

STRUCTURAL INFLUENCES ON THE LIGHT STABILITY OF 2-SUBSTITUTED AMINOANTHRAQUINONES AND HYDROXYANTHRAQUINONES IN MAN-MADE POLYMERS

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Summary

The fluorescence and phosphorescence spectra and quantum yields of 2-amino-, 2-hydroxy- and 2-amino-3-hydroxyanthraquinones have been recorded in a variety of solvents and these data have been linked to studies on the light stabilities of the compounds in man-made polymers. Strong fluorescence is observed only from the 2-amino derivative and strong phosphorescence only from the 2-hydroxy derivative while the 2-amino-3-hydroxy derivative is non-luminescent. On flash photolysis in 2-propanol, the 2-amino and 2-hydroxy derivatives gave strong transient absorption due to the radical anion $A^{\cdot-}$ whereas the 2-amino-3-hydroxy derivative gave strong transient absorption due to the semiquinone radical AH^{\cdot} . These results are discussed in relation to the photostabilities of the compounds in polyester and nylon 6,6 film and fabric.

1. Introduction

In earlier papers we found a relationship between structure, spectroscopic properties and lightfastness of simple anthraquinone model dyes used in man-made fibres [1 - 7]. Among the model dyes studied was 1,2-dihydroxyanthraquinone which has very high lightfastness in both polyester and nylon substrates [7]. In this case 2-hydroxy substitution appeared to stabilize the dye in nylon 6,6 since 1-hydroxyanthraquinone had low lightfastness in this substrate. On flash photolysis in polar 2-propanol there was a significant difference that explained the high photostability of the 1,2-derivative in nylon polymer.

[†]Dr. McKellar died suddenly on May 3, 1979, following a long period of illness.

A study of the luminescence properties of anthraquinone model dyes provided a guide to the assessment of lightfastness [1 - 6]. Of particular interest were some experiments in which we found remarkable differences in the quantum yields of fluorescence and phosphorescence for simple 2-hydroxy- and 2-aminoanthraquinones [1 - 3]. We have studied the effect of these two substituents in detail using luminescence, flash photolysis and steady state photolysis techniques and these lead to some interesting and important conclusions on the influence of these particular groups on the light stability of the anthraquinone chromophore in man-made polymers.

2. Experimental

The 2-amino-, 2-hydroxy- and 2-amino-3-hydroxyanthraquinones were supplied by the Fine Chemicals Service of I.C.I. Ltd. and were purified on a silica column using dimethylformamide as the eluant. The compounds were then watered out of solution, filtered and recrystallized from ethanol. The melting points of the compounds were in good agreement with the literature values.

The model dyes were applied to poly(ethylene terephthalate) (PET) (Crimplene fabric and Melinex film, 100 μm thick, I.C.I. Ltd) and nylon 6,6 (Bri-nylon fabric and Maranyl film, 100 μm thick, I.C.I. Ltd) using the standard pressure dyeing method.

The dyed fabrics and films were irradiated in a Xenotest-150 weatherometer (Original Hanau, Quartzlampen, G.m.b.H.) and the lightfastness was assessed by the standard ISO test method [9].

UV and visible absorption spectra were recorded using a Perkin-Elmer Model 554 spectrometer. The fluorescence and phosphorescence excitation and emission spectra, quantum yields and flash photolysis results were obtained as described earlier [1 - 7].

3. Results

3.1. Luminescence and lightfastness

From the photophysical data in Table 1 three points are of interest. First, it is seen that the 2-amino derivative is fluorescent but the quantum yield decreases rapidly with an increase in solvent polarity. Second, the 2-hydroxy derivative in contrast to the 2-amino derivative is phosphorescent and again very weakly fluorescent at high polarity. Third, the 2-amino-3-hydroxy derivative is completely non-luminescent.

The last observation is very interesting since all other 2,3-substituted derivatives studied previously [1 - 7] have exhibited fluorescence or phosphorescence. Furthermore, the occurrence of these emissions was related to the light stability of the model dye in its polymeric environment. To extend this comparison the fluorescence/phosphorescence emissions seen

TABLE 1
Luminescence properties of 2-substituted aminohydroxyanthraquinones

Anthraquinone	Fluorescence			Phosphorescence		
	Benzene Em λ (nm) ^a	ϕ_F ^b	Ethyl acetate Em λ (nm)	2-Propanol Em λ (nm)	EPA ^c glass Em λ (nm)	ϕ_P
2-Amino- 2-Hydroxy- 2-Amino-3-hydroxy.	529 Insol. ^d N.O. ^e	0.08	563 Insol. N.O.	N.O. 472 500 N.O.	— 515 N.O.	— $<10^{-5}$ $\sim 10^{-5}$ 0.06

^a Em λ = emission wavelength maximum.

