

POSSIBLE EMISSION FROM AN UPPER TRIPLET STATE OF AN ANTHRAQUINONE DYE

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Summary

The luminescence properties of 1-amino-2-carboxy-, 1-amino-3-carboxy- and 2-amino-3-carboxy anthraquinone are examined. The 2-amino-3-carboxy derivative exhibits anomalous phosphorescence emission which may originate from an upper $n\pi^*$ triplet state.

1. Introduction

In our work over the years [1 - 5] we have examined the luminescence properties of many anthraquinone dyes. During some recent work on aminocarboxyanthraquinones we found one particular derivative to be exceptional in its emission properties. Here we report on the emission behaviour of this dye and some analogues.

2. Experimental

2.1. Materials

The aminocarboxyanthraquinones were supplied by I.C.I. Ltd.

As will be seen later 2-amino-3-carboxyanthraquinone gives interesting phosphorescence results and for this reason particular attention was given to its purification. All the compounds were purified on a silica column using dimethylformamide as the eluant. The compounds were then watered out of solution, filtered and recrystallized from ethanol. The melting points of the 1-amino-2-carboxy- and 1-amino-3-carboxy-anthraquinones were 295 - 296 °C and 335 °C respectively in agreement with the literature values.

Because of the results given later the 2-amino-3-carboxy derivative was further purified by conversion to the sodium salt followed by acidification with sulphuric acid to give the original compound. The compound was then bound to an alumina column from solution in dimethylformamide. Fresh solvent was then drawn through the column to remove any unbound impu-

TABLE 1
Luminescence properties of some aminocarboxyanthraquinones

Anthraquinone	Fluorescence		Ethyl acetate		2-propanol		Phosphorescence EPA glass	
	Ether		λ_{EM} (nm)		ϕ_F		λ_{EM} (nm)	
	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	
1-amino-3-carboxy	558	7.8×10^{-3}	565	10^{-2}	585	3.5×10^{-3}	none	
2-amino-3-carboxy	520	6.0×10^{-2}	535	5×10^{-2}	573	1.4×10^{-3}	455, 492, 534.5, 585, 610	10^{-2} 5×10^{-4}

^aEmission wavelength maximum.

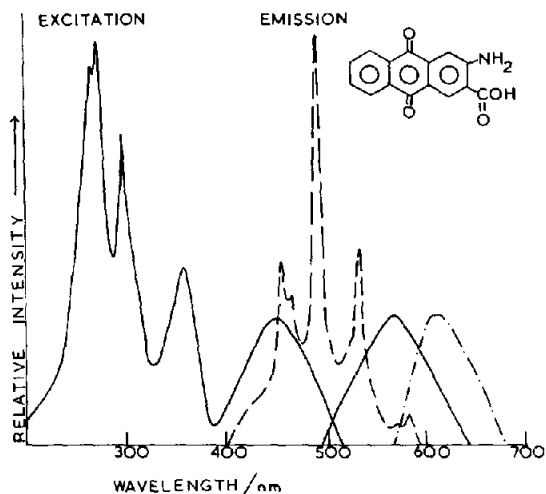


Fig. 1. Fluorescence excitation and emission spectra (—) and phosphorescence emission spectra (---) (excitation wavelength = 275 nm) and (-·-) (excitation wavelength = 450 nm) for 2-amino-3-carboxyanthraquinone in EPA solvent (300 K) and glass (77 K) respectively.

rities. The compound was then extracted from the alumina by boiling in dimethylformamide. Finally, the compound was watered out of solution, filtered and recrystallized from ethanol. The whole process was repeated. The melting point of the 2-amino-3-carboxy derivative was 362 - 363 °C in agreement with the literature value.

Also, because of the results given later very careful mass spectral analysis was carried out by I.C.I. Ltd. Particular attention was paid to the possibility of the presence of anthraquinone but none was found. We are indebted to Mr. A. E. Williams for his work on this analysis.

All solvents used were of Analar or Spectroscopic quality.

2.2. Luminescence properties

Fluorescence and phosphorescence spectra were obtained using a double grating Hitachi Perkin-Elmer MPF-4 spectrofluorimeter as described earlier [2 - 4]. Fluorescence quantum yields ϕ_F were obtained by the relative method using quinine sulphate in 0.05 M H_2SO_4 as a standard [5]. The quantum yield of quinine sulphate was assumed to be 0.55 [7, 8]. Phosphorescence quantum yields ϕ_P were obtained using benzophenone in EPA glass (ether-isopentane-ethanol, 5:2:2 parts by volume) as a standard. The quantum yield of benzophenone was assumed to be 0.74 [7].

3. Results and discussion

The fluorescence and phosphorescence emission wavelength maxima and quantum yields for the aminocarboxy substituted anthraquinones are

shown in Table 1. It is seen that all three derivatives exhibit fluorescence in ether, ethyl acetate and 2-propanol with similar quantum yields. The dyes were insoluble in solvents of lower polarity than ether. 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-aminocarboxy derivatives [2].

However, the outstanding feature of the results shown in Table 1 is the observation of two quite different phosphorescence emissions from the 2-amino-3-carboxy derivative. This compound exhibits normal weak phosphorescence emission at longer wavelengths than its fluorescence and an anomalous phosphorescence emission at shorter wavelengths (Fig. 1). The latter emission is produced only on excitation with light of wavelengths shorter than 350 nm. At present the only explanation we can propose is that this emission occurs from an upper $n\pi^*$ triplet state. The splitting of the vibrational structure (1640 cm^{-1}) is in accord with this assignment [8, 9].

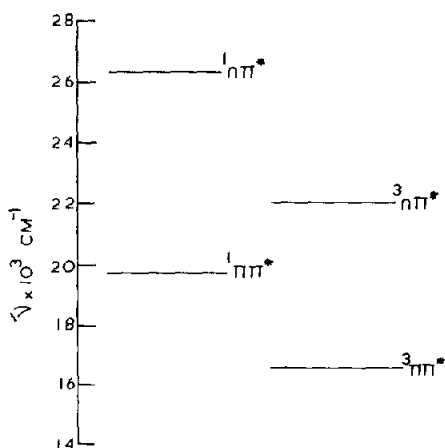


Fig. 2. Energy levels of 2-amino-3-carboxyanthraquinone in EPA.

The relative positions of the energy levels of 2-amino-3-carboxyanthraquinone in EPA solvent are shown in Fig. 2. In this case it would appear that intersystem crossing from the upper singlet $n\pi^*$ state to the upper triplet $n\pi^*$ state must compete with internal conversion to the lower singlet $\pi\pi^*$ state. Owing to the large energy gap, emission from the upper triplet $n\pi^*$ state must then compete with internal conversion to the lowest triplet $\pi\pi^*$ state. The observation of normal weak phosphorescence also indicates that intersystem crossing from the lowest singlet $\pi\pi^*$ state to the lowest triplet $\pi\pi^*$ state must also occur.

4. Conclusion

In comparison with all the anthraquinone dyes studied in this and previous work [1 - 5] the 2-amino-3-carboxyderivative is anomalous in that it appears to exhibit phosphorescence emission from an upper triplet $n\pi^*$ state.

Acknowledgments

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