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

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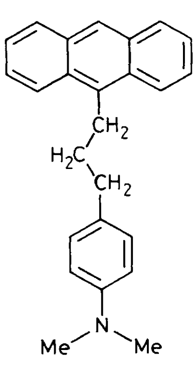
9-(2-Diethylaminomethylphenyl)anthracene exhibits exciplex luminescent behaviour in solution, in a rigid polymer film, and in the solid state, owing to the restricted conformation of the phenylanthracene ring system as indicated from its *X*-ray crystal structure.

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.

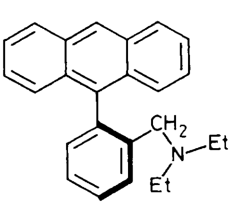
Efficient exciplex emission has been observed for certain D/A combinations connected with a trimethylene group,[4] for example. This linking group allows efficient orbital overlap through space in a folded conformation. Owing to the lack of any specific interaction between D and A in the ground state 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



(**1**)



(**2**)

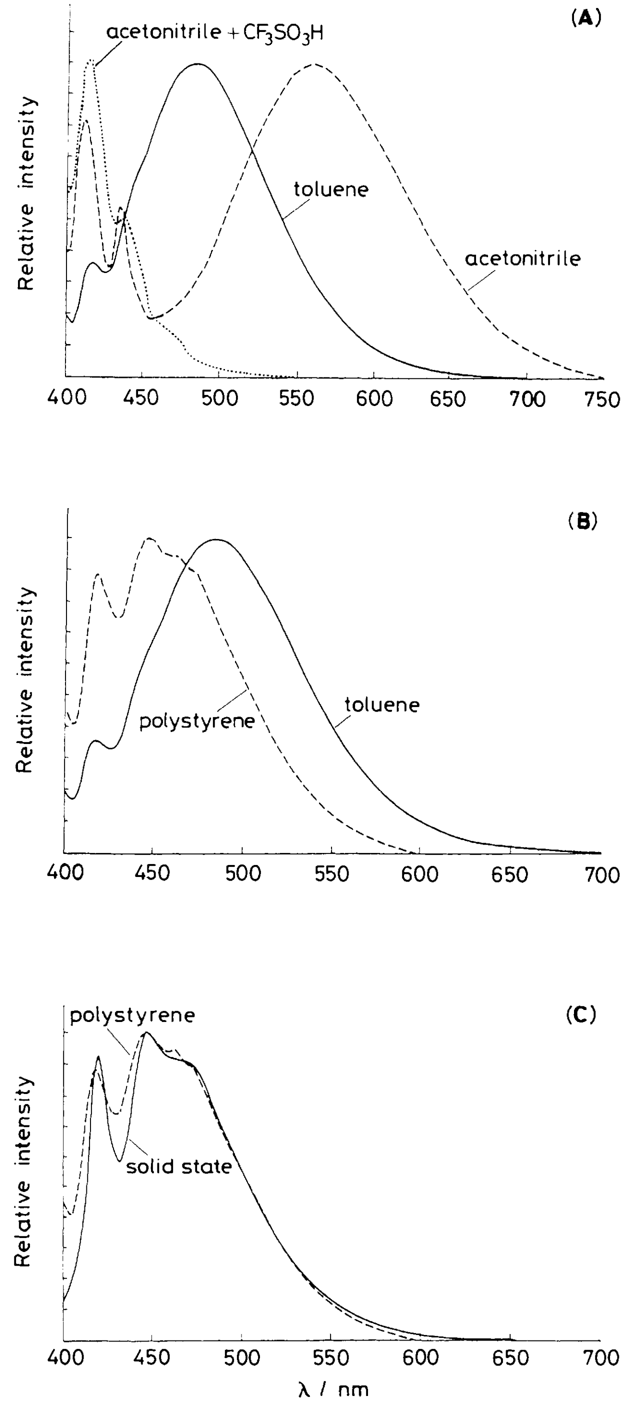


Figure 1. Fluorescence spectra for (**2**) (A) in toluene and acetonitrile solution, (B) in toluene solution and polystyrene film, and (C) in polystyrene film and the microcrystalline solid state.

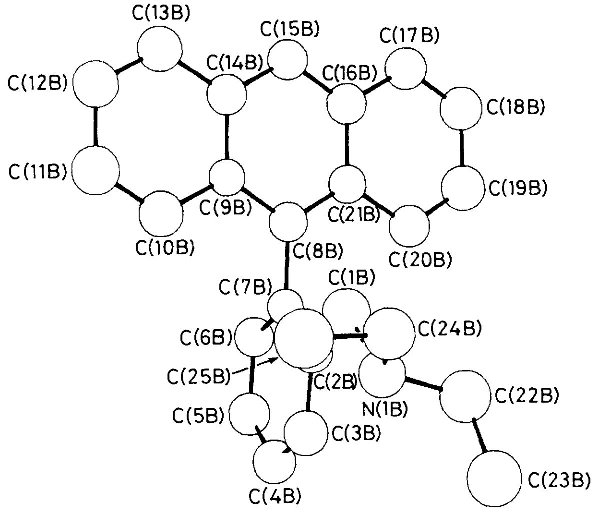


Figure 2. The solid state conformation of compound (**2**).

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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† Polystryene (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, α = 85.11(2), β = 88.20(2), γ = 79.43(2)°, U = 1959(1) Å^3, Z = 4, D_c = 1.151 g cm^{-3}, μ = 0.61 cm^{-1}. ω–2θ Scan technique to 2θ = 49°. 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 co-ordinates, 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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