FLUORESCENCE, PHOSPHORESCENCE AND LIGHT FASTNESS OF HYDROXYANTHRAQUINONES

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Summary

The fluorescence and phosphorescence spectra and quantum yields of nine 1-and 2-substituted hydroxyanthraquinones were determined in isopropanol and EPA glass respectively. Their light fastness on polyester fabric were also measured. Fluorescence is observed from all the hydroxyanthraquinones whereas phosphorescence is observed only from the 2-hydroxy derivatives. The fluorescence quantum yields of the 1-hydroxy derivatives are much higher than those of the 2-substituted derivatives. These results are discussed in relation to the light fastness of the hydroxyanthraquinones on polyester fabric.

Introduction

Many hydroxyanthraquinones are used in the dyeing of both natural and synthetic fibres [1]. In particular, a number of 1-hydroxy-substituted derivatives are of considerable commercial importance because of their very high light stabilities on poly(ethylene terephthalate) (PET) fibres [2]. Recently we reported on the influence of different structural features that affect the light fastness of a wide range of anthraquinone disperse dyes on PET [3]. With the simple aminoanthraquinone dyes it was possible to explain quite remarkable differences in their light fastness on PET from a study of their photophysical properties [4]. A similar study of a selected range of hydroxyanthraquinones is reported here.

Experimental

The hydroxyanthraquinones were obtained from the Fine Chemicals Service of ICI Ltd. They were purified by chromatography using a silica packed column and dimethylformamide as eluant. Finally they were

TABLE 1

Fluorescence and phosphorescence maxima and quantum yields for hydroxy-anthraquinones in relation to their light fastness

Anthraquinone	Fluorescence		Phosphorescence			Light fastness 1/1 depth
	λ/nm	ϕ_f	λ/nm	ϕ_p	τ_p/s	
2-hydroxy	472,500	$\sim 10^{-5}$	515	0.06	0.05	<1RD
2,6-dihydroxy	463,505	$\sim 10^{-5}$	532(s),560	0.23	0.16	1
1-hydroxy	570,597(s)	0.004	NO	—	—	>8
1,2-dihydroxy	570(s),590	0.004	NO	—	—	7 - 8
1,4-dihydroxy	536,565	0.05	NO	—	—	>8
1,5-dihydroxy	575,605(s)	0.006	NO	—	—	>8
1,8-dihydroxy	530,570	0.015	NO	—	—	7
1,4,5-trihydroxy	543,572	0.073	NO	—	—	>8
1,2,5,8-tetrahydroxy	550,561,591	0.004	NO	—	—	8

τ_p = phosphorescence lifetime; NO = not observed; RD = redder; (s) = shoulder.

repeatedly recrystallized from ethanol until their melting points were in good agreement with the literature.

The dyes were applied to PET (Crimplene, ICI) using the standard pressure dyeing method [3].

The fluorescence, phosphorescence and light fastness data were all obtained as described earlier [3, 4].

Because of the restricted solubility of the hydroxyanthraquinones in non-polar solvents the fluorescence measurements were made in iso-propanol only. The quantum yields were obtained from solutions in free equilibrium with air. No significant change in the values of the quantum yields were obtained from solutions previously saturated with nitrogen containing less than 5 ppm of oxygen. The phosphorescence measurements were obtained in EPA glass (diethyl ether/2-methylbutane/ethanol 5:2:2 by vol.). All solvents used were of spectroscopic quality.

Results and Discussion

Table 1 summarizes the fluorescence, phosphorescence and light fastness data. By far the most interesting feature is the clear cut difference between those dyes with a hydroxyl group in the 1-position and those without. This is apparent both from the photophysical and from the light fastness data. Since photophysical properties such as fluorescence and phosphorescence quantum yields are determined by the relative rates of deactivation of the various excited states of the dye, it will be our purpose here to examine the data to determine which are the most probable deactivation processes. Having determined these, they will then be related to the light fastness properties of the dyes. This method has been successful in explaining large differences in light fastness that have been observed

with many of the structurally simple aminoanthraquinone [4] and benzanthrone [5] disperse dyes on PET.

If we consider the light fastness data in Table 1, two points are of interest. First, since light fastness is assessed on an approximately geometric scale [6], it is seen that the difference between the 1- and 2- hydroxy derivatives is greater than two orders of magnitude. Second, irrespective of the position or number of other hydroxyl groups in the anthraquinone nucleus, provided the 1-position is hydroxy-substituted the dye light fastness is high. Interestingly, the corresponding light fastness values on PET for the 1- and 2-aminoanthraquinones are 4 - 5 and 1 respectively [3]. This difference is thus an order of magnitude less. It is known [7], however, that the basicity of an amino group, in addition to where it is located on the anthraquinone nucleus, contributes significantly to light fastness. This basicity effect results in an approximately linear relationship between light fastness grade and pK_a of the protonated dye [3].

