

## Short Communication

### Time-resolved fluorescence studies of *trans*-1,2-di-(2-naphthyl)ethylene

K. P. GHIGGINO

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

(Received July 14, 1979)

#### 1. Introduction

Recent spectroscopic evidence has suggested that certain *trans*-diaryl-ethylenes may exist in solution as a dynamic equilibrium between two or three conformers [1 - 3]. In the simplest case of *trans*-stilbene there is only one stabilized planar configuration that the molecule may assume. However, for certain substituted stilbenes it is possible to assign several non-identical coplanar structures [2]. In principle the *trans* isomer of 1,2-di-(2-naphthyl)-ethylene may exist as a mixture of two or three coplanar and almost iso-energetic conformers (Fig. 1).

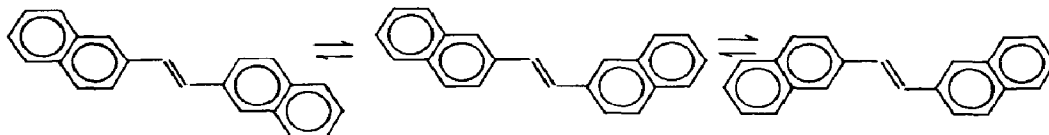


Fig. 1. Conformers of *trans*-1,2-di-(2-naphthyl)ethylene.

Observations of anomalies in the emission characteristics of this molecule have recently been reported [1 - 3] and have been ascribed to the presence of such a dynamic equilibrium. In the present communication further details of the conformational behaviour of this molecule in solution were obtained using time-resolved fluorescence techniques.

#### 2. Experimental

Samples of *trans*-1,2-di-(2-naphthyl)ethylene (DNE) were kindly supplied by Professor E. Fischer, Weizmann Institute of Science, Rehovot, Israel, and were purified by methods outlined elsewhere [3]. Spectroscopic grade cyclohexane (BDH) was further purified by distillation and by passing three times through a silica column to remove any fluorescent impurities. Solutions of DNE, approximately  $2 \times 10^{-5}$  M, in cyclohexane were degassed by freeze-pump-thaw cycles before use.

The picosecond laser–streak camera apparatus used for the fluorescence decay measurements has been described previously [4]. The fourth harmonic of a single pulse selected from the output of an  $\text{Nd}^{3+}$  glass laser was used for excitation ( $\lambda_{\text{exc}} = 265 \text{ nm}$ ,  $\tau \approx 6 \text{ ps}$ ) and the decay was recorded by a streak camera–optical multichannel analyser arrangement. Because of the heavy flint glass optics of the streak camera, only fluorescence above approximately 400 nm could be monitored. Time-resolved fluorescence spectra were obtained on an instrument also described in detail elsewhere [5, 6], using frequency-doubled cavity-dumped pulses from a dye laser for excitation and single-photon counting detection techniques. Steady state fluorescence spectra were recorded on a Perkin–Elmer MPF-44A spectrofluorimeter.

### 3. Results and discussion

The absorption spectrum of DNE has been reported previously [3] and consists of a structured band with an onset at about 380 nm. In agreement with other work [2, 3], the shape of the total fluorescence spectrum is strongly dependent on the excitation wavelength (Fig. 2). Excitation with

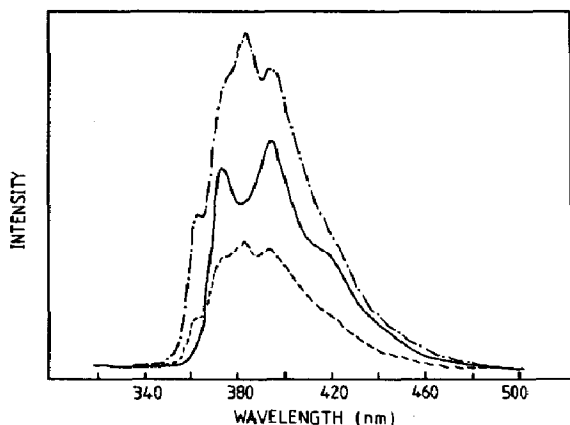


Fig. 2. Total fluorescence spectra of DNE in cyclohexane at 20 °C with various excitation wavelengths; —, 365 nm; - - -, 340 nm; - · - · -, 260 nm.

wavelengths above 360 nm produces a structured emission with fluorescence maxima at 373 and 395 nm, whereas with lower excitation wavelengths new peaks appear at 360 and 382 nm. This behaviour has been interpreted [3] to indicate that the various conformers have different emission spectra and slightly shifted absorption spectra. Thus, at the longest excitation wavelength only one conformer is excited and emits, whilst at lower wavelengths of excitation light is absorbed by all conformers to varying extents and the resulting fluorescence is a superposition of at least two sets of emission peaks.

Fluorescence decay curves for DNE in cyclohexane recorded on the picosecond laser–streak camera system were clearly non-exponential (Fig. 3), but they could be adequately described by a double exponential function of

