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The effect of diphenylamine on the photochemical properties of di(α-naphthyl)ethylene

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Diphenylamine in toluene solution was found to accelerate the isomerization reaction of the *trans*-isomer of the title compound and to retard the cyclization reactions of the *cis*-isomer, thus decreasing the concentration of dihydropicene in a photostationary equilibrium mixture.

The effect of amines on the photochemical properties of diarylethylenes (DAEs) has been extensively investigated.[1] Depending on the nature of the amine and solvent polarity, addition of amine to DAE can either result in formation of a fluorescent exciplex or give rise to DAE–amine adducts of different structures.

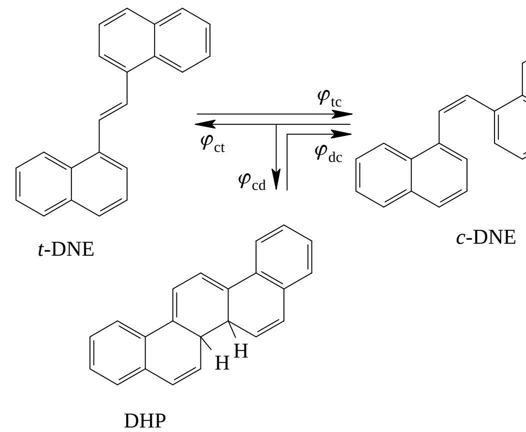
On the other hand, little is known about the influence of amines on the intrinsic photochemical transformations of diarylethylenes, such as isomerization and cyclization reactions.[2]

In this communication we report on the effect of diphenylamine (DPA) on the photochemical properties of *trans*-di(α-naphthyl)ethylene (*t*-DNE), its *cis*-isomer (*c*-DNE) and dihydropicene (DHP), the last two compounds being photochemically generated from *t*-DNE.

Unlike many diarylethylenes,[3] the photochemical behaviour of *t*-DNE is not complicated by the existence of several rotamers in solution. The main photochemical reaction of *t*-DNE is isomerization to the *cis*-isomer. The latter can both isomerize back to *t*-DNE and cyclize to DHP, the cyclization reaction being reversible (Scheme 1). In the presence of oxidants DHP is oxidized to condensed arene (picene); however, under the experimental conditions used this reaction can be neglected.

Thus, on steady irradiation, the system achieves equilibrium with photostationary values of reagent concentrations. The position of the equilibrium is dependent on the relationship between the quantum yields of four reactions and on the realtionship between the molar extinction coefficients of the three compounds at the irradiation wavelength (see Scheme 1).

Toluene solutions of *t*-DNE (10^{-5} M) were irradiated at 365 nm (light intensity 1.6×10^{-6} einstein dm^{-3} s^{-1}, extinction coefficients are 12880, 1790 and 6880 dm^3 mol^{-1} cm^{-1} for *t*-DNE, *c*-DNE and DHP, respectively). Spectrum (*1*) on Figure 1 belongs to pure *t*-DNE, whereas final spectrum (*6*) is a sum of three spectra – *t*-DNE, *c*-DNE and DHP. Monitoring the reaction mixture at two wavelengths (357 and 410 nm) enabled us to evaluate the concentrations of the three main components (insert on Figure 1).



Scheme 1

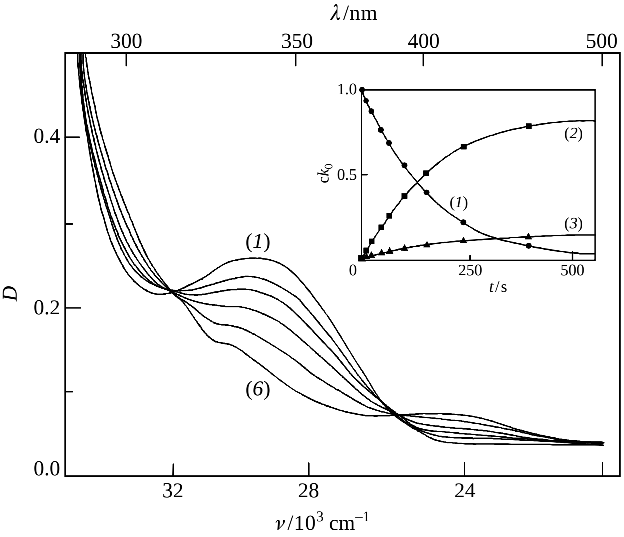


Figure 1 Spectral changes during irradiation of a 10^{-5} M toluene solution of *t*-DNE: irradiation time (*1*)–(*6*)/s: 0, 20, 40, 80, 160, 600. Insert: relative concentration changes: (*1*) *t*-DNE, (*2*) *c*-DNE, (*3*) DHP; experimental points and theoretic curves; c_0 initial concentration of *t*-DNE = 10^{-5} M.

A kinetic treatment of the experimental curves according to the scheme for the series–parallel reactions gives a value of $\varphi_{tc} = 0.12$, which coincides with that determined from initial concentration changes. Since the back reaction for *cis* → *trans* isomerization proceeds much more slowly than the forward reaction for *trans* → *cis* isomerization, only an estimate of φ_{ct} can be obtained: $\varphi_{ct}\varepsilon_{c,365} << \varphi_{tc}\varepsilon_{t,365}$, from which $\varphi_{ct} << 7\varphi_{tc}$. For the same reason, only the ratio $\varphi_{cd}/\varphi_{dc}$ can be obtained from this experiment, $\varphi_{cd}/\varphi_{dc} = 0.75$.

