Short Communication

Lightfastness and spectroscopic properties of aminocarboxyanthraquinones

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1. Introduction

The aminoanthraquinones are a commercially important class of compounds used as disperse dyes for synthetic fibres [1, 2]. In previous studies [3, 4] we found that a knowledge of the luminescence properties of the simpler aminoanthraquinones makes a valuable contribution to our understanding of the relation between structure and lightfastness (LF). More recently we found a correlation between the spectroscopic properties of aminochloroanthraquinones and their LF on polyester and nylon substrates [5]. These derivatives had a moderate LF [5] on polyester but low LF [1] on nylon.

In this paper the aminocarboxyanthraquinones have been examined by luminescence spectroscopy and conventional flash photolysis in different solvents so that any environmental influence on the photochemical behaviour of the dyes may be established. In this case, substitution of a carboxyl group in the anthraquinone nucleus markedly improves the LF of the dye in a polyester [8] compared with that of chloro-substitution.

2. Experimental

All the dyes were supplied by I.C.I. Ltd. and were purified by column chromatography. The LF, luminescence and flash photolysis results were obtained as described in earlier papers [5 - 9].

3. Results and discussion

If we consider the LF data in Table 1 two points are of interest. First, it is seen that in a polyester substrate the LF values of the two 1-aminocarboxy derivatives are significantly greater than that of the 2-amino-3-carboxy derivative. Second, in a nylon (polyamide) substrate the LF values of all the aminocarboxy derivatives are low.

TABLE 1

Luminescence and LF properties of some aminocarboxyanthraquinones

Anthraquinone	Ether		Fluorescence				Phosphorescence		LF	
			Ethyl acetate		2-Propanol		EPA glass		Polyester	Nylon
	λ_{EM}^a (nm)	Φ_F	λ_{EM} (nm)	Φ_F	λ_{EM} (nm)	Φ_F	λ_{EM} (nm)	Φ_P		
1-Amino-2-carboxy	562	2.4×10^{-3}	572	1.5×10^{-2}	590	4×10^{-3}	none		8	2
1-Amino-3-carboxy	558	7.8×10^{-3}	565	10^{-2}	585	3.5×10^{-3}	none		8	3
2-Amino-3-carboxy	520	6.0×10^{-2}	535	5×10^{-2}	573	1.4×10^{-3}	455, 492 534.5, 584 610	10^{-2} 5×10^{-4}	1	1

[a] Emission wavelength maximum.

The fluorescence and phosphorescence emission wavelength maxima and quantum yields for the aminocarboxy-substituted anthraquinones are shown in Table 1. It is seen that the fluorescence emission wavelength maximum of the 2-amino-3-carboxy derivative is more solvent dependent than those of the two 1-aminocarboxy derivatives. This indicates that the 2-amino-3-carboxy derivative possesses more charge transfer content in its first excited singlet state than the 1-amino derivatives. The fluorescence quantum yields of all three compounds are very similar.

However, the most interesting feature of the results shown in Table 1 is that phosphorescence is observed only from the 2-amino-3-carboxy derivative. In fact, this compound exhibits two quite different phosphorescence emissions. These are the normal weak phosphorescence emission at longer wavelengths than its fluorescence and an anomalous structured phosphorescence emission at shorter wavelengths. The latter emission is produced only on excitation with light of wavelengths shorter than 350 nm. We recently suggested that this emission occurs from an upper $n\pi*$ triplet state [6]. The splitting of the vibrational structure (1640 cm^{-1}) is in accord with this assignment [10, 11].

From the flash photolysis results shown in Table 2 it is seen that for all three derivatives whereas only very weak transient absorption is observed in nitrogen-saturated ethyl acetate strong transient absorption is observed in 2-propanol. The transient absorption spectra of all three derivatives in 2-propanol are shown in Fig. 1. It is seen that the transient species produced on flash photolysis of the 1-amino-2-carboxy and 1-amino-3-carboxy derivatives have wavelength maxima at 415 and 390 nm respectively whereas that of the 2-amino-3-carboxy derivative has a wavelength maximum at 530 nm. Both transients for the 1-aminocarboxy derivatives have a mean lifetime ($\tau_{1/e}$) of the 15 ms whereas that of the 2-amino-3-carboxy derivative has a mean lifetime of 30 ms.

A comparison of the results obtained here with earlier flash photolysis studies on anthraquinone and its derivatives [12 - 15] 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·) whereas transient absorption in the spectral region 450 - 550 nm is normally associated with the radical anion (Q·$^-$). Further, after one flash all three

