

LIGHTFASTNESS AND SPECTROSCOPIC PROPERTIES OF AMINO-CHLOROANTHRAQUINONES

NORMAN S. ALLEN, BRYAN HARWOOD and JOHN F. McKELLAR

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

(Received April 6, 1978; in revised form May 18, 1978)

Summary

The fluorescence and phosphorescence spectra and quantum yields of 1-amino-2-chloro-, 1-amino-3-chloro- and 2-amino-3-chloroanthraquinones have been recorded in a variety of solvents and these data have been linked to studies of the dyes in solution flash photolysis and to their lightfastness on polyester and nylon fabrics. Fluorescence is observed from all the compounds whereas phosphorescence is observed only from the 2-amino-3-chloro derivative. Interestingly, in less polar solvents the fluorescence quantum yield of the 2-amino-3-chloro derivative is higher than those of any of the other dyes. These results are discussed in relation to the lightfastness of the dyes on polyester and nylon fabrics.

1. Introduction

Anthraquinone derivatives are widely used as commercial dyes for both natural and synthetic fibres [1, 2]. In previous studies we found that a knowledge of the luminescence properties of the simpler amino- and hydroxyanthraquinones makes a valuable contribution to our understanding of the relation between structure and lightfastness (LF) [3 - 5]. However, as well as this influence of structure on LF many earlier workers have shown that the nature of the polymeric (fabric) environment may also have a significant effect on LF [6, 7]. For example, anthraquinone disperse dyes may in some instances have poor LF on nylon substrates but good LF on polyesters.

In this paper we have extended our previous luminescence studies [3 - 5] to the more complex amino-chloro derivatives with a two-fold objective. First, substitution of chlorine atoms in many cases improves the LF of the dye while differing substrates may have a greater or lesser effect. Further, we have examined these dyes by flash photolysis in different solvents so that any environmental influence on the photochemical behaviour of the dyes may be established.

2. Experimental

2.1. Materials

The aminochloroanthraquinones were obtained from the Fine Chemicals Service of I.C.I. Ltd. and were purified by chromatography using an alumina packed column with chloroform as eluant. Finally they were recrystallized from ethanol until their melting points were in good agreement with the literature values.

Quinine sulphate was crystallized three times from distilled water and dried over silica gel. All solvents used were normally of either spectroscopic or Analar reagent quality.

The dyes were applied to poly(ethylene terephthalate) (PET) (Crimplene, I.C.I.) and nylon 6,6 (Bri-nylon, I.C.I.) using the standard pressure dyeing method [8].

2.2. Lightfastness determination

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 [9]. The irradiation conditions were set up for simulated sunlight exposure out of doors [10].

2.3. Luminescence measurements

Fluorescence and phosphorescence excitation and emission spectra were obtained using a double grating ($1200 \text{ lines mm}^{-1}$) Hitachi Perkin-Elmer MPF-4 spectrofluorimeter equipped with two red-sensitive R-446F photomultiplier tubes. Fluorescence measurements were made in n-hexane, toluene, ethyl acetate and 2-propanol. Phosphorescence measurements were made in EPA glass (ether, isopentane and ethanol, 5:2:2 parts by volume) at 77 K.

Fluorescence quantum yields were determined by the relative method using quinine sulphate (in 0.25 M sulphuric acid) as a standard [11]. The fluorescence quantum yield of quinine sulphate was assumed to be 0.55. The quantum yields were obtained for solutions in free equilibrium with air. No significant increase in the fluorescence intensity was observed on saturating the solutions with nitrogen.

Phosphorescence quantum yields were obtained using benzophenone (in ethanol) as a standard [12]. The phosphorescence quantum yield of benzophenone was assumed to be 0.74.

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 $10 \mu\text{s}$.

