Fluorescence Quenching of 2-Piperidinoanthraquinone

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Fluorescence solvent shift data indicate the first excited singlet state of 2-piperidinoanthraquinone [2-PA] to be considerably more polar than its ground state. Amines quench the fluorescence of [2-PA] in cyclohexane by electron transfer. Alcohols also quench the fluorescence but by a different mechanism involving hydrogen bonding between the alcohol and the ground state of [2-PA] to form a complex that is itself fluorescent.

RECENTLY we reported a study of the photochemistry of the piperidinoanthraquinones in connection with the problem of the phototendering of cellulosic fabrics by vat dyes.[1] An important feature of this work was that in contrast to the 1-piperidinoanthraquinone [1-PA], the photoactive excited state of the 2-derivative [2-PA] in aqueous alcoholic solution reacted by the electron transfer processes (1) and (2).

$$[\text{2-PA}]^* + \text{OH}^- \longrightarrow [\text{2-PA}]^{-\cdot} + \text{OH}\cdot \qquad (1)$$

$$[\text{2-PA}]^* + R_2\text{CHO}^- \longrightarrow [\text{2-PA}]^{-\cdot} + R_2\text{CHO}\cdot \qquad (2)$$

In general, intersystem crossing is very efficient with the anthraquinones and their normal reactions occur *via* the triplet state.[2] However during our work we observed that, again in contrast to [1-PA] which is only weakly fluorescent,[3] [2-PA] exhibits strong fluorescence in non-polar solvents. This suggested possible photochemical reaction *via* the first excited singlet state of [2-PA] in, for example, a polymeric environment.[4] Here we report fluorescence quenching experiments with both electron-donating compounds (amines) and hydrogen-bonding compounds (alcohols) to examine this possibility.

EXPERIMENTAL

Preparation and purification of [2-PA] were as previously described.[1] The cyclohexane was MFC grade and purified by passing down an alumina column before distillation. All other reagents were of AnalaR or Spectrosol grade and distilled prior to use.

Absorption spectra were recorded using a Pye–Unicam SP 1800 spectrophotometer. Emission spectra were recorded using a Baird Atomic Fluorispec spectrofluorimeter equipped with an 1P28 photomultiplier.

RESULTS AND DISCUSSION

Earlier[1] we found that the longest wavelength band of [2-PA] is intramolecular charge transfer (CT) in character, showing a marked red shift with increasing solvent polarity. A plot of $E_{\lambda_{\text{max.}}}$ of absorption against a function of the static dielectric constant of the solvent, *i.e.* $f(D) = 2(D - 1)/(2D + 1)$[5] gave a slope of 28·6 kJ mol^{-1}. Figure 1 shows a similar plot for the fluorescence emission which gives a slope of 86·7 kJ mol^{-1}. Thus, the red shifts in both absorption and emission clearly show that the first excited singlet state of [2-PA] is considerably more polar than the ground state.

The quantum yield of fluorescence for [2-PA] in cyclohexane was found to be 0·35 in comparison with that of quinine sulphate ($\phi_f = 1$). A further feature was that the fluorescence intensity of [2-PA] in nitrogen and in oxygen saturated cyclohexane was the same. This indicates a life-time for the first excited singlet of $\leqslant 3 \times 10^{-9}$ s. This value was confirmed by single photon counting techniques which gave a first-order rate constant of $2{\cdot}31 \times 10^8$ s^{-1}.

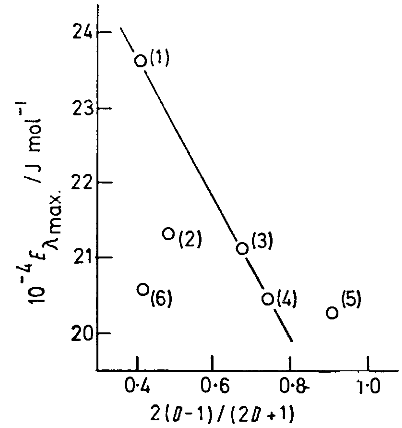

FIGURE 1 Plot of $E_{\lambda_{\text{max.}}}$ against $2(D - 1)/(2D + 1)$ for [2-PA]. Solvents: (1) cyclohexane; (2) toluene; (3) diethyl ether; (4) ethyl acetate; (5) acetone; (6) dioxan

The fluorescence of [2-PA] in cyclohexane was found to be quenched by the addition of a small amount of an amine. Even with relatively large amounts of amine present the fluorescence spectrum was identical to that of unquenched [2-PA]. Stern–Volmer plots of $I_0/I - 1$ against concentration of amine in all cases gave good straight lines. Quenching constants and rates of quenching based on the fluorescence lifetime of [2-PA] indicated by single photon counting are given in the Table. No change in shape or intensity of the longest wavelength absorption band of [2-PA] was observed with addition of amine.

