

Unique Intramolecular Exciplex Luminescent Behaviour of 9-(2-Diethylaminomethylphenyl)anthracene in Rigid Media

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9-(2-Diethylaminomethylphenyl)anthracene exhibits exciplex luminescent behaviour in solution, in a rigid polymer film, and in the solid state, owing to the restricted conformation of the phenylanthracene ring system as indicated from its X-ray crystal structure.

Electron transfer (ET) processes are important in photosynthesis,¹ solar energy schemes,² and many biochemical reactions. Investigations of intramolecular electron donor (D)/electron acceptor (A) systems, which exhibit charge transfer (CT) absorption,³ CT luminescence, fluorescence quenching, and exciplex emission in solution,⁴ can provide valuable mechanistic insight towards the understanding of electron transfer processes in general. The linking group between D and A is crucially important, in addition to the redox properties of D and A and the media (*e.g.*, solvent, polymer film, and solid state), in determining the D/A interactions in the ground and excited state.

Efficient exciplex emission has been observed for certain D/A combinations connected with a trimethylene group,⁴ for example. This linking group allows efficient orbital overlap through space in a folded conformation. Owing to the lack of any specific interaction between D and A in the ground state of exciplex systems, a conformational change must occur within the lifetime of the molecular excited state. In fluid solution, rapid conformational changes are possible, in contrast to the situation in rigid media, such as a polymer film below the glass transition temperature, T_g , and the solid state, where conformational mobility is prevented. Exciplex emission in nonpolar rigid media is not expected unless a preformed folded structure exists or CT can occur through the σ -bond framework.⁵ For example, compound (1) exhibits a combination of exciplex and monomer emission in toluene solution, and only monomer emission in a polystyrene film below T_g , owing to the existence of a frozen-in, extended-chain conformation.⁶

We report the unique exciplex or excited-complex luminescent behaviour of 9-(2-diethylaminomethylphenyl)anthracene (2) in solution, in a polystyrene (PS) film, and in the solid state, which is due to the conformational rigidity of the phenylanthracene ring system.

Compound (2) (E_p^ox 0.99 V, E_p^{red} -2.07 V, CH_2Cl_2 , standard calomel electrode, scan rate 100 mV s⁻¹)⁷ exhibits solvent-dependent exciplex behaviour in solution. Exciplex emission shifts from 485 nm in toluene to 557 nm in acetonitrile [see

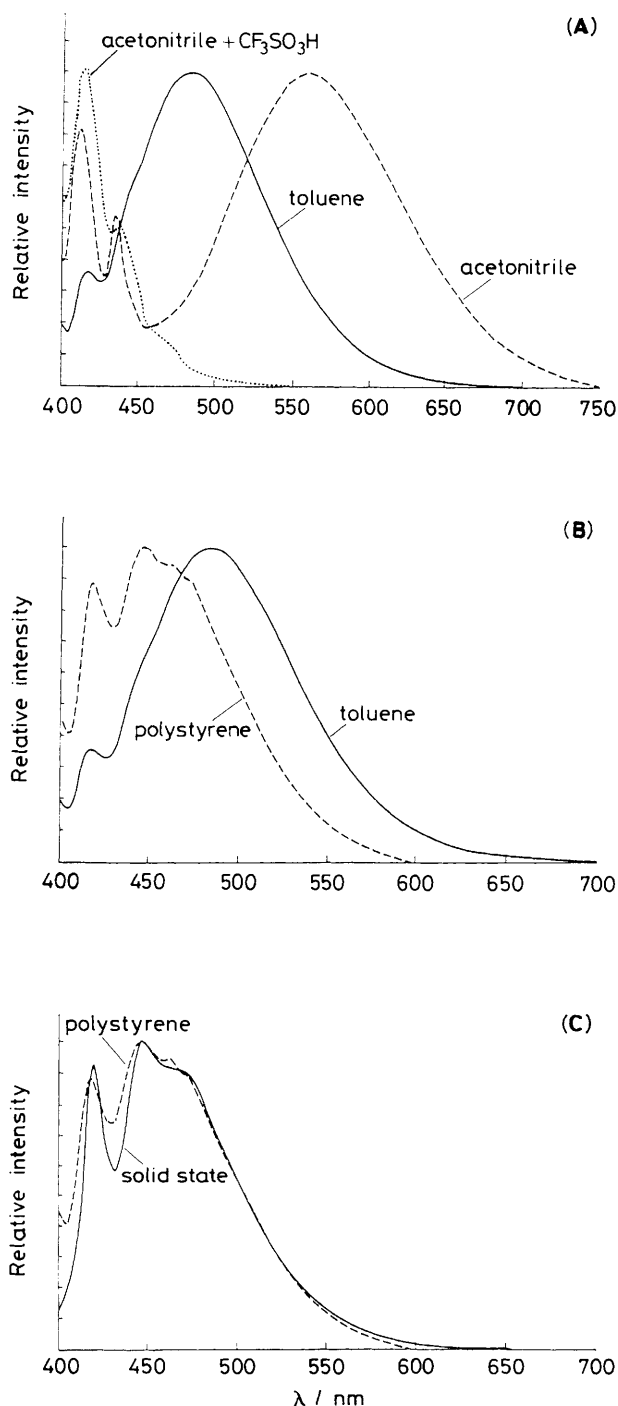
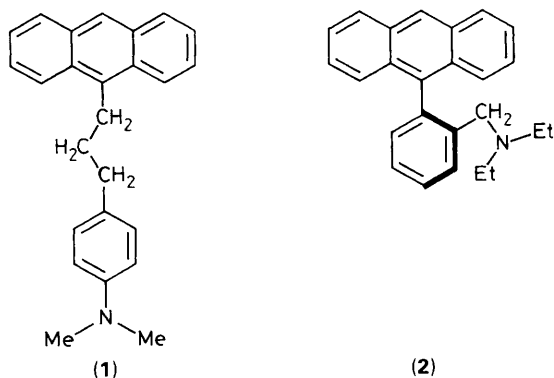


