The Photochemistry of Benz[*de*]anthracen-7-ones. Part I. Electronic Absorption and Emission Spectroscopy

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The electronic absorption and emission spectra of benz[*de*]anthracen-7-one and some of its 3-, 4-, 6-, and 8-substituted derivatives have been investigated. The lowest excited singlet states of the benzanthracenone derivatives are all π–π^* in nature. 8-Aminobenz[*de*]anthracen-7-one has a broad, structureless, longest wavelength absorption band which disappears on protonation of the ground state. In contrast, the 6-amino-derivative possesses marked vibrational structure in its absorption spectrum and is much more resistant to protonation of the ground state

THE photochemistry of benz[*de*]anthracen-7-one (benzanthrone) (I) and its derivatives has received little attention.[1] A recent preliminary communication,[2] however, described a study of benzanthrone and its 6-substituted derivatives and several interesting features were noted. Surprisingly, although substitution of hydroxy- or amino-groups led to some increase in photostability, on substitution of an anilino-group the increase in photostability was much greater.

The amount of information in the literature on the nature of the excited states of benzanthrone and its derivatives is limited.[3] Therefore, we have examined in

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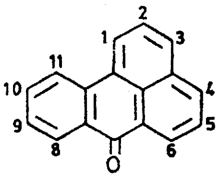
[1] K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5417; K. M. Joshi and A. B. Karnik, *Indian J. Chem.*, 1968, **6**, 540.

[2] A. H. Berrie, J. F. McKellar, and E. Young, *Chem. and Ind.*, 1973, 791.

[3] N. S. Proskuryakova and R. N. Nurmuknametov, *Optics and Spectroscopy*, 1969, **27**, 119.

detail the absorption and emission spectra of benzanthrone and its 3-, 4-, 6-, and 8-substituted derivatives.



(I)

EXPERIMENTAL

Synthesis of Benzanthrones.—Samples of benzanthrone, 3-methoxybenzanthrone, 4-hydroxybenzanthrone, 4-anilinobenzanthrone, 8-aminobenzanthrone, and 8-hydroxybenzanthrone in highly purified form were the kind gift of Imperial Chemical Industries Ltd. and the m.p.s corresponded to the literature values where available.

6-Hydroxybenzanthrone was prepared from 2-naphthyl benzoate by a method similar to that of ref. 4. Purification was by four successive crystallizations from hexane to give yellow needles, m.p. 178—179° (lit., 176°,[4] 177—178° [5]).

6-Aminobenzanthrone was prepared from the 6-hydroxy-derivative by the method of Bradley and Jadhav.[5] Three crystallizations from hexane gave yellow needles, m.p. 186—187° (lit.,[5] 186—187°).

6-Anilinobenzanthrone was prepared by a method[6] involving the reaction of 6-hydroxybenzanthrone and aniline at 280°. Chromatographic purification followed by crystallization from hexane gave golden yellow needles, m.p. 158° (lit.,[7] 156—157°).

Spectroscopic Measurements.—The absorption and fluorescence spectra were measured on a Unicam SP 800 spectrophotometer and a Baird Atomic model SF 100E spectrofluorimeter respectively. Phosphorescence measurements were made at 77 K by means of the phosphorescence attachment in the spectrofluorimeter. The phosphorescence lifetime of 6-aminobenzanthrone was determined from a photograph of the decay curve displayed on an oscilloscope.

Spectrosol grade hexane was used without further purification. Other solvents, which were normally of spectroscopic or AnalaR quality were dried and fractionated before use. Water was distilled from alkaline permanganate.

pK_a *Determination at Low* pH.—Anhydrous acetic acid was prepared by azeotropic distillation of the commercial (*ca*. 99%) material with ethyl acetate through a fractionating column. AnalaR sulphuric acid was used without further treatment but the precise quantity of H_2SO_4 in the sulphuric acid, determined by titration of diluted portions against standard sodium hydroxide solution, was taken into account in the calculation of the H_2SO_4 content of each solution measured. The pK_a values were calculated using equation (1)[8] where H_0 is the acidity function and ε,

$$\mathrm{p}K_a = H_0 + \log[(\varepsilon_B - \varepsilon)/(\varepsilon - \varepsilon_{BH^+})] \qquad (1)$$

ε_B, and ε_{BH^+} are the extinction coefficients of the solution measured, unprotonated form, and protonated form respectively. The values of extinction coefficient were obtained at 385 nm, the wavelength of the maximum of the second absorption band of 6-aminobenzanthrone. The H_0 values were obtained from the data of Roček.[9]

RESULTS AND DISCUSSION

The absorption spectra observed for benzanthrone and 3-methoxybenzanthrone were in agreement with the literature.[3,10] The longest wavelength absorption band of benzanthrone derivatives must be due to a π–π* transition since the extinction coefficients of the absorption maxima are high (1—2·7 × 10^4) and these bands, in general, shift to longer wavelengths with increasing solvent polarity (Figure 1 and Table 1). Similarly, the emission maxima of the fluorescence spectra show the same type of shift (Tables 1 and 2).

