

## STRUCTURAL INFLUENCES ON THE FLUORESCENCE OF AMINOANTHRAQUINONES

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(Received December 17, 1976; in revised form January 24, 1977)

### Summary

The fluorescence spectra and quantum yields of 1-amino, 2-amino, 1,5-diamino, 1,4-diamino and 1,4,5,8-tetraamino substituted anthraquinones in solvents of varying polarity have been measured. The data are related to the influence of structural features on the nature of the charge transfer (CT) content of the first excited singlet state and an interesting correlation with the light fastness of the more complex derivatives is noted.

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### Introduction

Anthraquinone derivatives are widely used as commercial dyes for both natural and synthetic fibres [1, 2]; in recent studies we have found that a knowledge of the luminescence properties of simple anthraquinones makes a valuable contribution to an understanding of the relationship between structure and light fastness [3 - 5]. Unfortunately, fluorescence data on the more complex anthraquinone derivatives are sparse and there are serious discrepancies reported in the literature. For example, Shcheglova *et al.* [6] have reported that 1,8-dihydroxyanthraquinone exhibits different emission spectra when excited at 313 nm and at 365 nm. We observed no such effect in our recent study of highly purified hydroxyanthraquinones [5]. This shows that factors such as the presence of fluorescent impurities may influence the nature of the observed emission.

In this paper we have extended our luminescence studies to cover examples of commercially important di- and tetra-substituted amino derivatives [1] so that the influence of structural variations on light fastness may be more clearly understood.

## Experimental

### *Materials*

The aminoanthraquinones 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 repeatedly recrystallised from ethanol until their melting points were in good agreement with the literature values.

Quinine sulphate was recrystallised three times from distilled water and dried over silica gel. The weight absorptivity of the purified samples was in good agreement with the values obtained by Fletcher [7]. All solvents used were normally of either spectroscopic or analytical reagent quality.

### *Fluorescence measurements*

The excitation and emission spectra were obtained using a double grating (1200 lines  $\text{mm}^{-1}$ ) Hitachi-Perkin-Elmer MPF-4 spectrofluorimeter equipped with two red-sensitive R-446F photomultipliers. The measurements were made in benzene, ethyl acetate and isopropanol. Solvents of lower polarity than benzene were found to be unsatisfactory because of solubility problems. Quantum yields were determined by the relative method using quinine sulphate ( $10^{-2}$  mol  $\text{m}^{-3}$  in sulphuric acid 500 mol  $\text{m}^{-3}$ ) as a standard [8]. The fluorescence quantum yield of quinine sulphate was assumed to be 0.55 [8]. A refractive index correction was applied by multiplying the integrated fluorescence intensity of each sample by the square of the refractive index of the solvent. The quantum yields were obtained on solutions in free equilibrium in air. No significant increase in the fluorescence intensity was observed on saturating the solutions with nitrogen.

### *Phosphorescence measurements*

No phosphorescence emissions at 77 K were observed from any of the aminoanthraquinones examined.

## Results and discussion

The fluorescence data for the five aminoanthraquinones studied are summarised in Table 1. If we compare the results obtained from the 1- and 2-derivatives it may be seen that with the two less polar solvents a greater variation in the wavelength maxima ( $\lambda_{\text{max}}$ ) is found with the 2-derivative. This is in agreement with earlier work [9, 10] and suggests that with the 2-derivative there is a greater charge transfer (CT) content in the  $\pi\pi^*$  first excited singlet state. Furthermore, the higher fluorescence quantum yield of the 2-amino derivative in the less polar solvents is probably due to its inability to form an intramolecular hydrogen bond, thereby increasing the probability of radiative deactivation [4, 5].

TABLE 1

Fluorescence emission ( $\lambda_{\max}$ ) and quantum yield ( $\phi_F$ ) data

Anthraquinone	Benzene		Ethyl acetate		Isopropanol	
	$\lambda_{\max}$ (nm)	$\phi_F$	$\lambda_{\max}$ (nm)	$\phi_F$	$\lambda_{\max}$ (nm)	$\phi_F$
1-amino	548	0.022	567	0.008	590	0.003
2-amino	529	0.08	563	0.024	N.O.	$< 10^{-5}$
1,5-diamino	550	0.013	555	0.007	575	0.0047
1,4-diamino	612, 635	$\sim 10^{-5}$	614, 640	$\sim 10^{-5}$	N.O.	$< 10^{-5}$
1,4,5,8-tetraamino	672	0.004	672	0.0024	684	0.002

N.O. indicates not observed.