^b ϕ_F and ϕ_P indicate fluorescence and phosphorescence quantum yields.

^c EPA = ether:2-methylbutane:ethanol, 5:2:2 parts by volume at 77 K.

^d Insol. = insoluble.

^e N.O. indicates not observed.

All compound are chromatographically pure.

TABLE 2

Comparison of fluorescence and phosphorescence observations with lightfastness on polyester and nylon 6,6 fabric

Anthraquinone	Fluorescence ^a	Phosphorescence ^b	Lightfastness ^c 1/1 depth polyester nylon 6,6	
2-Amino-	Strong	None	1	1
2-Hydroxy-	V. weak	Strong	1	1
2-Amino-3-hydroxy	None	None	4	3 - 4

^a See ref. 1.

^b See ref. 2.

^c ISO standard test BS. 1006:1971.

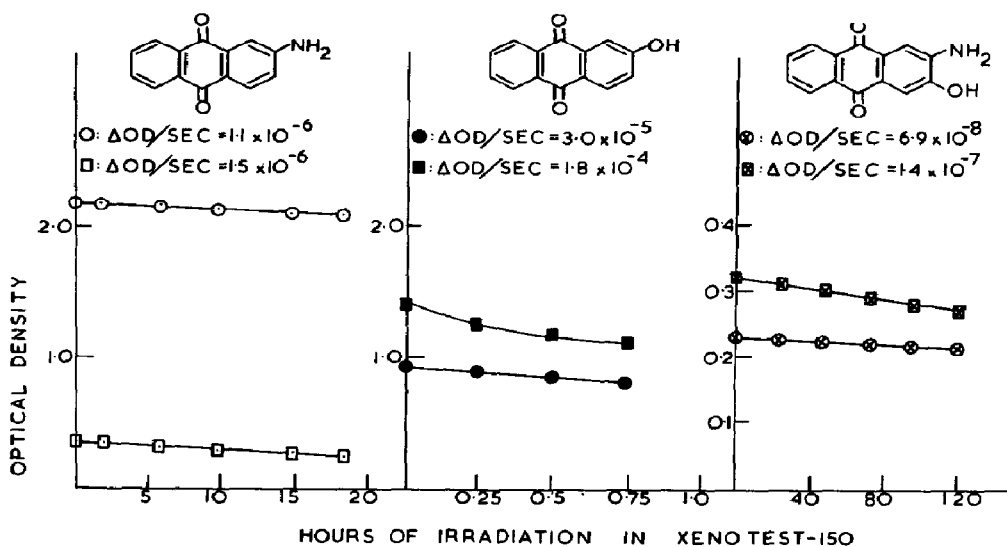


Fig. 1. Change in the optical densities of the longest wavelength absorption bands of 2-amino, 2-hydroxy- and 2-amino-3-hydroxyanthraquinone in polyester (○, 435 nm; ●, 385 nm; ⊙, 480 nm) and nylon 6,6 (□, 460 nm; ■, 375 nm; ⊞, 475 nm) films respectively during irradiation in a Xenotest-150 weatherometer.

under the conditions of Table 1 indeed match the stability of the model dye in the polymer, as found earlier. However, the discovery of a simple 2,3-substituted derivative with no fluorescence or phosphorescence was of great interest in this respect since it allowed exploration of its light stability as a model dye on a fabric such as polyester and polyamide. Table 2 shows the significant result that if no fluorescence and phosphorescence is observed then this is reflected in a marked improvement in the lightfastness of the dye in both polyester and nylon 6,6 fabrics. To demonstrate this clearly we have compared in the table only the relative intensities of the emissions from the model dyes with their lightfastness.