TABLE 1

Effect of solvent on the wavenumber of the longest wavelength absorption maximum $\sigma^a_{max.}$ and the fluorescence maximum $\sigma^f_{max.}$ of benzanthrone derivatives

	Benzanthrone		3-Methoxy-		4-Anilino-		6-Amino-		6-Anilino-		8-Amino-	
Solvent	σ^a_{max}/µm⁻¹	σ^f_{max}/µm⁻¹	σ^a_{max}/µm⁻¹	σ^f_{max}/µm⁻¹	σ^a_{max}/µm⁻¹	σ^f_{max}/µm⁻¹	σ^a_{max}/µm⁻¹	σ^f_{max}/µm⁻¹	σ^a_{max}/µm⁻¹	σ^f_{max}/µm⁻¹	σ^a_{max}/µm⁻¹	σ^f_{max}/µm⁻¹
Hexane	2·656	N.o.	2·453	2·110	2·353	2·026	2·265	2·110	2·176	1·961	2·210	1·862
Cyclohexane	2·639	N.o.	2·442	2·096	2·346	1·992	2·260	2·105	2·174	1·953	2·208	1·845
Carbon tetrachloride	2·623	N.o.	2·407	2·041	2·328	2·032	2·252	2·101	2·158	1·946	2·179	1·812
Toluene	2·600	N.o.	2·395	2·020	2·288	1·976	2·245	2·070	2·160	1·942	2·162	1·779
Triethylamine	2·642	N.o.	2·421	2·087	2·222	1·946	2·240	2·088	2·174	1·942	2·174	1·786
Furan	2·611	N.o.	2·392	1·992	2·282	1·965	2·252	2·096	2·169	1·938	2·169	1·808
Diethyl ether	2·584	N.o.	2·427	2·049	2·220	1·957	2·250	2·083	2·179	1·953	2·155	1·770
Ethyl acetate	2·571	N.o.	2·392	2·000	2·208	1·890	2·250	2·083	2·176	1·957	2·153	1·748
Acetone	2·574	N.o.	2·373	1·961	2·191	1·887	2·250	2·079	2·174	1·946	2·142	1·739
Methanol	2·538	2·083	2·299	1·835	2·130	1·887	2·232	2·062	2·167	1·916	2·126	1·695
NN-Dimethylformamide	2·578	N.o.	2·326	1·905	2·146	1·876	2·230	2·070	2·162	1·919	2·128	1·712

N.o. = Not observed.

The marked effect of solvent on the location of the longest wavelength absorption band of benzanthrone (Table 1) suggests that the lowest excited singlet state of benzanthrone must have some charge-transfer character. Support for this view comes from the fact that the pK_a value of the equilibrium between benzanthrone and its conjugate acid is greater by a value of *ca*. 8 in the first excited singlet state compared with the ground state,[10] an observation which indicates that on photon absorption the electron density on the carbonyl oxygen atom is considerably increased. As would be expected, the effect of solvent on the position of the

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[4] G.P. 453,280.

[5] W. Bradley and G. V. Jadhav, *J. Chem. Soc.*, 1948, 1622.

[6] E. Young, personal communication.

[7] W. Bradley and G. V. Jadhav, *J. Chem. Soc.*, 1948, 1746.

[8] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

[9] J. Roček, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1.

[10] R. Zahradnik, M. Tichy, and N. H. Reid, *Tetrahedron*, 1968, **24**, 3001.

longest wavelength absorption band of the 3-methoxy- and 4-anilino-derivatives is greater than the effect on benzanthrone itself showing that the charge-transfer character is enhanced by the introduction of electron-donating substituents.

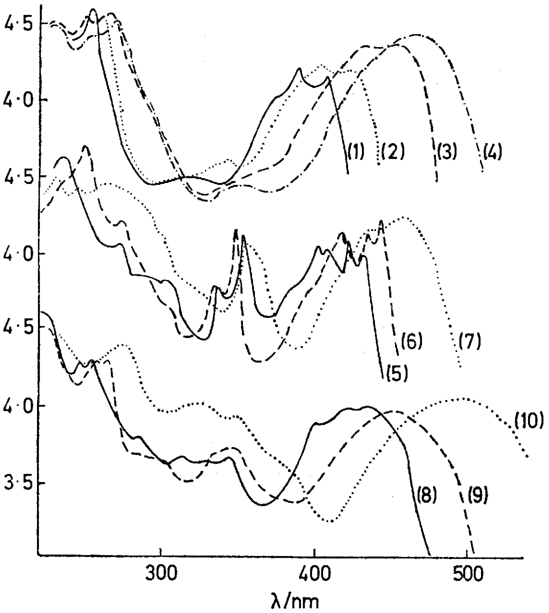


FIGURE 1 Absorption spectra of benzanthrone derivatives: (1) 4-hydroxy- in diethyl ether; (2) 4-hydroxy- in methanol; (3) 4-anilino- in diethyl ether; (4) 4-anilino- in methanol. All other spectra in hexane: (5) 6-hydroxy-; (6) 6-amino-, (7) 6-anilino-; (8) 8-hydroxy-; (9) 8-amino-; (10) 8-anilino-