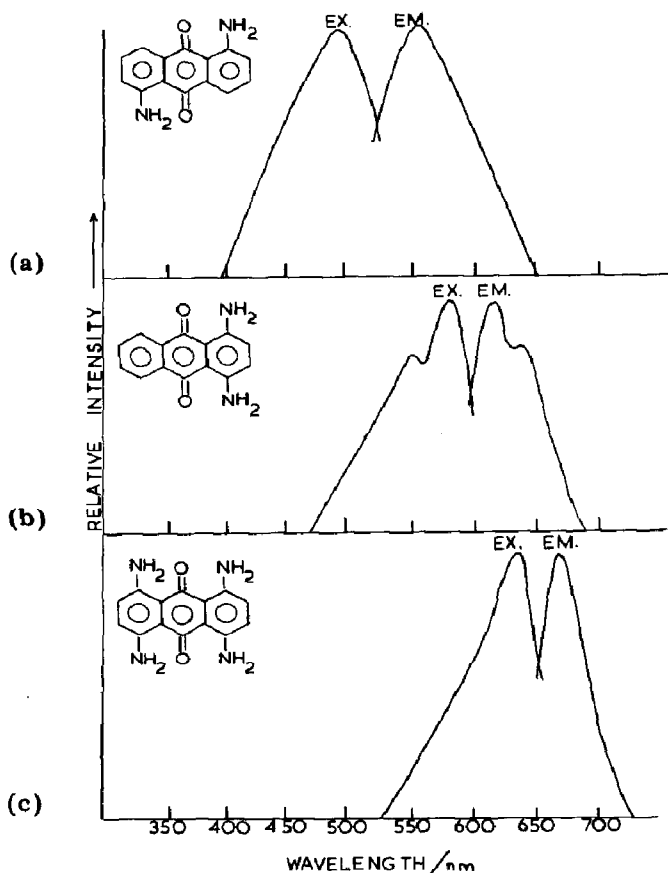
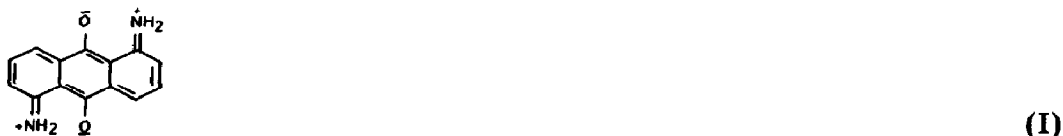


Fig. 1. Fluorescence excitation and emission spectra of (a) 1,5-, (b) 1,4- and (c) 1,4,5,8-substituted aminoanthraquinones in ethyl acetate. For clarity, only the longest wavelength absorption band is shown.

The two di-substituted aminoanthraquinones also show interesting differences in their fluorescence properties. This is shown in Table 1 and in Fig. 1 where the excitation and emission spectra are contrasted. Whereas only

one broad emission band is seen with the 1,5-derivative, a structured emission spectrum at longer wavelengths is seen with the 1,4-derivative. A similar effect has been noted in their absorption spectra [11].

A possible explanation for this interesting effect is that while the CT content of the  $\pi\pi^*$  excited singlet of the 1,5-derivative (I) may be of the type proposed earlier for the 1-substituted derivatives [9, 10]

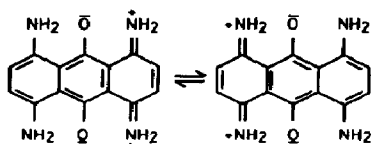


the corresponding CT shift for the 1,4-derivative results in a structure of the type

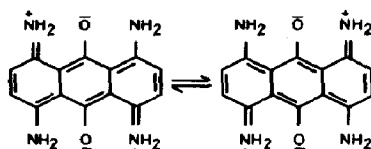


Since there is little change in the  $\lambda_{\max}$  values for the 1,4-derivative with solvent polarity, this would suggest that its first excited singlet state must possess greater molecular rigidity than that of the 1,5-derivative. On the basis of absorption data other workers [11, 12] have suggested similar structures to (I) and (II).

Finally, it may be seen from Table 1 and Fig. 1 that with the 1,4,5,8-derivative the emission properties appear to contain the features of both the 1,5- and 1,4-derivatives. The insensitivity of the 1,4,5,8-derivative to solvent polarity resembles that of the 1,4-derivative (Table 1). This would indicate that the CT content of the  $\pi\pi^*$  first excited singlet state is influenced by a contribution from the canonical structures



However, the 1,4,5,8-derivative also shows lack of structure in the excitation spectrum and a fluorescence quantum yield which is closer to that of the 1,5-derivative. This indicates a further contribution to the CT content from the structures



It would appear, therefore, that there is an element of both types of charge transfer in the  $\pi\pi^*$  first excited singlet state of the tetra-substituted derivative. Interestingly, the light fastness (LF) of the 1,4,5,8-derivative on poly-

ester fabric on the I.S.O. scale is 4 - 5 [1] which lies between that of the 1,4-derivative (LF = 5) and that of the 1,5-derivative (LF = 3) [3].

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