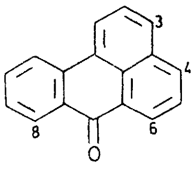
The Photochemistry of Benz[*de*]anthracen-7-ones. Part III.[1,2] Fluorescence Quantum Yield and Continuous Photolysis Studies.

By **Peter Bentley** and **John F. McKellar,*** Department of Chemistry and Applied Chemistry, University of Salford, Salford M54 WT

Fluorescence quantum yields are reported on benzanthrone and a range of its 3-, 4-, 6-, and 8-substituted derivatives in solvents of differing polarity. With benzanthrone and the 3-methoxy-derivative the quantum yields obtained in alcoholic solutions are in general higher than those in other solvents and this effect is discussed in the light of estimated potential energy levels and configurations of the lowest excited states. The continuous photolysis results are in accord with the configuration assignments and with earlier flash photolysis results on the same compounds.

IN Parts I and II we reported on the electronic absorption and emission spectroscopy[1] and flash photolysis[2] of benz[*de*]anthracen-7-ones (benzanthrones). Both this and other work[3,4] has shown that the spectroscopic and photochemical properties of benzanthrones (I) are very sensitive to small changes in molecular structure, particularly where there is substitution at positions 3, 4, 6, and 8. Here we report on the fluoroescence quantum yield and continuous photolysis of benzanthrone and a range of derivatives substituted at these positions. Amongst these is 3-methoxybenzanthrone, a compound to which we have paid particular attention because of its commercial importance as a disperse dye (C. I. Disperse Yellow 13) for polyester fabrics.[5]



(I)

EXPERIMENTAL

Flurescence Quantum Yields and Lifetimes.—The fluorescence measurements were carried out on a Baird-Atomic Fluorispec 100E and a Hitachi–Perkin-Elmer MPF-4 Spectrofluorimeter. These were calibrated using compounds whose corrected emission spectra have been accurately determined.[6] Fluorescence quantum yields were determined using the relative method[7] with quinine sulphate ($\leqslant 10^{-2}$ mol m^{-3}) in sulphuric acid (500 mol m^{-3}) as standard.[7,8] The refractive index correction was applied.[7] With the exception of 3-methoxybenzanthrone in alcohols and of 4-anilinobenzanthrone in aromatic hydrocarbons, the quantum yields obtained from air-equilibrated and nitrogen-saturated solutions were the same, within the sensitivity limits of the instruments. The quantum yield data reported here were from air-equilibrated solutions.

Approximate fluorescence radiative lifetimes τ_s° (in seconds) were calculated from the area under the long-wavelength absorption band by means of equation[9] (1)

$$1/\tau_s^\circ = 2.88 \times 10^{-9}\, \bar{\nu}^2_{\text{max.}}\, n^2 \int \varepsilon(\bar{\nu})\mathrm{d}\bar{\nu} \qquad (1)$$

where ε ($\bar{\nu}$) is the absorption coefficient (in l mol^{-1} cm^{-1}) at wavenumber $\bar{\nu}$ (in cm^{-1}), $\bar{\nu}_{\text{max.}}$ is the wavenumber of the maximum of the absorption band and n is the refractive index of the solvent.

Actual fluorescence lifetimes, τ_s, were estimated from the radiative lifetimes and fluorescence quantum yield, ϕ_f. In

$$\tau_s = \tau_s^\circ \phi_f$$

view of the inherent approximations in this equation the actual lifetimes are expected to be accurate to little more than an order of magnitude. However, since the τ_s values obtained in this work are spread over several orders of magnitude this error does not detract from our comparison between the τ_s values of the benzanthrones studied.

Steady State Photolysis.—The experiments were performed in cells of 10 or 100 mm length and with solutions between 0.1 and 0.01 mol m^{-3}. The solutions in the 10-mm cells were deoxygenated by either nitrogen saturation or by the freeze-pump-thaw method. The solutions in the 100-mm cells were only deoxygenated by nitrogen saturation.