This quenching of the fluorescence of [2-PA] can be

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readily explained by a mechanism of electron transfer from the amine to the highly polar first excited singlet state of [2-PA]. Further evidence for this mechanism is that the rate of quenching increases with decrease in the ionisation potential of the amine (Table).

Quenching of fluorescence of [2-PA] in cyclohexane

Quencher	Ionisation potential (e.v.)*	Stern–Volmer quenching constant	Quenching rate constant (10^{10} l mol^{-1} s^{-1}) [b]
Triphenylamine	6·9	53·3	1·8
Triethylamine	7·9	36·8	1·2
Quinoline	8·3	31·2	1·0
Methanol		80·6	2·7
[$^2H_4$]Methanol		78·0	2·6
Ethanol		78·1	2·6
Isopropanol		59·4	2·0

* Data from V. I. Vedenseyer, 'Bond Energies, Ionisations Potentials, and Electron Affinities,' Arnold, New York, 1966.
[b] Values are ±0·1.

The fluorescence spectrum of [2-PA] in cyclohexane was also found to be quenched by addition of a small amount of an alcohol. However, in this instance, the quenched fluorescence spectrum differed from that of [2-PA] in cyclohexane. While the fluorescence intensity at 507 nm was quenched by alcohol addition there was a distinct growth of a second emission at 535 nm (Figure 2). The area of the fluorescence spectrum attributed to this second band, when expressed as a percentage of the area of the composite emission band was found to increase with alcohol concentration. Stern–Volmer plots gave fairly linear relationships at low alcohol concentration enabling rates for the quenching process to be calculated (Table). However, at concentrations of alcohol above 0·04M there was significant deviation from the normal linear Stern–Volmer plot (inset, Figure 2). A further interesting feature of these solutions is that the longest wavelength band of the absorption spectrum of [2-PA] showed a red shift with increasing alcohol concentration. This shift we consider to be more than would be expected solely by a change in solvent polarity.

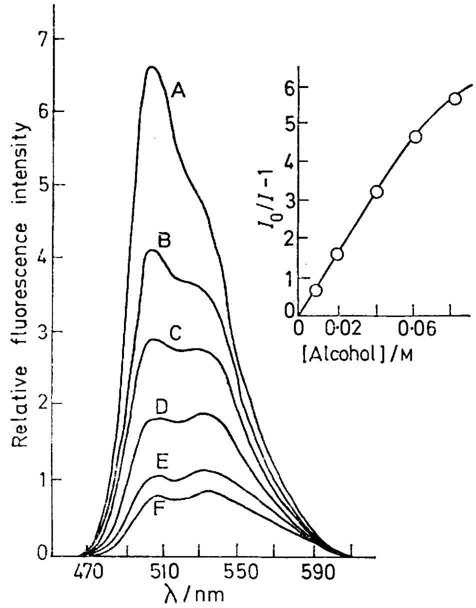

FIGURE 2 Quenching of fluorescence of [2-PA] by an alcohol in cyclohexane. [2-PA] = 5 × 10^{-4}. [Ethanol]: A 0·00; B 0·005; C 0·01; D 0·02; E 0·04; F 0·06. Inset shows typical Stern–Volmer plot

The fluorescence quenching by an alcohol can be explained by a mechanism of hydrogen bonding between ground state [2-PA] and the alcohol forming a complex that is itself fluorescent. This would account for the appearance of the longer wavelength emission at 535 nm and also for the decrease in the quenching constants with decreasing hydrogen-bonding ability of the alcohol (Table).

An alternative mechanism to that proposed for alcohol quenching is that of a proton transfer from the alcohol to the first excited singlet state of [2-PA]. However this mechanism of proton transfer is reported[6,7] to show a marked deuterium effect, but in our experiments this was not found when CH_3OH was replaced by CD_3OD.

Conclusions.—The quenching experiments with amines indicate that the first excited singlet state of [2-PA] can readily participate in electron transfer processes. This observation enhances our view[1] that the greater rate of degradation of nylon polymer reported by Egerton[4] for [2-PA] as compared to [1-PA], is due to electron transfer from the polymer to [2-PA] in either its first excited singlet or triplet states.[2]

The concept that an anthraquinone in its ground state can hydrogen bond to an alcohol thus forming a complex which is itself fluorescent may well be important in relation to the mechanism of phototendering. Such a situation is readily envisaged where an anthraquinone dye is hydrogen bonded to the substrate *via* the hydroxy-groups present in the cellulosic structure.

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