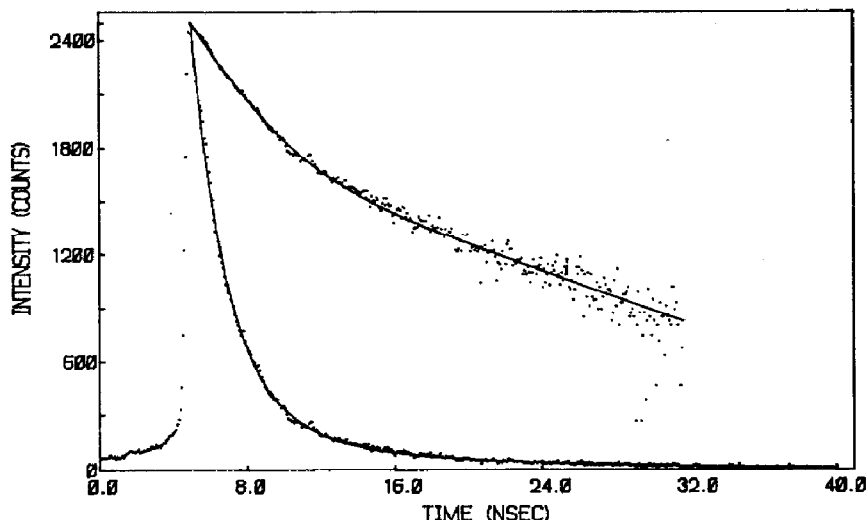


Fig. 3. The fluorescence decay curve for DNE excited at 265 nm (all emissions above 400 nm were monitored): ●, experimental data; —, non-linear least-squares fit to a double exponential decay with  $\tau_1 = 1.92$  ns and  $\tau_2 = 8.6$  ns. The upper data points are a semilogarithmic plot of the data.

the form

$$I(t) = A\{f\exp(-t/\tau_1) + (1 - f)\exp(-t/\tau_2)\} + B$$

where  $\tau_1$  and  $\tau_2$  are the lifetimes,  $f$  is the fraction of the component having a lifetime  $\tau_1$ ,  $A$  is the amplitude and  $B$  is a baseline parameter. A typical decay curve is shown in Fig. 3, for which  $\tau_1$  and  $\tau_2$  are  $1.92 \pm 0.04$  and  $8.6 \pm 0.7$  ns respectively and  $f = 0.9$ . These data suggest that the decay of the fluorescence above 400 nm can be attributed to emission from at least two species which have overlapping fluorescence spectra and different decay rates.

In order to obtain further information about the nature of the emitting species, time-resolved fluorescence spectra were recorded at various delay times after excitation. The spectra observed coincident with the excitation pulse and at a 30 ns delay after excitation are shown in Fig. 4. The spectral distribution of photons emitted initially should be weighted towards any short-lived species, whilst only the long-lived component of fluorescence will be observed after 30 ns.

Comparison of the time-resolved spectra in Fig. 4 with the total fluorescence spectra presented in Fig. 2 provides an insight into the spectral and temporal characteristics of the species responsible for emission. The maxima occurring at 373 and 395 nm in the total fluorescence spectrum recorded with 365 nm excitation are major features of the early-gated time-resolved spectrum but they are absent from the late-gated spectrum. The new peaks which appear in the total fluorescence spectrum when excitation wavelengths below 360 nm are used may be readily identified as belonging to the long-lived species described by the late-gated spectrum. Thus the spectrum of

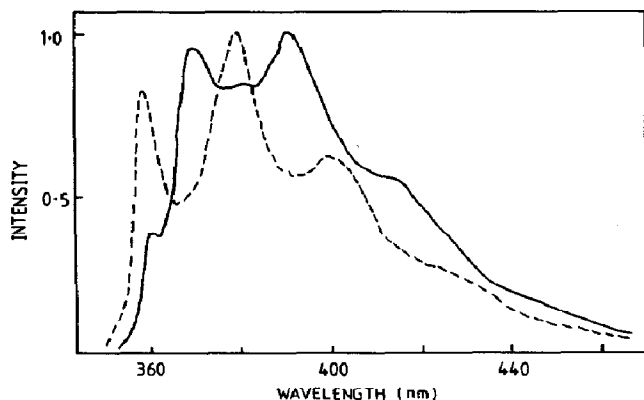


Fig. 4. Time-resolved emission spectra for DNE excited at 297 nm: —, early-gated spectrum with time delay  $\Delta t = 0$  and gate width  $\delta t = 3$  ns; ---, late-gated spectrum with  $\Delta t = 30$  ns. The spectral resolution was 1 nm. The spectra were normalized to their maxima to emphasize differences between them.

the pure short-lived component corresponds to the total fluorescence spectrum at long excitation wavelengths, whereas the spectral character of the long-lived fluorescence species is depicted in the late-gated time-resolved emission spectrum.

Even with the high time 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. Rather these results, together with the excitation wavelength dependence of the fluorescence spectra, are consistent with the existence of different ground state conformational species of DNE with characteristic emission and absorption spectra and characteristic excited state lifetimes. Although it is possible to assign three different conformers which could exist in equilibrium, there was no indication in the present investigation of more than two emitting species. However, the presence of a third conformer cannot be discounted on this evidence, since it is not necessary for all conformers to differ in their emission spectra and lifetimes.

The present time-resolved fluorescence studies thus support the existence of at least two discrete conformers of DNE on the time scale of electronic excitation. It is probable that the different photophysical properties of each conformational species will influence the overall photochemical behaviour of the molecule in solution.

#### *Acknowledgments*

The author would like to thank Professor E. Fischer for helpful discussions and the University of Melbourne for the award of an Emergency Research Grant.

- 1 Yu. B. Sheck, N. P. Kovalenko and M. V. Alfimov, *J. Lumin.*, 15 (1977) 157.
- 2 E. Haas, G. Fischer and E. Fischer, *J. Photochem.*, 9 (1978) 277.
- 3 E. Haas, G. Fischer and E. Fischer, *J. Phys. Chem.*, 82 (1978) 1638.
- 4 G. R. Fleming, J. M. Morris and G. W. Robinson, *Aust. J. Chem.*, 30 (1977) 2337.
- 5 K. P. Ghiggino, D. Phillips, K. Salisbury and M. D. Swords, *J. Photochem.*, 7 (1977) 141.
- 6 K. P. Ghiggino, A. J. Roberts and D. Phillips, in *Laser Induced Processes in Molecules*, Springer Series in Chemical Physics, Vol. 6, Springer, Heidelberg, 1979, p. 98.