The light source was a 200 W medium-pressure mercury arc from which the 365 nm line was isolated using a Chance OX1 filter and a 3 mm Pyrex glass plate. The intensity of the light was determined by ferrioxalate actinometry[10] and was normally in the range 10^{-3} to 10^{-2} mol s^{-1} m^{-3}.

Since in neutral solution the photolysis products did not absorb at wavelengths longer than 350 nm it was possible to monitor the rate of benzanthrone disappearance by the change in absorbance of the long-wavelength band. At high pH where there was some spectral overlap benzanthrone radical anion formation was monitored at 475 nm using a value of $\varepsilon = 1.0 \times 10^3$ m^3 mol^{-1}. The absorption coefficient was obtained from the absorption spectrum of the radical anion formed on complete photolysis of benzanthrone at high pH.

Materials.—The benzanthrone and its derivatives were obtained and purified as described earlier.[2]

---

[1] Part I, P. Bentley, J. F. McKellar, and G. O. Phillips, *J.C.S. Perkin II*, 1974, 523.

[2] Part II, P. Bentley, J. F. McKellar, and G. O. Phillips, *J.C.S. Perkin II*, 1975, 1259.

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

[4] P. Bentley, J. F. McKellar, and G. O. Phillips, *Chem. and Ind.*, 1974, 919.

[5] 'Colour Index,' Society of Dyers and Colourists, Bradford, 1971, 3rd edn.

[6] C. E. White and R. J. Argauer, 'Fluorescence Analysis,' Marcel Dekker, New York, 1970, ch. 3; W.H. Melhuish, *J. Res. Nat. Bur. Stand., Sect. A*, 1970, **76**, 547.

[7] J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

[8] B. Gelernt, A. Findeisen, A. Stein, and J. A. Poole, *J.C.S. Faraday II*, 1974, 939.

[9] J. B. Birks and I. H. Munro, *Progr. Reaction Kinetics*, 1967, **4**, 239.

[10] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.

RESULTS AND DISCUSSION

Fluorescence Quantum Yields and Lifetimes.—Benzanthrone. In agreement with earlier workers,[11,12] no fluorescence was detected in non polar solvents while in alcoholic solvents weak fluorescence was observed (Table 1). Proskuryakova and Nurmuknametov [12] attributed this to a change in the relative energies of the lower excited states from $S_{n\pi^*} > S_{\pi\pi^*} > T_{n\pi^*} > T_{\pi\pi^*}$ in non polar solvents to $S_{n\pi^*} > T_{n\pi^*} > S_{\pi\pi^*} > T_{\pi\pi^*}$ in alcoholic solvents since intersystem crossing is faster between states of unlike configuration.[13] Indeed, these workers assumed that the first excited singlet state of benzanthrone is ππ* rather than nπ* in both polar and non-polar solvents. However, as can be seen from Figure 1, this general assumption is open to question because in hexane the shoulder of the $S_{n\pi^*} \leftarrow S_0$ transition lies to longer wavelength than the apparent limit of the $S_{\pi\pi^*} \leftarrow S_0$ band. Further evidence to question their assumption is given later.

TABLE 1

Fluorescence quantum yields for benzanthrones.