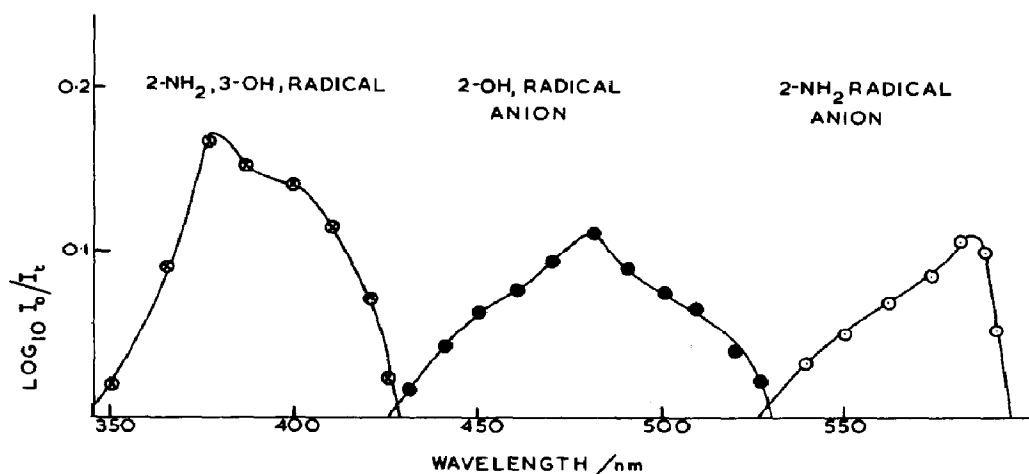


Fig. 2. Transient absorption spectra produced in the flash photolysis of nitrogen-saturated (less than 5 ppm oxygen) 10^{-4} M solutions of 2-aminoanthraquinone (○), 2-hydroxyanthraquinone (●) and 2-amino-3-hydroxyanthraquinone (⊙) in 2-propanol.

3.2. Continuous photolysis in polymer films

To compare the remarkable differences in the light stability of these model dyes, further experiments were carried out to monitor quantitatively their fading in polymer films. Essentially the reason for this was that the ISO test is not of sufficient accuracy to give the degree of light stability comparison that we needed for our further experiments. The model dyes were therefore applied to polyester and nylon 6,6 films and irradiated in a Xenotest-150 weatherometer (at wavelengths greater than 300 nm).

Figure 1 compares the change in the optical density of the longest wavelength absorption bands for the three model dyes in polyester and nylon 6,6 films during irradiation in a Xenotest-150 weatherometer. It is seen that all three dyes fade faster in nylon 6,6 than in polyester. Furthermore, the 2-hydroxy derivative fades by an order of magnitude faster than the 2-amino derivative in polyester and by at least two orders of magnitude faster in nylon 6,6. In contrast, the 2-amino-3-hydroxy derivative fades three orders of magnitude slower than the least stable 2-hydroxy derivative in both polymer films.

3.3. Flash photolysis in solution

Figure 2 compares the absorption spectra of the transient species produced on flash photolysis of the three model dyes in anaerobic 2-propanol. It is seen that the 2-amino, 2-hydroxy and 2-amino-3-hydroxy derivatives exhibit strong transient absorptions with wavelength maxima at 580, 480 and 375 nm respectively. The transients had mean lifetimes τ^1/e of 5, 20 and 80 ms respectively. Furthermore, after one flash the 2-amino-3-hydroxy derivative exhibited a very strong blue-green fluorescence emission whereas the 2-amino and 2-hydroxy derivatives exhibited a weaker fluorescence emission (Fig. 3). These emissions are very probably due to the hydro-

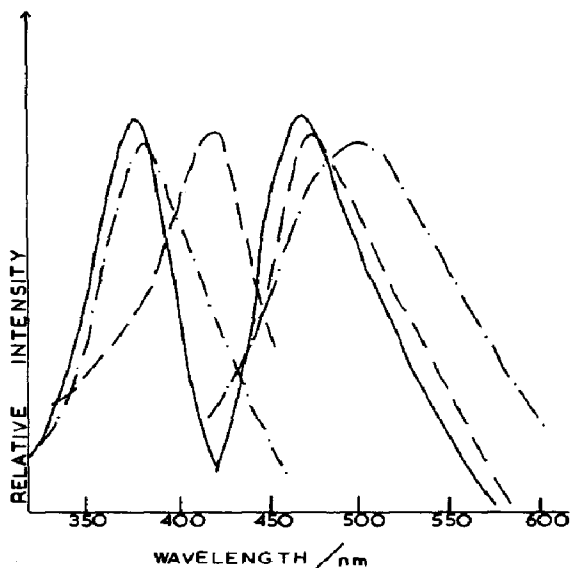


Fig. 3. Fluorescence excitation and emission spectra of the corresponding anthrahydroquinone photoproducts produced after photoflashing 10^{-4} M solutions of 2-aminoanthraquinone (—, $S_x = 30$), 2-hydroxyanthraquinone (---, $S_x = 30$) and 2-amino-3-hydroxyanthraquinone (-.-, $S_x = 3$) in 2-propanol, where S_x = sample sensitivity.

quinones since on admitting air into the solutions they disappeared because of oxidation [4 - 7].

