm.
[b]Fluorescence decay data fitted to a double-exponential function of the form

$$I(t) = F \exp\left(-\frac{t}{\tau_1}\right) + (1 - F) \exp\left(-\frac{t}{\tau_2}\right)$$

The emission above 400 nm was monitored.
[c]The fluorescence spectra of these compounds varied with the excitation wavelength.

fluorescence decay behaviour of stilbene, but the lifetime measured by pico-second techniques in the present work agrees closely with recent measurements [13] and is not consistent with the double-exponential behaviour reported by some workers [3, 14]. The room temperature fluorescence spectra of PNE, DPE, DNE and NQE showed distinct changes with a variation in the excitation wavelength (e.g. Fig.3). For the case of DPE (Fig. 3(a)) excitation with wavelengths above 390 nm produces a structured emission with maxima at 398 and 424 nm, while new maxima are observed as progressively shorter excitation wavelengths are used. For NQE (Fig. 3(b)) excitation above 370 nm yields a fluorescence spectrum with maxima at 380 and 403 nm, while with shorter excitation wavelengths new peaks appear at 366 and 387 nm. PNE and DNE displayed similar behaviour in good agreement
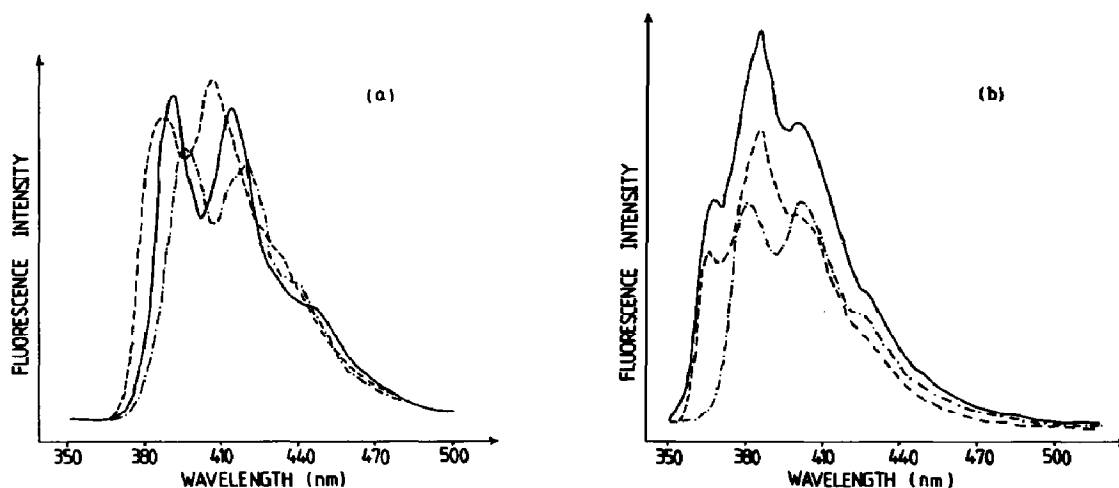

Fig. 3. Fluorescence spectra of DPE and NQE in cyclohexane at 20 °C with various excitation wavelengths: (a) DPE (——, 385 nm; – – –, 375 nm; – · –, 395 nm); (b) NQE (——, 265 nm; – – –, 350 nm; – · –, 375 nm).

with earlier results [5, 8]. The emission spectrum of 3-DMS showed no detectable excitation wavelength dependence at room temperature but at lower temperatures (below 150 K) a significant dependence was observed. As argued previously [5 - 10], these observations are consistent with the existence of distinct ground state conformational species in these molecules with different emission spectra and slightly shifted absorption spectra. By selectively exciting different regions of the absorption spectrum it is possible to alter the relative excited state populations of each conformational species. Thus at the longest excitation wavelength it is likely that only one conformer is excited and emits, whilst at shorter excitation wavelengths light is absorbed by all conformers to varying degrees and the observed fluorescence is a superposition of at least two sets of emission maxima.