TABLE 2

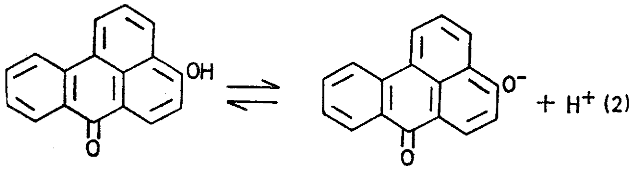
Fluorescence (λ^f) and phosphorescence (λ^p) emission data for benzanthrones

Compound	λ^f_{max}/nm	λ^p_{max}/nm
Benzanthrone	N.o.,[a] 480 [b]	N.o. [c]
3-Methoxy-	476,[a] 545 [b]	N.o. [c]
4-Hydroxy- *	453,[b] 496 [a]	608 [c]
4-Anilino-	490,[a] 430 [b]	N.o. [c]
6-Hydroxy-	455,[a] 474 [b]	586 [c]
6-Amino-	474,[a] 485 [b]	557 [c]
6-Anilino-	512,[a] 552 [b]	N.o. [c]
8-Hydroxy-	472,[a] 485 [b]	N.o.[c]
8-Amino	537,[a] 590 [b]	N.o.[c]
8-Anilino-	547,[a] 547 [b]	N.o.[c]

N.o. = Not observed. [a] In hexane. [b] In methanol. [c] In ether–isopentane–ethanol 5 : 5 : 2 (v/v).

* Fluorescence of this derivative is sensitive to pH. Values are for un-ionized and ionized forms respectively and observed on addition of small amounts of acid or base.

Recently, Bhujle *et al.*[11] reported that the absorption and fluorescence emission spectrum of 4-hydroxybenzanthrone changed with concentration in alcoholic solvents. The change was attributed to molecular aggregation. We observed no such change. Beer's law plots of ethanol solutions at 404 nm for the concentration range 10^{-6}—10^{-4}M, gave good straight lines. We observed, however, that both the absorption and emission spectra were sensitive to pH and this can be attributed to equilibrium (2). By measuring the change in absorbance at 476 nm in buffered aqueous solutions of small and constant ionic strength,[12] the pK_a of



equilibrium (2) was found to be 5·6 ± 0·1. From the absorption and fluorescence emission spectra of the 4-hydroxy-derivative and its conjugate base in ethanol solution together with the ground state pK_a above, application of the Förster cycle[13] gives a value of 0·4 for the pK_a of equilibrium (2) for the lowest excited singlet state. Thus as in the case of the 3-methoxy- and 4-anilino-derivatives there is a large shift of electron density on photon absorption.

In the case of the intramolecularly hydrogen bonded 6- and 8-substituted benzanthrones, the effect of solvent polarity on the absorption and emission spectra was relatively small (Tables 1 and 2). Indeed, the position of the longest wavelength maxima in the absorption spectra of the 6- and 8-hydroxy-derivatives were the same in both hexane and methanol. A similar effect has been reported for intramolecularly hydrogen-bonded benzophenone and nitrobenzene derivatives.[14] A further feature is the highly resolved vibrational structure of the longest wavelength absorption bands of the 6-hydroxy- and 6-amino-benzanthrones (Figure 1). In contrast, the longest wavelength absorption bands of the 6-anilino-derivative and of the 8-substituted derivatives are broad and almost structureless.

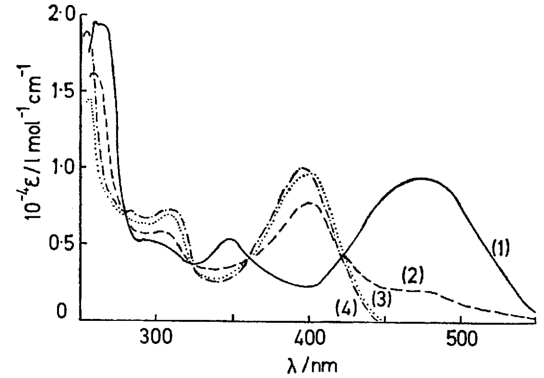


FIGURE 2 Absorption spectra in 3 : 2 methanol–water of 8-aminobenzanthrone at pH 7·0 (1); 0·3 (2); and <0 (3) compared with benzanthrone (4)