Separated values of quantum yields φ_{cd} and φ_{dc} are obtained using *c*-DNE as a starting substance for photochemical transformations, $\varphi_{cd} = 0.53$ and $\varphi_{dc} = 0.70$. The last experiment also confirms the relatively small value of φ_{ct}; the ratio obtained was $\varphi_{ct} << \varphi_{cd}$.

For di(α-naphthyl)ethylene studied, *cis* → *trans* isomerization was reported[4] to be much slower than *cis* → DHP cyclization, which coincides with our findings.

DPA displays no measurable absorption above 350 nm (the DPA band maximum lies at 284 nm). On addition of DPA the absorption spectrum of *t*-DNE (at $\lambda > 350$ nm) is not changed, consequently these two compounds do not form a ground-state complex. Selective excitation of the substrate (DNE) on irradiation at 365 nm is thus ensured in further experiments.

Luminescence of *t*-DNE is reduced in the presence of DPA, however, quenching is not accompanied by a new red-shifted emission band, *i.e.* an exciplex, if formed, is not fluorescent. The measured Stern–Volmer constant is equal to 24.7 M^{-1}, testifying that quenching occurs with a rate constant within the limit of diffusion control (the lifetime of singlet-excited *t*-DNE is known to be 2 ns[5]).

Photochemical transformations of *t*-DNE in the presence of DPA (0.1 M) are accelerated, quantum yield $\varphi_{tc} = 0.49$. At the same time the ratio $\varphi_{cd}/\varphi_{dc}$ is reduced to 0.13, so formation of DHP in this case is hardly observed (< 3% compared to 15% in the absence of amine). It should be noted that prolonged irradiation of the DNE–DPA mixture led to gradual consumption of DNE due to the occurrence of a chemical reaction, whose nature was not further studied.

One can see that in the presence of amine the quantum yield for *trans* → *cis* isomerization increases by ~4 fold, whereas the value of $\varphi_{cd}/\varphi_{dc}$ decreases by ~6 fold. The diminishing of the $\varphi_{cd}/\varphi_{dc}$ ratio can generally be explained by φ_{cd} decreasing and/or by φ_{dc} increasing. Since the quantum yield for ring opening φ_{dc} in pure DNE is near unity, the main reason for $\varphi_{cd}/\varphi_{dc}$ decreasing in the presence of amine is the decreasing of the quantum yield for ring closure φ_{cd}. Therefore, amine quenches the excited reactive state of *c*-DNE.

The data obtained can be explained as follows. DPA and *t*-DNE form no complex in the ground state, however, luminescence quenching and photochemical measurements testify to the interaction of excited DNE with amine. The reaction appears to occur with participation of an encounter complex, *i.e.* exciplex (though nonfluorescent), by analogy with the interaction of other DAEs with aliphatic amines.[1]

Isomerization of *trans*-stilbene is known to take place in the singlet excited state,[6] whereas that of higher *trans*-diarylethylenes proceeds mainly in the triplet excited state.[7] Therefore, acceleration of *trans* → *cis* isomerization can be explained by an electron-transfer/triplet mechanism:[8] i, singlet-excited *t*-DNE forms an encounter complex with DPA with electron transfer from amine to diarylethylene; ii, exciplex undergoes back electron-transfer to give a triplet *t*-DNE; iii, the latter isomerizes to *c*-DNE.

Compared to the *trans* → *cis* isomerization reaction, the back reaction for *cis* → *trans* isomerization has been much less studied. The reaction appears to occur in the singlet excited state, as well as reaction of ring closure.[4] Thus, DPA produces a different effect on the reactivity of *trans*- and *cis*-isomers of DNE: it increases the reactivity of the former and decreases that of the latter.

This fact suggests that *trans* → *cis* isomerization reactions do not proceed through a common intermediate state with a perpendicular configuration of the two aryl planes (traditional one-dimension picture), and for a description of the reactions a multidimensional model should be used. This is in accordance with the recent results of computer simulation of the photoisomerization dynamics of stilbene.[9]

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References

1 F. D. Lewis, D. M. Bassani, E. R. Burch, B. E. Cohen, J. A. Engleman, G. D. Reddy, S. Schneider, W. Jaeger, P. Gedeck and M. Gahr, *J. Am. Chem. Soc.*, 1995, **117**, 660.

2 U. Mazzucato, G. G. Aloisi, G. Bartocci, F. Elisei, G. Galiazzo and A. Spalletti, *Med. Biol. Environm.*, 1995, **23**, 69.

3 U. Mazzucato and F. Momicchioli, *Chem. Rev.*, 1991, **91**, 1679.

4 T. Wismontski-Knittel, G. Fischer and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1930.

5 T. Wismontski-Knittel, I. Sofer and P. K. Das, *J. Phys. Chem.*, 1983, **87**, 1745.

6 D. H. Waldeck, *Chem. Rev.*, 1991, **91**, 415.

7 G. G. Aloisi, F. Elisei and H. Gorner, *J. Phys. Chem.*, 1991, **95**, 4225.

8 M. Goes and G. Eckert, *J. Am. Chem. Soc.*, 1996, **118**, 140.

9 V. D. Vachev, B. A. Grishanin, J. H. Frederick and V. N. Zadkov, in *Fast Elementary Processes in Chemical and Biological Systems*, ed. A. Tramer, AIP Press, Woodbury, New York, 1996, p. 54.

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