Compound	Solvent	ϕ_f	Compound	Solvent	ϕ_f
Benzanthrone	Hexane	$<10^{-3}$	4-Anilino	Diethyl ether	0.082
Benzanthrone	Acetone	$<10^{-3}$	4-Anilino	Ethyl acetate	0.008
Benzanthrone	*NN*-Dimethylformamide	$<10^{-3}$	4-Anilino	Acetone	0.006
Benzanthrone	Propan-2-ol	0.009	4-Anilino	Methanol	0.006
Benzanthrone	Ethanol	0.017	6-Hydroxy	Hexane	0.049
Benzanthrone	Methanol	0.027	6-Hydroxy	Toluene	0.087
3-Methoxy	Hexane	0.02	6-Hydroxy	Propan-2-ol	0.091
3-Methoxy	Benzene	0.16	6-Hydroxy	Methanol	0.071
3-Methoxy	Toluene	0.16	6-Amino	Hexane	0.006
3-Methoxy	Dioxan	0.23	6-Amino	Toluene	0.030
3-Methoxy	Propan-2-ol [a]	0.71	6-Amino	Propan-2-ol	0.033
3-Methoxy	Methanol	0.76	6-Anilino	Hexane	$<10^{-4}$
4-Anilino	Hexane	0.052	6-Anilino	Propan-2-ol	6×10^{-5}
4-Anilino	Cyclohexane	0.065	8-Hydroxy	Hexane	$<10^{-4}$
4-Anilino	Dioxan	0.26	8-Hydroxy	Propan-2-ol	$<10^{-4}$
4-Anilino	Benzene	0.49	8-Hydroxy	Methanol	$<10^{-4}$
4-Anilino	Toluene [b]	0.48	8-Amino	Hexane	2×10^{-4}
4-Anilino	Furan	0.35	8-Amino	Propan-2-ol	2×10^{-3}

[a] In nitrogen-saturated solution $\phi_f = 0.73$. [b] In nitrogen-saturated solution $\phi_f = 0.50$.

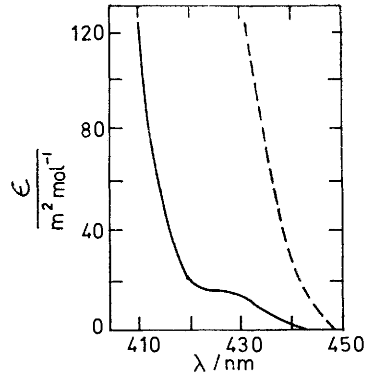


FIGURE 1 Long-wavelength electronic absorption of benzanthrone in hexane —— and methanol - - - -

It is possible to estimate the location of the $S_{\pi\pi^*} \leftarrow S_0$ transition in hexane by the following procedure. In methanol, both the intersection of the absorption and fluorescence curves and the average of the long-wavelength absorption and fluorescence maxima show that in this solvent the purely electronic $S_{\pi\pi^*} \leftarrow S_0$ transition occurs at 2.32 ± 0.01 μm^{-1}.[1,14] The absorption solvent shift of the band maximum is 0.12 μm^{-1} (ref. 1) so that in hexane the *0,0* transition is *ca.* 2.44 μm^{-1}. On the other hand, the pronounced $S_{n\pi^*} \leftarrow S_0$ shoulder occurs at 2.35 μm^{-1} so that in hexane the $S_{n\pi^*}$ state of benzanthrone must be of lower energy than that of the $S_{\pi\pi^*}$ state.

If we make the following assumptions we get the energy-level diagram for benzanthrone shown in the left-hand side of Figure 2. (1) The energy difference between the $S_{n\pi^*}$ and $T_{n\pi^*}$ states of benzanthrone, like that of many other aromatic carbonyl compounds [15] is close to 27 kJ mol^{-1}. (2) The solvent shift of the $S_{n\pi^*} \leftarrow S_0$ and $T_{n\pi^*} \leftarrow S_0$ transitions are similar to that of the $S_{n\pi^*} \leftarrow S_0$ transition in acetone