Fluorescence decay curves collected for the total emission above 400 nm from 3-DMS, PNE, DPE, DNE and NQE were clearly non-

exponential (*e.g.* Fig. 4) but all were better fitted to a double-exponential function of the form

$$I(t) = F \exp\left(-\frac{t}{\tau_1}\right) + (1 - F) \exp\left(-\frac{t}{\tau_2}\right)$$

where τ_1 and τ_2 are the lifetimes and F is the initial fraction (*i.e.* the fraction at zero time) of the component having lifetime τ_1. The results of these analyses from data collected on the picosecond laser streak camera using an excitation wavelength of 265 nm are presented in Table 1. For the case of PNE, for which only two non-equivalent conformers could be envisaged, analysis of the decay curves recorded on the photon counting apparatus using different excitation wavelengths yielded similar decay times but varying initial fractions of the short and long-lived components (Fig. 4). These observations suggest that the decay of fluorescence can be attributed to emission from at least two species which have different absorption spectra, overlapping fluorescence spectra and different decay rates. Double-exponential fits to the fluorescence decays for 3-DMS, DPE, DNE and NQE gave slightly non-random weighted residual distributions and high reduced χ^2 values (*i.e.* $\chi^2 > 2$), providing some evidence that more than two kinetically distinct emitting species were present. However, the quality of our streak camera decay data did not justify the fitting of triple-exponential lifetimes. It should be noted that even with the high temporal resolution of the picosecond laser apparatus, no evidence was obtained for any "grow-in" of the emitting species with time which could indicate a conformational change or a reaction occurring in the excited state.

