

FLUORESCENCE AND LIGHT FASTNESS OF AMINOANTHRAQUINONES

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Summary

The fluorescence emission spectra and quantum yields of thirteen 1-amino-2-amino- and 1,4-diamino-anthraquinones in a variety of solvents have been determined. The quantum yield values for the 1-amino derivatives are decreased on *N*-alkylation and also by the *N*-substitution of acyl or aryl groups. Both emission wavelength maxima and quantum yields of the 2-substituted derivatives are markedly sensitive to solvent polarity. These observations are discussed in relation to the light fastness of the aminoanthraquinones on polyester fabric.

Introduction

The aminoanthraquinones are widely used as commercial dyes for both natural and synthetic fibres [1]. Recently we reported on the light fastness of a range of these compounds as disperse dyes on polyester fibre and discussed their light fastness in terms of their photochemical and spectroscopic properties [2].

In order to further our understanding of the relationship between dye structure and light fastness, however, it is necessary to have a better understanding of the rates of the photophysical processes following light absorption and therefore we must have an accurate knowledge of the fluorescence quantum yields of the dyes. Unfortunately, literature data for the aminoanthraquinones are sparse and there are also several serious discrepancies in the values reported (Table 1). Further, the quantum yield data are restricted to the 1- and 2- aminoanthraquinones and their simple alkyl derivatives. Here we have carried out a study of a much wider range of aminoanthraquinones including the commercially important [3] 1-acetylamino, 1-benzoylamino and 1,4-diamino derivatives whose fluorescence quantum yields have not previously been reported.

TABLE 1

Literature data on the fluorescence quantum yields of aminoanthraquinone derivatives.

Anthraquinone	Solvent	Φ_f	Literature source
1-amino	cyclohexane	0.01	1
	1,4-methylcyclohexane	0.24	2
	2-propanol	0.11	3
1-methylamino	cyclohexane	$\sim 10^{-4}$	1
1-dimethylamino		$\sim 10^{-5}$	1
2-amino		0.2	1
	benzene	0.06	1
		0.24	4
	2-propanol	0.007	3
		0.16	4
2-methylamino	benzene	0.05	1
	2-propanol	0.01	3
2-dimethylamino	cyclohexane	0.2	1
	benzene	0.06	1
2-piperidino	cyclohexane	0.19	5

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Experimental

Fluorescence spectra were obtained on a Perkin-Elmer MPF-4 double grating spectrofluorimeter (1200 lines/mm) equipped with two R446F photomultipliers. Fluorescence quantum yields were determined by the relative method using quinine sulphate (10^{-2} mol/m³ in sulphuric acid 500 mol/m³) as standard. The fluorescence quantum yield of quinine sulphate was assumed to be 0.55 [4, 5]. 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 [4].

The dyes used were the highly purified samples used in our earlier work [2]. Quinine sulphate was obtained from Hopkin & Williams, and was recrystallized three times from water and dried over silica gel. The weight absorptivity of the purified samples was in good agreement with the values obtained by Fletcher [6]. Solvents were normally of either spectroscopic or analytical quality. Propan-2-ol was dried over anhydrous magnesium sulphate and fractionally distilled under nitrogen from sodium borohydride. Hexane was treated with three successive portions of silica gel and then fractionated under nitrogen.

TABLE 2

Fluorescence maxima, λ_f , and quantum yields, Φ_f , for aminoanthraquinones.

Anthraquinone	Solvents					
	n-Hexane		Furan		2-Propanol	
	λ_f (nm)	Φ_f	λ_f (nm)	Φ_f	λ_f (nm)	Φ_f
1-amino	530	0.07	558	0.03	590	0.003
1-methylamino	560	0.003	588	0.002	612	10^{-4}
1-piperidino	N.O.	$<10^{-5}$	N.O.	$<10^{-5}$	N.O.	$<10^{-5}$
1-acetylamino	500	$\sim 10^{-5}$	505	0.02	518	0.004
1-benzoylamino	505	$\sim 10^{-5}$	510	0.005	528	~ 10
1-anilino	N.O.	$<10^{-5}$	N.O.	$<10^{-5}$	N.O.	$<10^{-5}$
1-N-methylanilino	N.O.	$<10^{-5}$	N.O.	$<10^{-5}$	N.O.	$<10^{-5}$
2-amino	a	—	532	0.05	N.O.	$<10^{-5}$
2-dimethylamino	495,535 (s)	0.2	590	0.04	610	$\sim 10^{-5}$
2-piperidino	510,545 (s)	0.27	615	0.04	630	$\sim 10^{-5}$
1,4-diamino ^b	610,630 (s)	$\sim 10^{-5}$	612,645	$\sim 10^{-5}$	N.O.	$<10^{-5}$
1,4-bismethylamino ^c	665,670 (s)	$\sim 10^{-5}$	670,710	$\sim 10^{-5}$	N.O.	$<10^{-5}$
1,5-dipiperidino	N.O.	$<10^{-5}$	N.O.	$<10^{-5}$	N.O.	$<10^{-5}$

N.O. = not observed; a = insoluble; b = in chloroform $\lambda_f = 614,648$ $\Phi_f = \sim 10^{-5}$; c = in chloroform $\lambda_f = 675,720$ $\Phi_f = 10^{-5}$; (s) = shoulder.

