The Unusual Fluorescence of 9-Cyano-10-*N,N*-dimethylaminoanthracene

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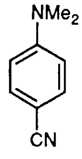
Three distinct fluorescence emission bands with maxima at 435, 497 and 615 nm are observed in acetonitrile for 9-cyano-10-*N,N*-dimethylaminoanthracene and are assigned as arising from a π,π*, an excimer, and a charge transfer state, respectively.

Since the discovery of dual fluorescence emission for 4-*N,N*-dimethylaminobenzonitrile **1** by Lippert *et al.*,[1] numerous studies have appeared on the photophysics of **1** and related benzene derivatives.[2,3] The long wavelength emission observed in these compounds was proposed to arise from a twisted intramolecular charge transfer (TICT) state.[3] Dual fluorescence was also observed for 1-dimethylamino-4-cyanonaphthalene and the long wavelength emission was interpreted as arising from a TICT state.[4] However, the emission properties of the anthracene analogue of **1**, 9-cyano-10-*N,N*-



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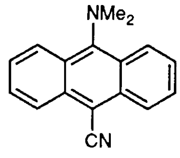

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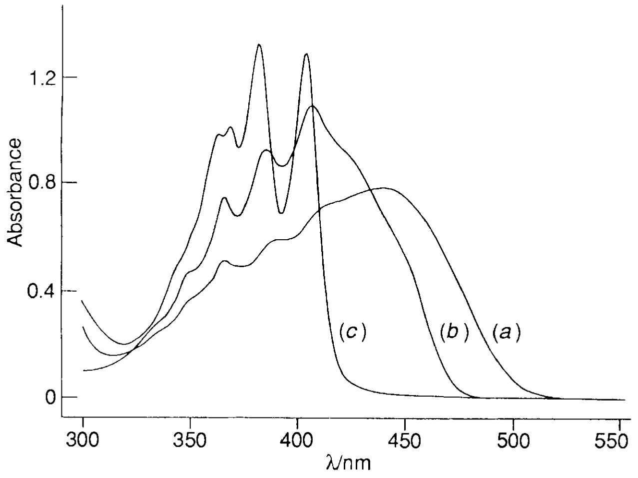

Fig. 1 Absorption spectra of **2** in acetonitrile and cyclohexane. (*a*) In acetonitrile (1.20×10^{-4} mol^{-1} dm^{-3}); (*b*) in cyclohexane (1.62×10^{-4} mol^{-1} dm^{-3}; (*c*) spectrum (*a*) on addition of acid (0.2 ml of conc. H_2SO_4).

dimethylaminoanthracene **2**, have not previously been investigated. We initiated this study to see if **2**† would also show a dual emission.

The absorption spectra of compound **2** in acetonitrile and cyclohexane are shown in Fig. 1. In acetonitrile, a long wavelength band with maximum at *ca.* 440 nm overlaps with the anthracene-like absorption band at *ca.* 350 nm [Fig. 1(*a*)]. This long wavelength absorption band is not observed following addition of acid to the solution [Fig. 1(*c*)] and the resulting spectrum resembles that of a 9,10-disubstituted anthracene derivative.[5] The absorption band at 440 nm (ε = 6800 ± 120 mol dm^{-3} cm^{-1}) is assigned as arising from ground-state charge transfer (CT) along the short molecular axis, since protonation of the $-NMe_2$ group removes this band. The absorption spectra in other polar solvents such as methanol, ethanol and 2-methoxyethanol show similar features. In hydrocarbon solvents such as cyclohexane, the CT band in the long wavelength region is insignificant [Fig. 1(*b*)] and the overall spectrum is predominantly anthracene like.

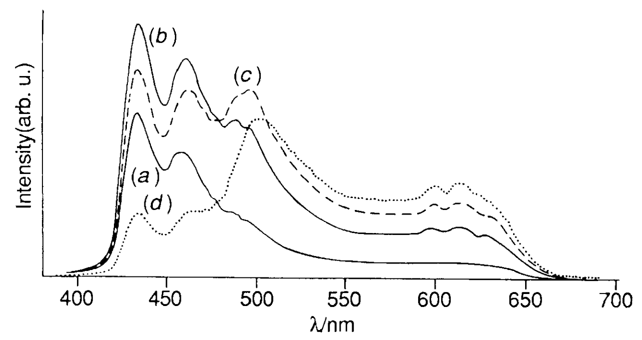

Fig. 2 Corrected fluorescence spectra of **2** as a function of concentration in acetonitrile at 23 ± 2 °C; excitation at 350 nm: (*a*) 1.37×10^{-5} mol^{-1} dm^{-3}; (*b*) 6.07×10^{-5} mol^{-1} dm^{-3}; (*c*) 1.12×10^{-4} mol^{-1} dm^{-3} and (*d*) 2.60×10^{-4} mol^{-1} dm^{-3}