Further information concerning the number of emitting species was obtained from quenching experiments using carbon tetrachloride. Quenching of stilbene and 4-DMS fluorescence by carbon tetrachloride was found to obey Stern–Volmer kinetics with a bimolecular quenching rate constant of 1.9×10^{10} dm^3 mol^{-1} s^{-1}. However, quenching of PNE, DPE, DNE and NQE fluorescence all showed deviations from Stern–Volmer behaviour, and the observed quenching efficiency varied with the excitation wavelength used. These observations are consistent with the proposed existence of distinct excited state species which are quenched to differing extents by carbon tetrachloride. In addition the differential quenching is reflected in changes in the spectral characteristics of fluorescence from these compounds. This is illustrated in Fig. 5 for the quenching of DNE fluorescence by carbon tetrachloride at two excitation wavelengths. For DNE, excitation near the onset of absorption at 362 nm results in a fluorescence spectrum with maxima at 373 and 395 nm while excitation at 297 nm produces additional new maxima at 360 and 382 nm. Thus at the longer excitation wavelength (362 nm) there is evidence that we are not exciting one species, yet differential quenching of the emission maxima by carbon tetrachloride is still observed, indicating the presence of more than one species (Fig. 5). These results suggest that there are at least three differently quenchable entities
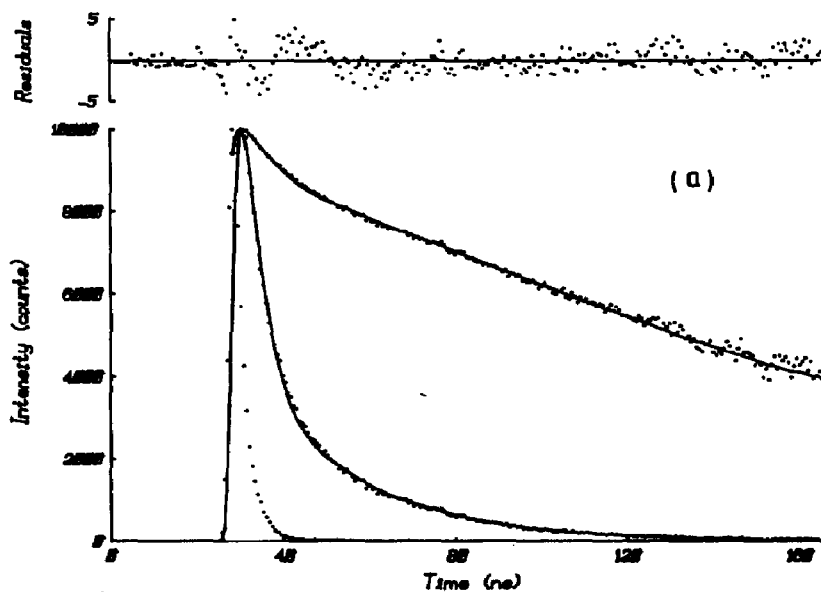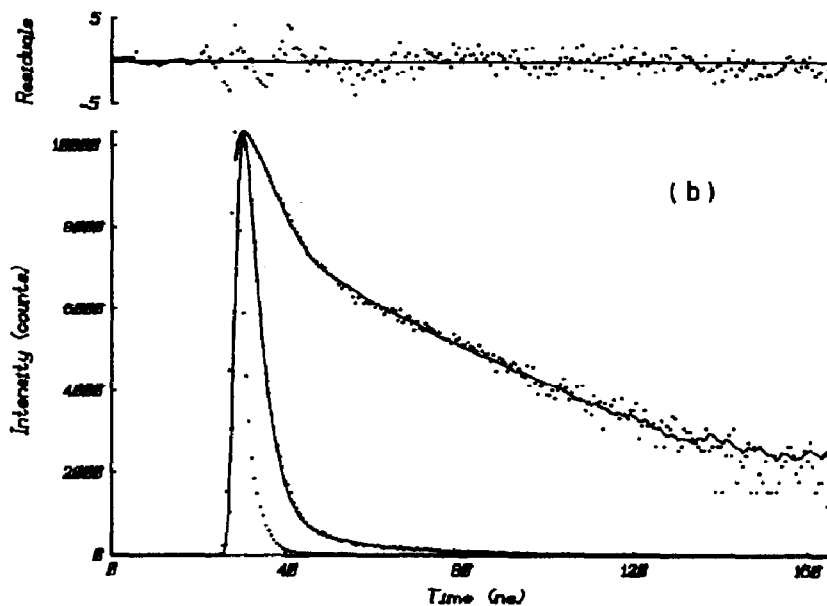
Fig. 4. Fluorescence decay curves and residuals plots for PNE recorded with excitation wavelengths of (a) 348 nm ($F = 0.79$, $\tau_1 = 3.23$ ns, $\tau_2 = 25.82$ ns) and (b) 365 nm ($F = 0.96$, $\tau_1 = 2.79$ nm, $\tau_2 = 19.88$ ns): ●, experimental data; ——, non-linear least-squares fit to double-exponential decay. The upper data points are a semilogarithmic plot of the data. Emissions above 400 nm are monitored.
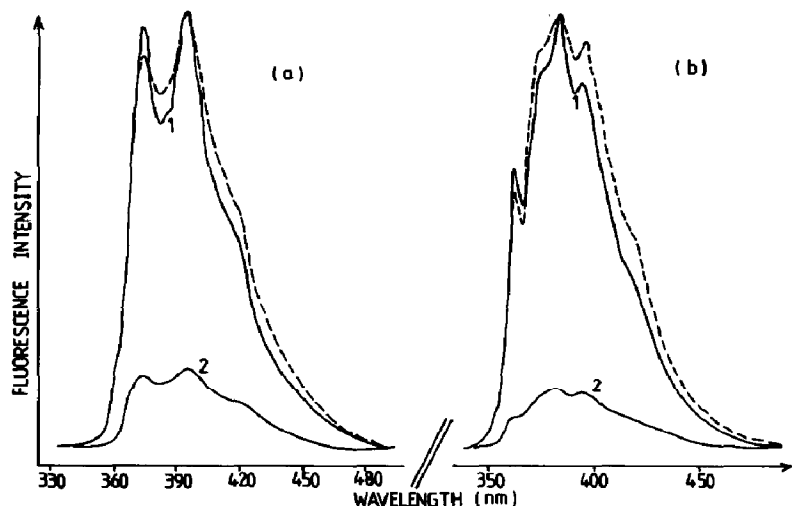
Fig. 5. Quenching of DNE fluorescence with carbon tetrachloride at excitation wavelengths of (a) 362 nm and (b) 297 nm: spectra 1, unquenched fluorescence spectra; spectra 2, with 1.18 mol CCl$_4$ dm^{-3}; – – –, spectra 2 normalized to the maximum of spectra 1 to emphasize spectral differences.

