LIGHTFASTNESS AND SPECTROSCOPIC PROPERTIES OF N-SUBSTITUTED 1-AMINOANTHRAQUINONES

N. S. ALLEN, B. HARWOOD and J. F. McKELLAR

Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT (Gt. Britain)

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Summary

The fluorescence spectra and quantum yields of 1-acetylamino-, 1-monochloroacetylamino-, 1-benzoylamino- and 1-anilinoanthraquinones have been recorded in a variety of solvents. The dyes have also been examined using microsecond flash photolysis in ethyl acetate and 2-propanol. Fluorescence is observed from all the dyes except the 1-anilino derivative. On flash photolysis, all the dyes give strong transient absorption in 2-propanol whereas no transient absorption is observed in ethyl acetate. Interestingly, the 1-anilino derivative gives a very strong transient absorption due to the semiquinone radical ($QH\cdot$) whereas the other three dyes give a strong transient absorption due to the radical anion ($Q^{\overline{\cdot}}$). These results are discussed in relation to the lightfastness of the dyes on polyester and nylon fibres.

1. Introduction

In previous papers [1 - 5] we found that a knowledge of the spectroscopic properties of aminoanthraquinone dyes makes a valuable contribution to our understanding of the relation between structure and lightfastness (LF). For example, substitution of an electron-withdrawing carboxyl group in the nucleus of 1-aminoanthraquinone results in a significant improvement in the LF of the dye in polyester but not in a highly polar environment such as nylon [5]. On flash photolysis strong transient absorption was observed only in polar solvents such as isopropanol.

In this paper we have examined the spectroscopic and LF properties of 1-aminoanthraquinone dyes substituted in the N-position by electron-withdrawing acetyl, monochloroacetyl, benzoyl and phenyl groups. This type of substitution also gives rise to dyes of high light stability in a polyester substrate [1, 2]. With chloro- and carboxyaminoanthraquinones we found a large difference in the LF values between polyester and nylon substrates [4, 5]. It is of interest therefore to examine the "substrate effect" on the LF values of N-substituted aminoanthraquinones since this may lead to a better understanding of their photochemistry.

2. Experimental

2.1. Materials

The dyes were supplied by the Fine Chemical Service of ICI Ltd. and were purified on an alumina column using chloroform as the eluant. Finally, they were recrystallized from ethanol until their melting points were in good agreement with the literature values.

The dyes were applied to poly(ethylene terephthalate) (PET) (Crimplene, ICI) and nylon 6,6 (Bri-nylon, ICI) using the standard pressure dyeing method [6].

All the solvents used were normally of either spectroscopic or Analar reagent quality.

2.2. Lightfastness

The dyed fabrics were irradiated in a Xenotest-150 fadeometer (Original Hanau, Quartzlampen, G.m.b.H) and the LF was assessed by the standard ISO test method [7].

2.3. Fluorescence measurements

Fluorescence excitation and emission spectra were obtained using a double grating (1200 lines mm^{-1}) Hitachi Perkin–Elmer MPF-4 spectrofluorimeter equipped with two red-sensitive R-446F photomultiplier tubes [2 - 5]. Fluorescence measurements were made in n-hexane, ethyl acetate and 2-propanol. Fluorescence quantum yields were determined by the relative method using quinine sulphate in 0.25 M sulphuric acid as a standard [8]. The fluorescence quantum yield of quinine sulphate was assumed to be 0.55. No phosphorescence was observed from any of the dyes studied here.

2.4. Flash photolysis

The flash photolysis experiments were carried out using a microsecond apparatus with a photoflash of 300 J and a half-life of 10 μs.

3. Results and discussion

If we consider the LF data in Table 1 three points are of interest. First, it is seen that the LF values of all the dyes are high in a polyester substrate. Second, in a nylon substrate the LF values of the 1-acetyl-, 1-monochloroacetyl- and 1-benzoylaminoanthraquinones are low. Third, the LF value of the 1-anilino derivative is little affected by the nature of the polymer substrate.

The fluorescence emission wavelength maxima and quantum yields for the dyes are shown in Table 1. It is seen that all the dyes except the 1-anilino derivative fluoresce. Further, the fluorescence quantum yields of the 1-acetyl, 1-monochloroacetyl and 1-benzoylamino derivatives are higher in polar solvents than in non-polar solvents.