With the 6- and 8-aminobenzanthrones marked differences in their spectra were observed on protonation of their respective ground states. On addition of a small amount of sulphuric acid to a solution of 8-aminobenzanthrone in aqueous methanol the longest wavelength absorption band disappears and the spectrum formed on complete protonation resembles that of benzanthrone (Figure 2). A similar effect is observed with many

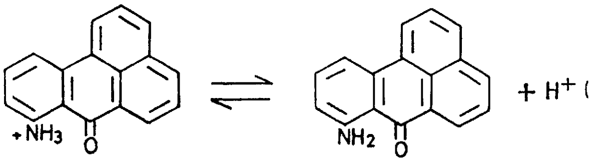
[11] V. V. Bhujle, R. R. Karnik, and M. R. Padhye, *Indian J. Pure Appl. Phys.*, 1971, **9**, 380.

[12] D. D. Perrin, *Austral. J. Chem.*, 1963, **16**, 572.

[13] E. Vander Donckt, *Progr. Reaction Kinetics*, 1970, **5**, 273.

[14] M. B. Ledger and P. Suppan, *Spectrochim. Acta*, 1967, **23A**, 641.

1-substituted anthraquinones.[15] By measuring the absorbance of 8-aminobenzanthrone at 472 nm in 3 : 2 v/v *methanol*-water containing various amounts of sulphuric acid the pK_a of equilibrium (3) was found to be 0·6 ± 0·1.



(3)

In contrast, the absorption spectrum of the 6-amino-derivative under these conditions remains unchanged even at a pH of 0. Protonation of 6-aminobenzanthrone was examined at low pH using solutions of 85% aqueous acetic acid–sulphuric acid and typical spectra observed are shown in Figure 3. The lack of isobestic points in the 400—500 nm region is probably due to the dependence of the extinction coefficient of the protonated form on the acidity of the media. It is clear, however, that since the absorption spectrum of benzanthrone is not observed at any stage, protonation takes place at the oxygen rather than the nitrogen atom. Calculation using equation (1) (see Experimental section), gives a value of —0·4 ± 0·1 for the pK_a of the equilibrium between 6-aminobenzanthrone and its conjugate acid.

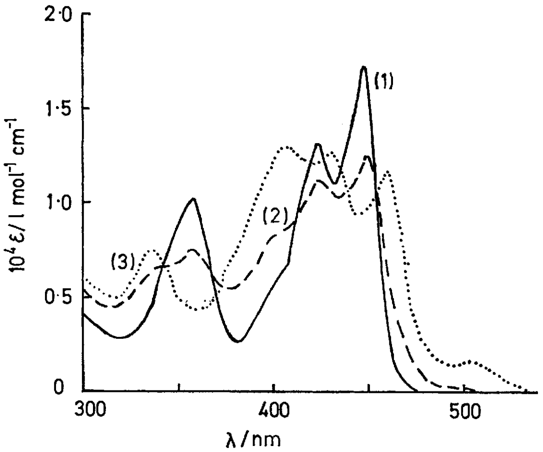


FIGURE 3 Absorption spectrum of 6-aminobenzanthrone in 85% aqueous acetic acid containing 0% (1); 4·39% (2); and 24·6% (3) sulphuric acid

Earlier [2] it was stated that 6-anilinobenzanthrone did not fluoresce whereas in this work fluorescence has been observed in a wide range of solvents (Table 1). This discrepancy is probably due to the fact that the measurements were made on different instruments. Here we found that fluorescence could only be observed under conditions of very low resolution and high amplifier gain. Since in methanol the quantum yield of fluorescence of the 6-anilino-derivative is *ca.* 500 times less than that of the 6-amino-compound the conclusions reached [2] on the photostability of the 6-substituted derivatives remain unchanged. In agreement with earlier work, whilst 6-hydroxy- and 6-amino-benzanthrone exhibited phosphorescence, no phosphorescence was observed from the 6-anilino-derivative. Furthermore, no phosphorescence was observed from any of the 8-substituted derivatives studied. The decay of the phosphorescence of 6-aminobenzanthrone obeyed first-order kinetics and the mean phosphorescence lifetime was 120 ms, a value consistent with the lowest triplet state being π–π* in nature.[16]

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[15] A. K. Davies, J. F. McKellar, and G. O. Phillips, *Proc. Roy. Soc.*, 1971, *A*, **323**, 69; V. V. Kratochvil and M. Nepras, *Coll. Czech. Chem. Comm.*, 1972, **37**, 1533; R. Ford, Ph.D. Thesis, University of Salford, 1973.

[16] G. Porter and P. Suppan, *Trans. Faraday Soc.*, 1965, **61**, 1664.