From the photophysical data in Table 1, it is seen that while all the hydroxyanthraquinones fluoresce, only the 2-hydroxy derivatives phosphoresce. Also the fluorescence quantum yields of the 2-hydroxy derivatives are much less than those of the 1-derivatives. If we construct a potential energy diagram comparing the relative levels, multiplicities and configurations for the excited states of the 1- and 2-hydroxy derivatives then a satisfactory explanation for the differences in the photophysical properties of the two dyes may be obtained. In constructing the diagram we have made the same assumptions as we made with the aminoanthraquinones, [4] namely:

(1) The energy of the first $^1n\pi^*$ and $^3n\pi^*$ levels are similar to those of anthraquinone [8]. This assumption is justified in view of the relative insensitivity of $n\pi^*$ energy levels to the extent of the π-system [9].

(2) The zeroth vibrational level of the $^1\pi\pi^*$ state corresponds to an average of the long wavelength absorption and the fluorescence maxima.

(3) The energy of the first $^3\pi\pi^*$ level of the 2-hydroxy derivatives is given by the highest energy vibrational maximum of the phosphorescence spectrum.

Figure 1 shows that for the 1-hydroxy derivative the level of the $^3n\pi^*$ state lies above that of the $^1\pi\pi^*$ and consequently intersystem crossing between these two states will not occur. The fact that no phosphorescence was detected from this derivative, within the wavelength range of our instrument (sensitive up to 1000 nm), indicates that a large potential energy gap must exist between the $^1\pi\pi^*$ state and any low lying $^3\pi\pi^*$ state, if indeed one exists. Thus radiationless deactivation from the first excited singlet state is probably relatively in efficient for these compounds and this would account for the low but significant quantum yields that are observed. The actual mechanism of deactivation is probably that common to many o-hydroxy substituted aromatic carbonyl compounds, rapid proton exchange in the first excited singlet state [10].

For the 2-hydroxy derivatives, this process of proton exchange deactivation cannot, of course, be significant. However, it is seen from

28 —

26 — ——————————————————— $^1n\pi^*$

24 —

$\langle \nu \rangle \times 10^{-3}$ CM^{-1}

22 — —————————— $^1\pi\pi^*$
$^3n\pi^*$

20 — —————————— $^3\pi\pi^*$
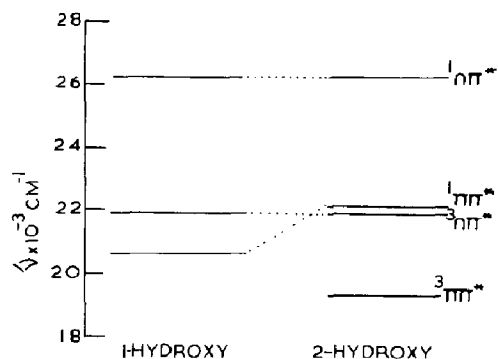
18 —

1-HYDROXY   2-HYDROXY

Fig. 1. Estimated energy levels, multiplicities and configurations of the excited states of 1- and 2- hydroxyanthraquinone.

Fig. 1 that the level of the $^3n\pi^*$ state lies just below that of the $^1\pi\pi^*$ state. In this case, therefore, rapid deactivation from the first excited singlet state, $^1\pi\pi^*$, by intersystem crossing to the $^3n\pi^*$ state will be strongly favoured by two factors; (a) the small size of the potential gaps between the two states, and (b) the fact that the crossing involves states of differing configuration. This clearly accounts for the very low fluorescence quantum yields of these derivatives. Following efficient intersystem crossing to the $^3n\pi^*$ state, further rapid deactivation will occur by internal conversion within the triplet manifold to the $^3\pi\pi^*$ state. At this point, however, further radiationless deactivation to the ground state is likely to be inefficient on both multiplicity and configuration grounds [11], and this would explain the substantial quantum yields and relatively long lifetimes of the phosphorescence from the 2-hydroxy derivatives.

To conclude, therefore, the above interpretation of the photophysical data leads to a ready explanation for the difference in light fastness between the 1- and 2- hydroxyanthraquinones. It shows that the former, and this includes all the other 1-hydroxy substituted derivatives in Table 1, are much more rapidly deactivated to their ground states, thus decreasing the chance of chemical reaction with their environment.

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