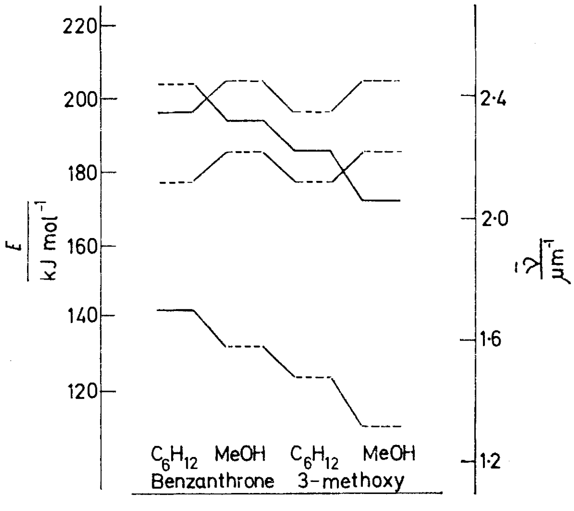


FIGURE 2 Energy-level diagram for benzanthrone and 3-methoxy-benzanthrone in hexane and methanol. Observed level —— and estimated level - - - -

---

[11] N. F. Levchenko and L. M. Podgornaya, *Zhur. priklad. Spektroskopii*, 1968, **8**, 164.

[12] N. S. Proskuryakova and R. N. Nurmuknametov, *Optika Spectroskopiya*, 1969, **27**, 224.

[13] M. A. El-Sayed, *J. Chem. Phys.*, 1963, **38**, 2834; V. G. Plotnikov, *Optika Spektroskopiya*, 1966, **22**, 735.

[14] P. Bentley, Ph.D. Thesis, University of Salford, 1975.

[15] D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, 1966, **88**, 5087.

and benzophenone.[16] (3) The shift in the energy of the $T_{\pi\pi^*} \leftarrow S_0$ transition with solvent is of a magnitude similar to that of the $S_{\pi\pi^*} \leftarrow S_0$ transition. The energy of the $T_{\pi\pi^*} \leftarrow S_0$ transition in non-polar solvents is taken from the data of Proskuryakova and Nurmuknametov.[12]

According to Figure 2 intersystem crossing in hexane occurs between like states ($S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$) so that the lack of fluorescence cannot now be attributed to spin-orbit coupling. However, $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ intersystem crossing is not necessarily slow. In the case of benzophenone in heptane the triplet is formed by an $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ process with a rate constant of 1.25×10^{11} s^{-1}.[17] Furthermore, because of its nπ^* configuration the S_1 state in hexane has a radiative lifetime of *ca.* 2.5 ms (Table 2) corresponding to a fluorescence rate constant of 4×10^5 s^{-1}. Thus even if the intersystem crossing rate were two orders of magnitude slower than that of benzophenone, fluorescence would still be uncompetitive with radiationless decay.

TABLE 2

Approximate radiative lifetimes, τ_s°, and actual lifetimes, τ_s, of the first excited singlet states of benzanthrones

	Hexane		Methanol	
	τ_s°/ns	τ_s/ns	τ_s°/ns	τ_s/ns
Benzanthrone [a,b]	2 500	2.5	7.6	0.21
3-Methoxy- [c]	8.0	0.16	6.8	5.1
4-Anilino- [d]	5.6	0.25	4.7	0.03
6-Hydroxy-	10.0	0.49	9.4	0.86
6-Amino- [e]	10.3	0.06	10.9	0.36
6-Anilino- [e]	8.5	$<10^{-3}$	8.2	$<10^{-3}$
8-Hydroxy-	8.9	$<10^{-3}$	8.2	$<10^{-3}$
8-Amino- [e]	12.2	2.4×10^{-3}	10.3	0.02

[a] Value estimated from the $S_{n\pi^*} \leftarrow S_0$ shoulder. [b] In 1 : 1 v/v propan-2-ol-water $\tau_s^\circ \approx 7.6$ ns and τ_s 0.62 ≈ ns. [c] In toluene $\tau_s^\circ \approx 6.1$ ns and $\tau_s \approx 0.98$ ns. [d] In toluene $\tau_s^\circ \approx 3.8$ ns; $\tau_s \approx 1.8$ ns. [e] Solvents are hexane and propan-2-ol.