Figure 1. Fluorescence spectra for (2) (A) in toluene and acetonitrile solution, (B) in toluene solution and polystyrene film, and (C) in polystyrene film and the microcrystalline solid state.

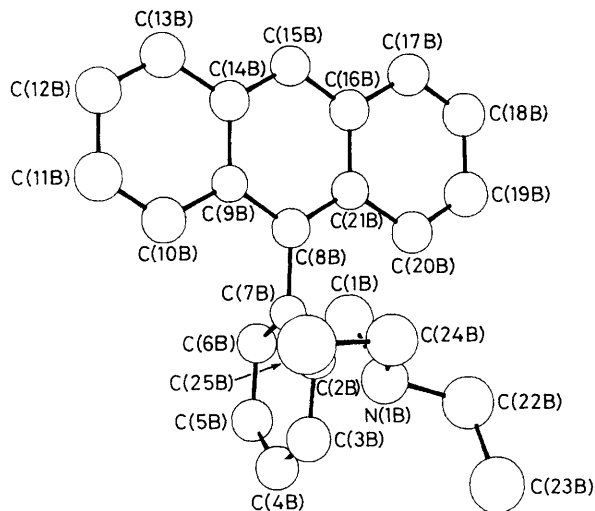


Figure 2. The solid state conformation of compound (2).

Figure 1 (A)]. Addition of trifluoromethanesulphonic acid to the acetonitrile solution of (2) protonates the amine moiety and eliminates exciplex luminescence while regenerating strong anthracene-like fluorescence.

When (2) is dissolved in a polystyrene film† (1 wt%), exciplex emission is observed at ~460 nm with a quantum yield of 0.013 [see Figure 1(B)] compared with 0.11 in toluene solution. The singlet lifetime of (2) in the PS film is <1 ns, whereas the lifetime of the 'exciplex-like' state is 14 ns.‡ The X-ray structure§ of (2) was obtained in order to determine the

solid state conformation. This information allows differentiation between the existence of a preformed molecular conformation and conformational mobility, to explain the observations on the PS film.

The solid state conformation of (2), as shown in Figure 2, has the nitrogen lone pair front lobe directed away from the π system of the anthracene ring. The C(2)–C(7)–C(8)–C(21) and N(1)–C(1)–C(2)–C(7) dihedral angles for molecule (A) are 89.5 and 177.7°, and for molecule (B) are 94.3 and –174.8°. The atom-to-atom distance between nitrogen N(1A) and the anthracene ring carbon C(8A) is 4.37 Å. The unit cell of (2) contains four molecules with similar conformations. Molecules (A) and (B) are approximately related by a pseudo-glide plane and the unit cell is approximately monoclinic $P2_1/a$ (*c*-axis unique).

An examination of the front-surface luminescence spectrum of (2) as a powder shows 'exciplex-like' emission similar to that observed for (2) in the PS film [see Figure 1(C)]. Owing to the similarity between the solid state and PS film fluorescence spectrum [Figure 1(C)], the PS film containing (2) was investigated by optical microscopy. There was no indication that (2) had crystallized within the PS at 1000× magnification. Further inspection of the unit cell of (2) shows the lack of intermolecular D/A and excimer interactions that would be expected to possess the proper orbital overlap to explain the solid-state luminescent behaviour. The photoexcited singlet phenylanthracene moiety appears to accept an electron from the back lobe of the nitrogen lone pair at a distance of 4.4 Å to produce an anion radical/cation radical pair, which provides exciplex emission as a consequence of back ET. The unique luminescent behaviour of (2) in rigid media is a result of the restricted conformation of the phenylanthracene ring system.

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† Polystyrene (Styron) of molecular weight 100 000 was used for the spectroscopic investigations.

‡ The singlet lifetimes were determined by the time-correlated single-photon counting technique using the PRA System 3000 (Photochemistry Research Associates, London, Ontario).

§ Crystal data: $C_{25}H_{25}N$, $M = 339.485$, triclinic, space group $P\bar{1}$, $a = 7.919(2)$, $b = 11.066(3)$, $c = 22.831(5)$ Å, $\alpha = 85.11(2)$, $\beta = 88.20(2)$, $\gamma = 79.43(2)^\circ$, $U = 1959(1)$ Å³, $Z = 4$, $D_c = 1.151$ g cm⁻³, $\mu = 0.61$ cm⁻¹. ω -2 θ Scan technique to $2\theta = 49^\circ$. 5436 Reflections were measured, of which 3880 with $I > 3\sigma(I)$ were used in the refinement. Enraf-Nonius CAD4 diffractometer. Mo- K_α radiation. Programs used are from the Structure Determination Package (SDP), 3.0, Enraf-Nonius Corporation. $R = 0.065$, $R_w = 0.070$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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