Fluorescence quantum yields were obtained on solutions in free equilibrium with air. No significant increase in fluorescence quantum yields was observed, however, on saturating the solutions with nitrogen.

Because of the better instrumentation employed and the higher purity of the dyes used we consider the data reported here to be more accurate than those obtained earlier in these laboratories (Table 1; data of Ford).

Results and Discussion

The fluorescence data for the range of aminoanthraquinones studied are summarized in Table 2. The fluorescence maxima and quantum yield were determined in three solvents of differing polarity so that the effect of this parameter on the potential energy levels of the first excited singlet states could be assessed (see later). Additional data for the 1,4-diamino and 1,4-bismethylamino derivatives in chloroform are included for the same purpose. The 2-amino derivative was found to be insoluble in both n-hexane and cyclohexane so we believe the value reported by Ford (Table 1) was due to the presence of an impurity. Our value for the quantum yield of 1-aminoanthraquinone in n-hexane lies between the values obtained by earlier workers and, in agreement with Ford (Table 1), the quantum yield decreases with increasing alkylation of the amino group.

It is interesting that the presence of electron withdrawing substituents

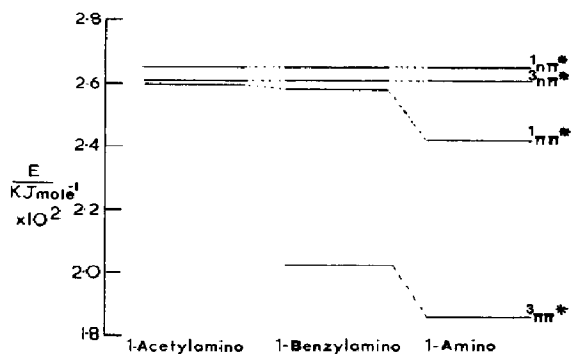


Fig. 1. Estimated energy levels of the excited states of 1-acetylamino, 1-benzoylamino and 1-aminoanthraquinones in a non-polar environment.

in the 1-amino groups also results in a decrease in the fluorescence quantum yield. This is found both with the anilino derivatives, which will be considered later, and with the acetyl and benzoyl derivatives. The lack of fluorescence from the latter two compounds is probably related to the effect of molecular structure on the energies of the first excited $^1\pi\pi^*$ states. These are compared with that of 1-aminoanthraquinone in Fig. 1. The values of the potential energy levels were estimated by: (1) assuming that the energy of the first $^1n\pi^*$ and $^3n\pi^*$ levels are similar to those in anthraquinone [7]. This assumption is justified in view of the relative insensitivity of $n\pi^*$ energy levels to the extent of the π -system [8]; (2) assuming that the zeroth vibrational level of the $^1\pi\pi^*$ state corresponds to an average of the long wavelength absorption and the fluorescence maxima; (3) taking the energies of the first excited $^3\pi\pi^*$ states from pulse radiolysis and flash photolysis data [9][†].

Figure 1 shows that in the non-fluorescent 1-acetylamino and 1-benzoylamino derivatives the $^1n\pi^*$ and $^1\pi\pi^*$ levels are very close. Vibronic coupling between almost degenerate $^1n\pi^*$ and $^1\pi\pi^*$ levels of heteroaromatic molecules is predicted to lead to pseudo Jahn-Teller distortion of the lower state leading to an enhanced Franck-Condon factor and consequently rapid deactivation (*via* either internal conversion or intersystem crossing) of the lowest excited singlet state [10]. This effect, which has been observed in studies on both aromatic carbonyl compounds [10] and nitrogen heterocycles [11], clearly explains the lack of fluorescence from the 1-acetylamino and 1-benzoylamino derivatives and, assuming that the enhanced deactivation involves rapid internal conversion also explains their high light stability [2] on polyester fabrics. In the case of the 1-amino derivative the energy difference between the

[†]We were unable to observe phosphorescence in EPA (diethyl ether/2-methylbutane/ethanol 5: 2: 2 by vol.) at 77 °K from any of the derivatives examined even though the detection system of the MPF-4 instrument is sensitive to light of wavelengths up to 1000 nm.