TABLE 1

Fluorescence and LF properties of N-substituted 1-amino-anthraquinones

Anthraquinone	Fluorescence						LF (one-third depth)	
	n-hexane		Ethyl acetate		2-propanol		Polyester	Nylon 6,6
	λ_{EM}(nm)	ϕ_F	λ_{EM}(nm)	ϕ_F	λ_{EM}(nm)	ϕ_F		
1-Acetylamino	500	$<10^{-4}$	515	6.9×10^{-3}	518	4×10^{-3}	6 - 7	1
1-Monochloroacetylamino	–	$<10^{-5}$	509	1.3×10^{-3}	515	1.1×10^{-3}	7	1
1-Benzoylamino	500	$<10^{-4}$	520	1.3×10^{-3}	528	$<10^{-4}$	7	<1
1-Anilino	–	$<10^{-5}$	–	$<10^{-5}$	–	$<10^{-5}$	7	5

TABLE 2

Flash photolysis of N-substituted 1-aminoanthraquinones

Anthraquinone	Transient absorption	
	Ethyl acetate	2-Propanol
1-Acetylamino	None	Strong
1-Chloroacetylamino	None	Strong
1-Benzoylamino	None	Strong
1-Anilino	None	Very strong

From the flash photolysis results shown in Table 2 it is seen that for all the derivatives whereas no transient absorption is observed in nitrogen-saturated ethyl acetate strong transient absorption is observed in 2-propanol. The transient absorption spectra of all four derivatives in 2-propanol are shown in Fig. 1. It is seen that the transient species produced on flash photolysis of the 1-acetyl, 1-monochloroacetyl and 1-benzoylamino derivatives have wavelength maxima at about 490 nm whereas that of the 1-anilino derivative has a wavelength maximum at 390 nm. The transients for the first three derivatives at 490 nm have a mean lifetime (τ^1/e) of 50 ms whereas that of the 1-anilino derivative has a mean lifetime of 100 ms.

A comparison of the results obtained here with earlier flash photolysis studies on anthraquinone and its derivatives [9 - 11] enables us to identify the transient species formed. Transient absorption in the spectral region 350 - 450 nm is normally associated with the semiquinone radical (QH·)
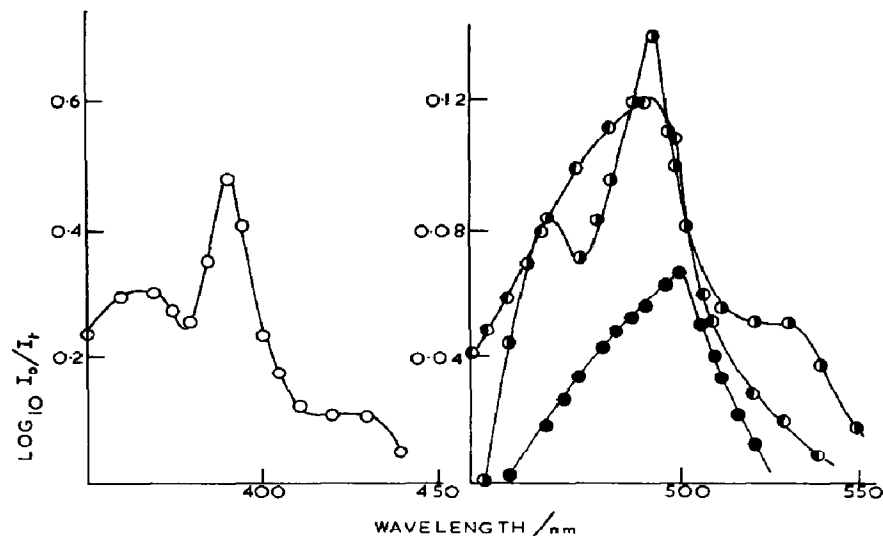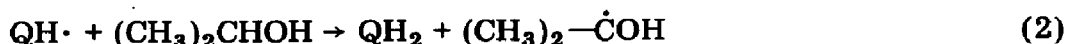

Fig. 1. Transient absorption spectra produced in the flash photolysis of nitrogen-saturated (less than 5 ppm oxygen) 10^{-5} M solutions of the following substituted anthraquinones in 2-propanol: o, 1-anilino; ◑, 1-benzoylamino; ◕, 1-acetylamino; ●, 1-monochloroacetyl-amino.