On transferring benzanthrones to an alcoholic solvent, weak but measurable fluorescence is observed. According to the energy-level diagram, the S_1 state gains a $\pi\pi^*$ configuration and thus intersystem crossing can occur between unlike states. The $\pi\pi^*$ configuration will make radiative decay more competitive with intersystem crossing. From Table 2, $k_f = 1/\tau^\circ \approx 1.2 \times 10^8$ s^{-1} which is closer to the rate constant for intersystem crossing. Presumably in alcoholic solution the rates of the two processes are close enough that the net result is weak fluorescence emission.

3-*Methoxybenzanthrone*.—In contrast, this derivative shows significant fluorescence in all the solvents used (Table 1). Indeed in alcoholic solution the quantum yield is quite high (0.7 to 0.8). If we make the same assumptions as we did for benzanthrone the energy-level diagram for this derivative is given in the right-hand side of Figure 2. In hexane the relative energies of the lower excited states of 3-methoxybenzanthrone are the same as those of benzanthrone in alcohols and, accordingly, the fluorescence quantum yield ($\phi_f \approx 2\%$) is similar. In alcoholic solvents however the fluorescence efficiency of 3-methoxybenzanthrone is much higher than that of benzanthrone. This difference is due to the change in the relative energies of the lower excited states so that for the 3-methoxy-derivative intersystem crossing now occurs between unlike states $S_{\pi\pi^*} \rightsquigarrow T_{n\pi^*}$. That the increased fluorescence efficiency of 3-methoxybenzanthrone in alcohols is associated with decreased triplet yield rather than a decrease in the rate of some other process such as internal conversion is consistent with our flash photolysis results [2] where it was found that the absorbance of 3-methoxybenzanthrone triplet in methanol was *ca.* one third of that in benzene.

The essential difference between the energy-level diagram shown in Figure 2 and the energy-level diagram of Proskuryakova and Nurmuknametov [12] lies in the energy of the nπ^* states. These workers estimated an $S_{n\pi^*}$ level of *ca.* 2.6 μm^{-1} in octane, by analogy with the $S_{n\pi^*}$ level of naphthalenecarbaldehyde, even though they attributed the shoulder at 2.35 μm^{-1} to an $S_{n\pi^*} \leftarrow S_0$ transition. While both schemes must, to some extent, be tentative we feel that Figure 2 gives a better representation of the nπ^* energy levels. Figure 2 also accounts for the solvent effect on the fluorescence quantum yield of 3-methoxybenzanthrone, a feature which Proskuryakova and Nurmuknametov's scheme cannot readily explain.

4- *and* 6-*Anilinobenzanthrone*.—The fluorescence quantum yield of 4-anilinobenzanthrone is also extremely solvent dependent (Table 1). The ten-fold increase in fluorescence quantum yield from hexane to benzene might be due to inversion of the $S_{\pi\pi^*}$ and $T_{n\pi^*}$ energy levels (*cf.* 3-methoxybenzanthrone), but the hundredfold decrease in fluorescence quantum yield on proceeding from benzene to methanol (Table 1) is more difficult to explain. The latter observation is also interesting in view of our earlier flash photolysis results [2] which show that the triplet yield of 4-anilinobenzanthrone decreases by more than an order of magnitude from benzene to methanol. Hence, the faster rate of singlet decay in the polar solvent (Table 2) must be due to an enhanced rate of internal conversion.

Another interesting property of 4-anilinobenzanthrone is that the absorption coefficient of the long-wavelength absorption band increases markedly with increasing solvent polarity. For example, in hexane the long-wavelength absorption band has an absorption coefficient, ε, of 1.78×10^3 m^2 mol^{-1} while in methanol it is 2.51×10^3 m^2 mol^{-1}. An explanation for this observation is that as the solvent polarity increases the molecule becomes more planar due to the amino-group of the anilino-substituent becoming coplanar with the benzanthrone nucleus. It is unlikely that the phenyl ring of the anilino-group would also become coplanar with the remainder of the molecule because this is strongly inhibited by steric interaction of the hydrogen atoms of the two ring systems. Thus, one possibility is that rapid internal conversion only occurs for 4-anilinobenzanthrone molecules in which the amino-group is in the same plane as the benzanthrone nucleus.