fluorescing in solutions of DNE. Similar conclusions were reached from fluorescence quenching experiments on solutions of DPE and NQE, while evidence for only two quenchable emitting species was obtained for PNE. These observations are entirely consistent with the proposed number of rotational conformers which might exist in these compounds (see Fig. 1).

In order to verify the existence of interconverting rotational conformers it is of interest to see whether the position of equilibrium might be shifted between the proposed structures. Temperature dependence studies provide a possible means of investigating this phenomenon. Analysis of the temperature dependence of the fluorescence intensity and lifetime for stilbene and 4-DMS yielded an activation energy for non-radiative decay of 14.6 ± 2 kJ mol^{-1} for both molecules in agreement with previous data for stilbene [13]. This activation energy is close to the energy barrier of 17.2 kJ mol^{-1} reported for the *trans–cis* photoisomerization of stilbene [15], suggesting that the major temperature-dependent non-radiative relaxation pathway in these molecules is photochemical isomerization. For the molecules which are expected to exist as an equilibrium mixture of several coplanar structures, deviations in the expected correlation between changes in the fluorescence lifetime and the emission intensity of each species might be observed if there is a temperature-dependent shift in the ground state equilibrium. Such behaviour could only be detected for PNE. For this compound, warming the solutions from 290 to 333 K resulted in a 30% decrease in the lifetime of the short-lived component but a negligible change in the contribution of this component to the total fluorescence intensity. Over the same temperature range the lifetime of the longer lived species decreased by only 10% but its contribution to the total fluorescence decreased by one-third.

The most reasonable explanation for these observations is that there is a shift in equilibrium between the two species as the temperature is raised in favour of the shorter lived component. Significant changes in the intensity and the lifetime could not be detected for DNE or DPE over the temperature range investigated and thus an equilibrium between ground state conformers could not be confirmed in these compounds.

4. Summarizing remarks and conclusion

The experimental results reported above support the existence, on the time scale of electronic excitation, of two or three distinct ground state rotational conformers in solutions of 3-DMS, DNE, NQE, DPE and PNE. No anomalous behaviour was observed for 4-DMS or stilbene where detectable conformational species are not expected. Of particular interest are the different photophysical properties observed (*e.g.* lifetime, spectra) for each conformer. It has been suggested above that the major non-radiative pathway in simple stilbenes is *trans–cis* photoisomerization about the ethylenic double bond, and it might be proposed that the different lifetimes observed for each conformer of a compound might be related to the ease of *trans–cis* isomerization for each species. Conservation-of-momentum rules can be employed to describe the motion of individual atoms of a molecule as it undergoes such an isomerization towards a certain critical rotation angle beyond which fluorescence from the excited state will no longer be observed. We have carried out such calculations which predict distinct differences in fluorescence decay times for each conformer. However, it is likely that each conformer has other relaxation pathways, including different radiative rates and intersystem crossing efficiencies, which complicate the above argument. Furthermore, each species will undergo unique interactions with the surrounding solvent. Nevertheless the identification of rotational conformers in the compounds examined in this study has important implications for understanding the photochemistry of related molecules including commercial fluorescent whitening agents and other stilbene-based dyes.

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