TABLE 2

Flash photolysis of aminocarboxyanthraquinones

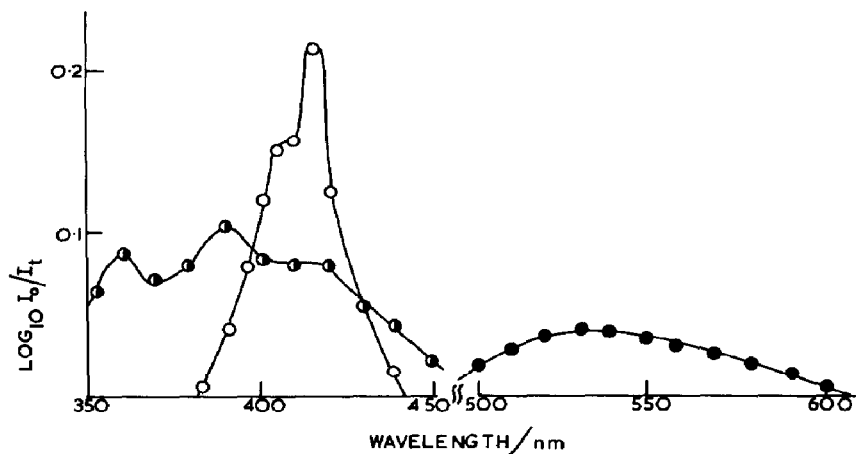| Anthraquinone	Transient absorption	
	Ethyl acetate	2-Propanol
1-Amino-2-carboxy	V. weak	Strong
1-Amino-3-carboxy	V. weak	Strong
2-Amino-3-carboxy	V. weak	Strong

Fig. 1. Transient absorption spectra produced in the flash photolysis of nitrogen-saturated (less than 5 ppm oxygen) 10^{-5} M solutions of 1-amino-2-carboxy- (○), 1-amino-3-carboxy- (◉) and 2-amino-3-carboxy-anthraquinone (●) in 2-propanol.

derivatives in anaerobic 2-propanol exhibited strong blue and green fluorescence emissions (Fig. 2). These are very probably due to the hydroquinones formed by the following established reaction mechanisms:

$$Q\cdot^- + H^+ \longrightarrow QH\cdot \quad (1)$$

$$2QH\cdot \longrightarrow Q + QH_2 \quad (2)$$

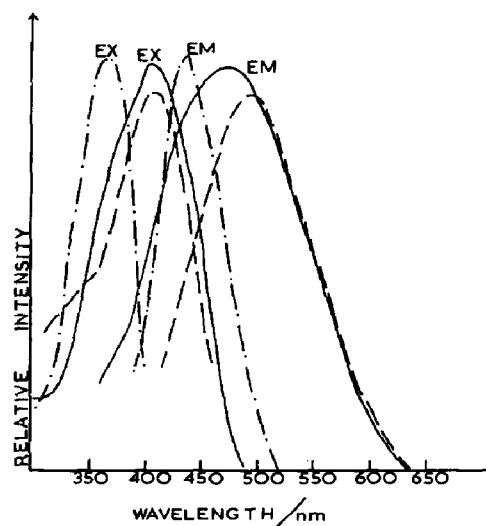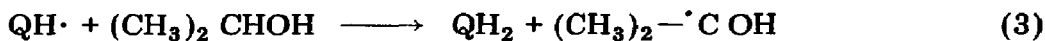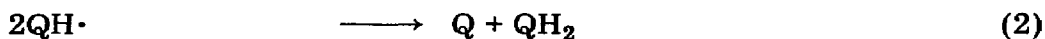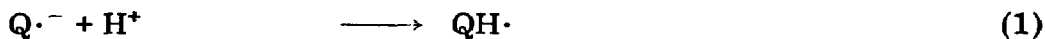$$QH\cdot + (CH_3)_2\,CHOH \longrightarrow QH_2 + (CH_3)_2{-}^{\cdot}C\,OH \quad (3)$$

Fig. 2. Fluorescence excitation and emission spectra of the corresponding anthrahydroquinone photoproducts produced after photoflashing 1-amino-2-carboxyanthraquinone (———), 1-amino-3-carboxyanthraquinone (-----) and 2-amino-3-carboxyanthraquinone (—·—·—) in 2-propanol (10^{-5} M).

since on admitting air into the solutions they disappeared owing to oxidation of the hydroquinones [12 - 15]:

$$QH_2 + O_2 \longrightarrow QH\cdot + HO_2^- \tag{4}$$

$$QH\cdot + O_2 \longrightarrow Q + HO_2^- \tag{5}$$

Reaction (3) has been introduced because no definite order of decay of QH· was found with the dyes. Reactions (1) - (3) apply in the case of the 2-amino-3-carboxy derivatives whereas only reactions (2) and (3) are applicable in the case of the two 1-amino-carboxy derivatives. The observation of the radical anion on flashing the 2-amino-3-carboxy derivative is crucial since this is exactly what would be expected from a dye of high charge transfer content in a polar environment [13 - 15].

The above luminescence and flash photolysis results are very useful in the interpretation of the LF properties of the compounds in both polyester and nylon substrates. The observation of two phosphorescence emissions from the 2-amino-3-carboxy derivative clearly accounts for its low LF value in both substrates compared with the 1-amino-3-carboxy derivatives. Also the greater charge transfer content in this derivative indicates that it is more likely to undergo chemical reaction with the substrate, *e.g.* electron abstraction [14]. In contrast, the observation of relatively strong transient absorptions for all three dyes in a polar solvent clearly accounts for their low LF value in a highly polar polymeric environment such as nylon 6,6 fabric [16].

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