4-Anilinobenzanthrone shows some similarities with the *N*-arylaminonaphthalene sulphonates which are 'non-fluorescent' in water but fluoresce strongly in organic solvents.[18] It has been reported that in non-polar solvents singlet excited 2-*N*-anilinonaphthalene-6-sulphonate is deactivated from a non-planar form by both fluorescence and intersystem crossing while in polar solvents, singlet decay occurs from a 'planar' charge-transfer form, mainly by non-radiative decay within the singlet manifold.

An explanation for the fluorescence quantum yield of 6-anilinobenzanthrone being considerably lower than that of the 6-amino-derivative in both polar and non-polar solvents

---

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

[17] R. W. Anderson, R. M. Hochstrasser, H. Lutz, and G. W. Scott, *Chem. Phys. Letters*, 1974, **28**, 153.

[18] E. M. Kosower, H. Dodiuk, K. Tanizawa, M. Oholenghi, and N. Orbach, *J. Amer. Chem. Soc.*, 1975, **97**, 2167.

is now apparent. In both these derivatives the amino-group is maintained in a coplanar orientation with respect to the benzanthrone nucleus by strong intramolecular hydrogen bonding.[14] Hence, photo-excited 6-anilinobenzanthrone can be deactivated within the singlet manifold by the same mechanism which de-excites the planar form of the 4-anilino-derivative present in polar solvents.

6- *and* 8-*Hydroxy- and Amino-benzanthrone.*—The 8-hydroxy- and 8-amino-benzanthrones have much lower fluorescence quantum yields and have excited singlet states which are deactivated much more rapidly than their 6-substituted analogues (Tables 1 and 2). This is interesting because while one might expect, by analogy with the benzophenones,[19] that substitution of hydroxy- or amino-groups *ortho* to carbonyl in the benzanthrone nucleus would cause rapid de-excitation of the photo-excited singlet states of the dyes, this behaviour only appears to apply to substitution in the benzene moiety rather than in the naphthalene part of the molecule. There is some evidence that this phenomenon may apply to a number of *ortho*-substituted aromatic carbonyl compounds.[4]

Steady State Photolysis.—*Photolysis of benzanthrone in neutral solution.* Photolysis of benzanthrone in deoxygenated methanol or propan-2-ol results in a decrease in the absorbance of the long-wavelength absorption band and an increase in absorbance in the 300—350 nm region. Isosbestic points are observed at 309 and 351 nm until *ca.* 90% of the benzanthrone has disappeared. The product, which is spectrally similar to that produced on repetitive microsecond flash photolysis,[14] is insensitive to oxygen and exhibits visible blue fluorescence. Comparison of the maxima of the absorption spectra of the product ($\varepsilon_{\text{max.}}$ = 315, 328, and 343 nm) with those of the long-wavelength absorption band of benzanthrone in 'alcohol'[20] ($\varepsilon_{\text{max.}}$ = 313, 329 and 344 nm) shows that the chromophoric system responsible for light absorption by the product is the same as that of benzanthrene.

Microsecond flash photolysis of benzanthrone in alcoholic solvents results in the formation of ketyl radicals which decay without detectable regeneration of ground-state benzanthrone.[2,3] This observation suggests that the ketyl radicals react by a dimerisation process

$$2\text{BH}\cdot \longrightarrow (\text{BH})_2$$

rather than by disproportionation

$$2\text{BH}\cdot \longrightarrow \text{BH}_2 + \text{B}$$

Hence, although the product formed on steady-state photolysis could be either benzanthrone pinacol $(\text{BH})_2$ or the hydrol, BH_2 (since both have the same π-system as benzanthrone and therefore are expected to have a similar absorption spectrum), the balance of the evidence favours the pinacol as the product of benzanthrone photolysis.