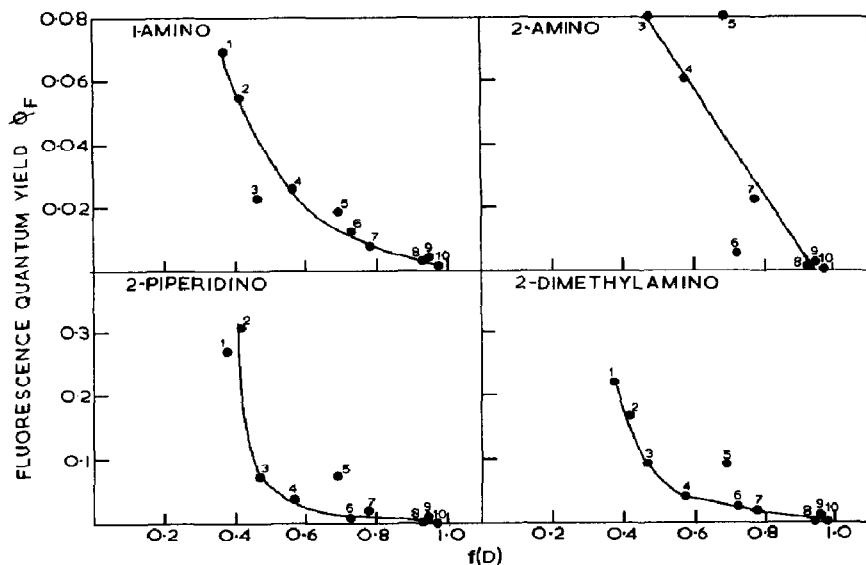


Fig. 2. Fluorescence quantum yields of aminoanthraquinones against solvent polarity function $f(D)$. $f(D) = 2(D - 1)/2D + 1$ [14]. Solvents: 1, hexane; 2, cyclohexane; 3, benzene; 4, furan; 5, diethylether; 6, chloroform; 7, ethyl acetate; 8, 2-propanol; 9, acetone; 10, dimethylformamide.

$^1n\pi^*$ and $^1\pi\pi^*$ levels is much greater (Fig. 1) so that the rate of deactivation of the $^1\pi\pi^*$ state is much slower, consequently relatively efficient fluorescence is observed and, interestingly, the light stability of 1-aminoanthraquinone is somewhat lower than that of the 1-acetylamino and 1-benzoylamino derivatives [2].

The lack of fluorescence emission from the 1-anilino and 1-*N*-methylanilino derivatives is more difficult to explain. However, our observations here bear a remarkable similarity to those already reported in our current work on the photochemistry of the benzanthrone disperse dyes [12]. There it was found that while 6-aminobenzanthrone has relatively efficient fluorescence the fluorescence from the 6-anilino derivative is extremely weak. Further, there is no observable phosphorescence emission nor is there any evidence of triplet formation on nanosecond laser flash photolysis of 6-anilinobenzanthrone. These observations have been attributed to a process of rapid deactivation within the singlet manifold and it appears likely that such a process may also occur with the corresponding aminoanthraquinones. On a more practical note, where this rapid deactivation process does occur due to the presence of an anilino group then the appropriate dye has a very high light fastness [2, 12].

As expected from the greater polarity of their first excited singlet states, [13] the wavelength of the fluorescence maximum of the 2-aminoanthraquinones is considerably more sensitive to solvent polarity than that of the 1-amino-derivatives (Table 2). Similarly, the fluorescence quantum yield of the 2-amino compounds is more solvent dependent than

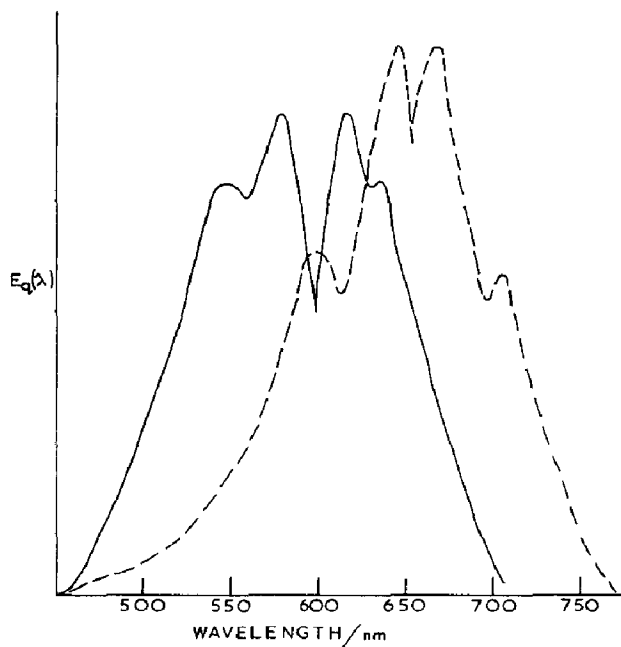
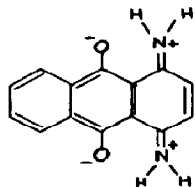


Fig. 3. Fluorescence and fluorescence excitation spectra of 1,4-diaminoanthraquinone (—) and 1,4-bis(methylamino)anthraquinone (---) in chloroform.

that of their 1-substituted analogues (Table 2 and Fig. 2). Finally, it is noteworthy that the fluorescence spectra of the 1,4-diaminoanthraquinones, like the absorption spectra [15, 16] possess marked vibrational structure (Fig. 3). The structured absorption spectra have been attributed [16] to the presence of a resonance form such as:



in the ground state. Similarly the structured fluorescence spectra, together with the small Stokes loss (Fig. 3), suggests that the first excited singlet state, like the ground state possess considerable molecular rigidity [17].

Acknowledgement

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