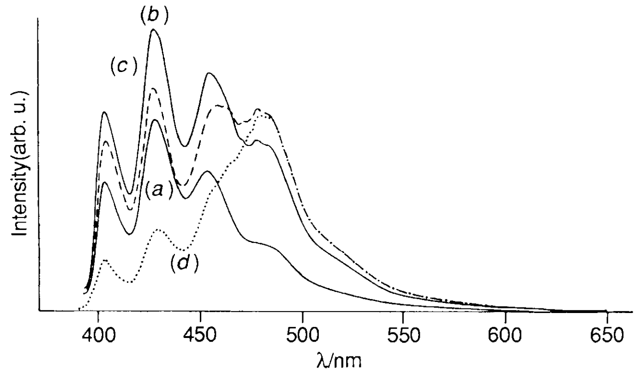

Fig. 3 Corrected fluorescence spectra of **2** as a function of concentration in cyclohexane at 23 ± 2 °C; excitation at 350 nm: (*a*) 2.80×10^{-5} mol^{-1} dm^{-3}; (*b*) 1.09×10^{-4} mol^{-1} dm^{-3}; (*c*) 1.88×10^{-4} mol^{-1} dm^{-3} and (*d*) 3.25×10^{-4} mol^{-1} dm^{-3}

Table 1 Lifetimes (τ/ns) of the emission bands of **2** in acetonitrile and cyclohexane[a]

	Acetonitrile	Cyclohexane
Monomer	14.1 ± 0.2 (440)	12.0 ± 0.1 (430)
Excimer	12.1 ± 0.3 (510)	9.3 ± 0.1 (480)
CT	0.4 ± 0.3 (600)	—

[a] Measured on a PTI time-correlated single photon counting instrument. The numbers in parentheses indicate the wavelength (in nm) at which the emission was monitored. Excitation wavelength = 350 nm.

Excitation of **2** in acetonitrile at 350 nm (*ca.* 10^{-5} mol dm^{-3}) gives a fluorescence band with maximum at 435 nm and a broad unstructured emission in the wavelength region 550–650 nm [Fig. 2(*a*)]. An increase in the concentration causes the intensity of the 435 nm emission to increase [Fig. 2(*b*)]. Further increase in concentration leads to a decrease in the intensity of the 435 nm emission, with the simultaneous appearance of a band with maximum at 497 nm [Fig. 2(*c*) and (*d*)]. The emission band with maximum at 435 nm is assigned as arising from a π,π^* excited state (locally excited anthracene moiety), since the shape of the band is similar to the emission spectrum of 9,10-dicyanoanthracene in acetonitrile (λ_{max} 436 nm). The new emission band with maximum at 497 nm is attributed to an excimer, as evidenced by the concentration dependence of the fluorescence spectra. The increase in concentration also increases the intensity of the emission in the region 550–650 nm and in Fig. 2(*d*), a band with maximum at 615 nm can be clearly seen. This emission is attributed to a CT state, since excitation into the CT absorption at 440 nm results in an emission with maximum at 615 nm. Similar behaviour was observed for **2** in other solvents such as methanol, ethylene glycol, dimethyl ether and dioxane.

On acidifying the acetonitrile solution with H_2SO_4, the emissions at 497 and 615 nm disappear and the resulting emission spectrum resembles that of 9,10-dicyanoanthracene. Fig. 3 shows the fluorescence emission in cyclohexane. Similar to the case in acetonitrile, an excimer band appears in the emission spectrum (λ_{max} 481 nm) on increasing the concentration of the substrate, though no emission is seen in the wavelength region 600–650 nm. The lack of a CT emission band in cyclohexane can be attributed to the fact that the stabilization offered to a polar excited state by a nonpolar solvent is negligible[6] and hence the absence of a CT emission.

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† The structure of **2** has been confirmed by standard spectroscopic techniques. The purity of the compound used for the fluorescence study is >99.5%, as checked by gas chromatographic methods. The preparation and characterization of **2** will be reported elsewhere.

The excitation spectra, monitored at λ 500 nm (high concentration) and 435 nm (low concentration) were identical and the spectrum monitored at 615 nm resembles the absorption spectrum. In the absorption spectra, the absorbance showed a linear relationship with substrate concentration, ruling out the possible formation of ground state dimeric species. The results of fluorescence lifetimes measured by the time-correlated single photon counting method in acetonitrile and cyclohexane are summarized in Table 1. The three emission bands show different lifetimes, indicating that each of them arises from a distinct excited state.

Similar to compound **1**, the anthracene analogue **2** shows long wavelength fluorescence emission. However, at the present time we have no reason to conclude that the long wavelength emission in the region 600–650 nm necessarily arises from a TICT state. Compound **1** and other *ortho*-substituted analogues of **1** do not show a long wavelength CT absorption band in the ground state. Thus, the CT (or TICT) state is not directly accessible to excitation; whereas in **2** there is a distinct CT state which could be excited. The origin of the *ca.* 600 nm emission in **2** and other related compounds is currently being investigated in our laboratory.

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