TABLE 1
Luminescence and LF properties of some aminochloroanthraquinones

Anthraquinone	Fluorescence			Ethyl acetate			2-Propanol			Phosphorescence EPA glass (77 K)		LF 1/1 depth
	n-hexane λ_{EM}^a (nm)	ϕ_F^b	Toluene λ_{EM} (nm)	λ_{EM} (nm)	ϕ_F	λ_{EM} (nm)	λ_{EM} (nm)	ϕ_F	λ_{EM} (nm)	ϕ_P	Polyester	
1-Amino-2-chloro	540	0.021	550	563	0.016	583	8.4×10^{-3}	583	8.4×10^{-3}	None	5	1
1-Amino-3-chloro	528	0.017	540	563	0.014	585	7.7×10^{-3}	585	7.7×10^{-3}	None	5	1
2-Amino-3-chloro	insoluble		512	545	0.018	558	2.2×10^{-3}	558	2.2×10^{-3}	8×10^{-4}	1	1

^aEmission maximum.

^bQuantum yield.

TABLE 2
Flash photolysis of aminochloroanthraquinones

Anthraquinone	Transient absorption	
	Ethyl acetate	2-Propanol
1-Amino-2-chloro	None	Strong
1-Amino-3-chloro	None	Strong
2-Amino-3-chloro	Very weak	Strong

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-aminochloro derivatives are much greater than that of the 2-amino-3-chloro derivative. Second, in a nylon (polyamide) substrate the LF values of all the aminochloro derivatives are low.

From the photophysical data in Table 1, it is seen that, while all three derivatives fluoresce, only the 2-amino-3-chloro derivative is phosphorescent. This observation of phosphorescence from the 2-amino-3-chloro derivative is interesting since no phosphorescence was observed from any of the aminoanthraquinone derivatives studied earlier [3 - 5]. A further interesting feature of Table 1 is that the fluorescence quantum yields of all three derivatives are dependent on solvent polarity and in less polar solvents the fluorescence quantum yield of the 2-amino derivative is higher than those of the 1-amino derivatives.

The flash photolysis results are summarized in Table 2 and it is seen that whereas no transient absorption is observed with the 1-aminochloro derivatives in nitrogen-saturated ethyl acetate the 2-amino-3-chloro derivative exhibits a very weak, but reproducible, transient absorption. In contrast, in nitrogen-saturated 2-propanol transient absorptions are observed with all three derivatives. Typical transient absorption spectra in 2-propanol are shown in Fig. 1. Finally it should be noted from the figure that the transient species produced on flash photolysis of both the 1-aminochloro derivatives are similar, having a wavelength maximum at 520 nm, whereas that of the 2-amino-3-chloro derivative has a wavelength maximum at 480 nm. Both transients have a mean lifetime (τ^1/e) of 20 ms.

The results presented here are also interesting when we compare them with earlier flash photolysis studies on anthraquinone and its derivatives [13 - 16]. These studies invariably gave strong transient absorption in the spectral region 450 - 550 nm (in alkaline solutions (pH > 7.0)) and this absorption was assigned to the radical anion species $Q^{\cdot-}$. Under our conditions (pH = 7.0), however, the intensity of the transient absorption was rather weak. Owing to the strong absorption of the compounds below 450 nm no transient absorption due to the semiquinone radical QH^{\cdot} could be detected.

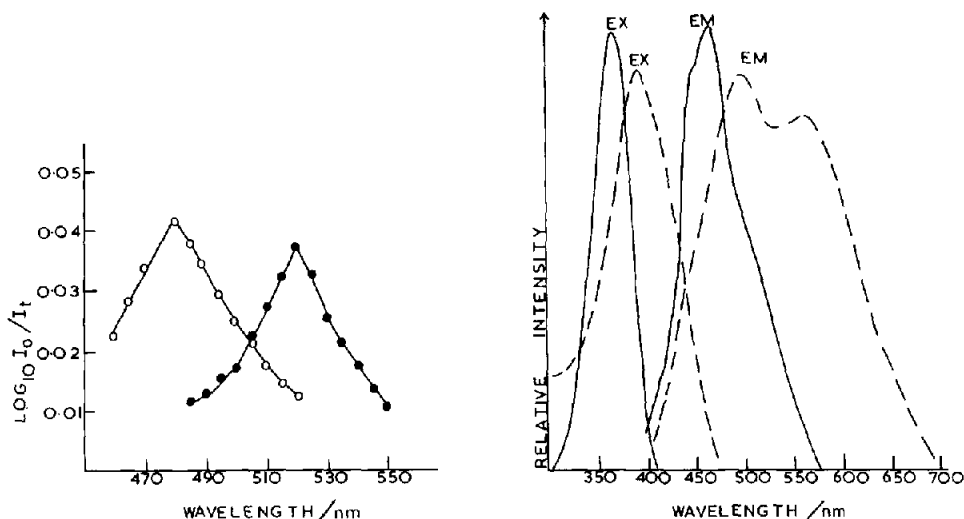
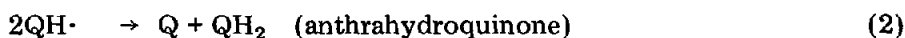