whereas transient absorption in the spectral region 450 - 550 nm is normally associated with the radical anion ($Q^{\bar{\cdot}}$). Further, after one flash the 1-anilino derivative in anaerobic 2-propanol exhibited a strong blue–green fluorescence emission whereas the 1-acetyl and 1-monochloroacetylamino derivatives exhibited only a very weak blue fluorescence (Fig. 2). The 1-benzoylamino derivative, however, exhibited no such fluorescence after flashing. These emissions are very probably due to the hydroquinones formed by the following established reaction mechanisms:

$$2QH\cdot \rightarrow Q + QH_2 \tag{1}$$

$$QH\cdot + (CH_3)_2CHOH \rightarrow QH_2 + (CH_3)_2-\overset{\cdot}{C}OH \tag{2}$$

$$Q^{\bar{\cdot}} + H^+ \rightarrow QH\cdot \tag{3}$$

This mechanism is postulated because, on admitting air into the solutions, the emissions disappear owing to oxidation of the hydroquinones [9 - 11] according to the reactions

$$QH_2 + O_2 \rightarrow QH\cdot + HO_2^{\bar{\cdot}} \tag{4}$$

$$QH\cdot + O_2 \rightarrow Q + HO_2^{\bar{\cdot}} \tag{5}$$

Both reactions (1) and (2) have been included since no definite order of decay of QH· was found with the 1-anilino derivative. Reaction (3) must contribute to only a minor extent to the disappearance of $Q^{\bar{\cdot}}$ for the 1-acetyl and 1-monochloroacetylamino derivatives since only a trace of hydroquinone could be detected as a photoproduct in anaerobic 2-propanol. In the case of the 1-benzoylamino derivative reaction (3) does not apply since no hydroquinone could be detected. Further, no definite order of decay of $Q^{\bar{\cdot}}$ was found with any of the dyes. One other possible mechanism for the decay of
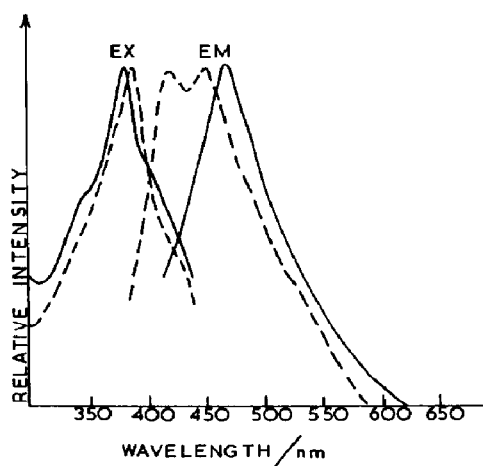

Fig. 2. Fluorescence excitation (EX) and emission (EM) spectra of the corresponding anthrahydroquinone photoproducts after photoflashing 1-anilino (——, × 10) and 1-acetyl and monochloroacetylaminoanthraquinones (---, × 100) in 2-propanol (10^{-5} M).

$Q^{\cdot-}$ is the formation of the stable dianion (Q^{2-}) and a molecule of the original dye by [9 - 11] the reaction

$$2Q^{\cdot-} \rightarrow Q^{2-} + Q \qquad (6)$$

The above fluorescence and flash photolysis results are very useful in the interpretation of the LF properties of the compounds in both polyester and nylon substrates. The higher fluorescence quantum yields of the 1-acetyl, 1-monochloroacetyl and 1-benzoylamino derivatives in polar solvents clearly account for their low LF values in a polar polymeric environment such as nylon 6,6. Similar observations were established with 3-methoxybenzanthrone in nylon 6,6 [12]. Also the observation of strong transient absorptions due to the radical anion for these three dyes in a polar solvent indicates that they must abstract an electron from the solvent. This would also account for their low LF value in a highly polar polymeric environment such as nylon 6,6 fabric where the probability of dye–substrate interaction by such a mechanism is enhanced [10, 11]. In the case of the 1-anilino derivative oxidation of the hydroquinone to the original dye must account for its relatively higher LF value in nylon 6,6 fabric.

Acknowledgment

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