4. Discussion

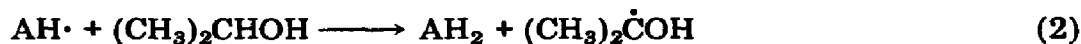
The outstanding result of this work is the observation of high light stability for the 2-amino-3-hydroxy derivative, particularly in a highly polar substrate such as nylon 6,6. This result is of both theoretical and practical interest since high stability in the anthraquinone molecule is normally achieved by 1-hydroxy substitution which gives rapid deactivation within the singlet and/or triplet manifolds through the formation of an intramolecular hydrogen bond with the carbonyl group [1 - 3]. Of further interest is the result that this improvement in light stability with 2,3-amino-hydroxy substitution is paralleled by the observation of the lack of fluorescence and phosphorescence from this particular dye. Thus, in this case deactivation of the excited states of the dye must occur through some other mechanism. A preliminary communication on this result has already been reported [10].

For the present, two possible pathways of deactivation for this other mechanism could be operative, of which the first appears to us the more probable. However, the second may make some contribution. The first mechanism is that substitution of both the amino and the hydroxy groups in the 2 position relative to both the carbonyl groups in some way produces a compensating effect in deactivating the singlet and triplet states of the

anthraquinone chromophore. For example, substitution of an amino group in the 2 position of the anthraquinone molecule will introduce an element of charge transfer resulting in the formation of an emissive $\pi\pi^*$ singlet state and non-emissive $\pi\pi^*$ triplet state [1, 3]. In contrast, substitution of a hydroxy group in the 2 position will deactivate the first excited $\pi\pi^*$ singlet state by intersystem crossing to the second excited $n\pi^*$ triplet state [2]. The second mechanism involves the formation of an intermolecular hydrogen bond between the carbonyl group of one molecule and the hydroxyl group of another. Although this mechanism may not occur in solution it could well be important in the solid phase where the dye molecules may form suitably orientated aggregates [8]. However, this type of bonding is unlikely to account for the increase in light stability of the dye in a highly polar substrate such as nylon 6,6 where such weak bonds would be easily broken. Furthermore, other 2,3 substituted derivatives studied previously [6] could also form intermolecular hydrogen bonds and yet have low light stability.

Another interesting result is the marked difference in light stability between the 2-amino and 2-hydroxy derivatives. Again, the luminescence results parallel their light stabilities. The phosphorescent 2-hydroxy derivative is, as expected, less stable to light than the fluorescent 2-amino derivative.

A comparison of the flash photolysis results shown in Fig. 2 with earlier flash photolysis studies on anthraquinone and its derivatives [4 - 7, 11] enables us to identify the transient species formed. Transient absorption in the spectral region 35 - 350 nm is normally associated with the semiquinone radical $AH\cdot$, whereas transient absorption in the spectral region 450 - 600 nm is normally associated with the radical anion $A^{\cdot-}$. The formation of the hydroquinones may be explained by the following established reaction mechanisms [4 - 7, 11]:



Both reactions (1) and (2) have been included since no definite order of decay of $AH\cdot$ was found with the 2-amino-3-hydroxy derivative. Reaction (3) must only contribute to a minor extent to the disappearance of $A^{\cdot-}$ since only a trace of hydroquinone could be detected as a photoproduct.

As found earlier for the substituted aminoanthraquinones [4 - 6] the flash photolysis results are also useful in the interpretation of the lightfastness properties of the model dyes in nylon 6,6 polymer. The observation of strong transient absorptions due to the radical anion for the 2-amino and 2-hydroxy derivatives in polar 2-propanol indicates that they must abstract an electron from the solvent. This would also account for their low lightfastness in a polar polyamide environment such as nylon 6,6 where the probability of dye-substrate interaction by such a mechanism is enhanced [12]. In the

case of the 2-amino-3-hydroxy derivative the observation of strong transient absorption due to the semiquinone radical indicates that this model dye must abstract a hydrogen atom from its environment. This result bears a strong similarity to our earlier work on 1-anilinoanthraquinone [5]. There we concluded that oxidation of the hydroquinone to the original dye must account for its higher light stability in the polymer.

5. Conclusions

Substitution in the 2 and 3 positions by an amino and a hydroxy group respectively leads to extremely rapid deactivation within the singlet and triplet manifolds. This gives a dye of much higher light stability than the corresponding individually 2-substituted compounds in which deactivation is obviously slower. This is a result of considerable significance, not only from a scientific point of view but also from a technological one and particularly with regard to the development of light-stable dyes for man-made polymers.

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