Fig. 1. Transient absorption spectra produced in the flash photolysis of nitrogen-saturated (less than 5 ppm oxygen) 10^{-5} M solutions of 2-amino-3-chloroanthraquinone (○) and 1-amino-2-chloro- and 1-amino-3-chloroanthraquinones (●) in 2-propanol.

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

Finally, after one flash all three dyes in anaerobic isopropanol exhibited strong green and blue fluorescence emissions (Fig. 2). These are very probably due to the presence of the corresponding hydroquinones formed by the established reaction mechanisms [16]



since on admitting air (or oxygen) into the solutions both disappeared due to oxidation of the hydroquinones [13 - 16]:



The above spectroscopic and flash photolysis experiments are very useful in the interpretation of the LF properties of the compounds in both polyester and nylon substrates. First, the higher fluorescence quantum yield coupled with the observation of phosphorescence and a weak transient absorption in less polar solvents clearly accounts for the lower LF value of the 2-amino-3-chloro derivatives in a less polar polymeric environment such as polyester fabric [17] compared with the 1-amino-2-chloro and 1-amino-3-chloro derivatives. In contrast, the observation of transient absorptions for all three dyes in a polar solvent clearly accounts for their poor LF value in a highly polar polymeric environment such as nylon 6,6 fabric [17].

Finally, 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 [15].

Acknowledgment

The authors thank Dr. C. W. Greenhalgh (I.C.I. Organic Division), Manchester, England, for helpful discussions.

References

- 1 Colour Index (3rd edn.), Society of Dyers and Colourists, Bradford, 1970.
- 2 E. R. Trotman, *Dyeing and Chemical Technology of Textile Fibres* (4th edn.), Griffin, London, 1970.
- 3 N. S. Allen, P. Bentley and J. F. McKellar, *J. Photochem.*, 5 (1976) 225.
- 4 N. S. Allen and J. F. McKellar, *J. Photochem.*, 5 (1976) 317.
- 5 N. S. Allen and J. F. McKellar, *J. Photochem.*, 7 (1977) 107.
- 6 C. H. Giles and R. B. McKay, *Text. Res. J.*, 33 (1963) 527.
- 7 Yu. A. Ershov and G. E. Krichevskii, *Russ. Chem. Rev.*, 43 (1974) 210.
- 8 N. S. Allen, P. Bentley and J. F. McKellar, *J. Soc. Dyers Colour*, 91 (1975) 366.
- 9 B. S. 1006: (1971).
- 10 N. S. Allen, J. F. McKellar and D. G. M. Wood, *Plast. Rubber Mater. Appl.*, 1 (1976) 57.
- 11 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 75 (1971) 991.
- 12 S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973.
- 13 N. K. Bridge and G. Porter, *Proc. R. Soc. London, Ser. A*, 244 (1958) 259.
- 14 G. O. Phillips, N. W. Worthington, J. F. McKellar and R. R. Sharpe, *J. Chem. Soc., Ser. A*, (1969) 767.
- 15 A. K. Davies, J. F. McKellar and G. O. Phillips, *Proc. R. Soc. London, Ser. A*, 323 (1971) 69.
- 16 I. V. Khudyakov and V. A. Kuzmin, *Russ. Chem. Rev.*, 44 (1975) 801.
- 17 R. W. Moncrieff, *Man-Made Fibres* (5th edn.), Heywood, London, 1970.