The quantum yield for the photolysis of benzanthrone in alcohols is relatively low (Table 3), in accordance with the $\pi\pi^*$ configuration of the lowest-energy triplet state.[14,21] The quantum yield is also independent of initial concentration, indicating that the low value is not due to self quenching of the photo-excited benzanthrone.

Photolysis of benzanthrone at high pH. On photolysis of benzanthrone in a 1 : 1 v/v propan-2-ol–water mixture at high pH the absorption spectrum changes through isosbestic points at 324, 382, and 432 nm and an oxygen-sensitive product is formed whose absorption spectrum ($\varepsilon_{\text{max.}}$ = 365, 475, and 568 nm) reveals its identity as the benzanthrone radical anion which we observed earlier on microsecond flash photolysis of benzanthrone at high pH.[2]

TABLE 3

Quantum yields for the disappearance of benzanthrone in de-oxygenated solutions on photolysis at 365 nm

Compound	Solvent	c/mol m^{-3}	ϕ_d
Benzanthrone	Propan-2-ol	0.1	2.1×10^{-3}
Benzanthrone	Propan-2-ol	0.01	2.2×10^{-3}
Benzanthrone	Methanol	0.1	1.6×10^{-3}
Benzanthrone	Propan-2-ol–water (1 : 1 v/v)	0.01	1.6×10^{-3}
Benzanthrone	Propan-2-ol–water (1 : 1 v/v) +NaOH (200 mol m^{-3})	0.01	*ca.* 1.6×10^{-2} [a]

[a] Quantum yield for the formation of the benzanthone ketyl anion.

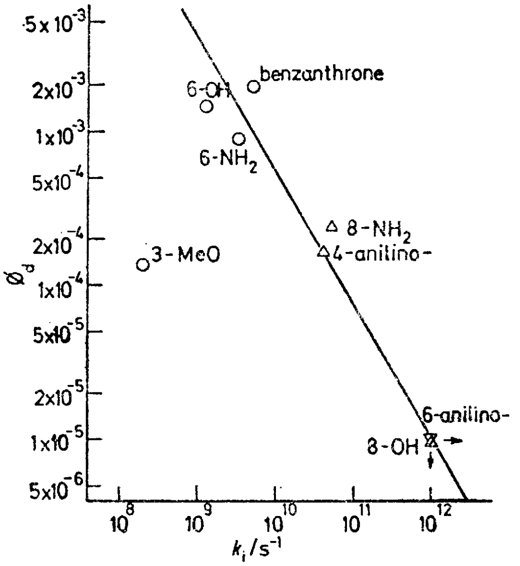


FIGURE 3 Relationship between the rate of singlet deactivation, k_i, and the quantum yield of disappearance at 365 nm, ϕ_d, of benzanthrones in methanol. The absorbance of the maximum, $A_{\max}$, in the spectrum of the transient observed at the end of the pulse on laser-flash photolysis[2] of each compound is denoted by ○ for $A_{\max} > 0.1$; △ for $0.1 > A_{\max} > 0.01$ and ▽ for $A_{\max} < 0.001$

Under similar conditions of light absorption, photolysis of benzanthrone at high pH occurs much more rapidly than in neutral solution. Furthermore, the quantum yield for the formation of the radical anion is an order of magnitude greater than that for photolysis of benzanthrone in neutral solution (Table 3) and, assuming that in neutral solution the quantum yield for hydrogen abstraction is similar to that for benzanthrone disappearance, then the radical anion cannot be formed to any significant extent by the reactions

$$\text{B}^* + \text{Me}_2\text{CHOH} \longrightarrow \text{BH}\cdot + \text{Me}_2\dot{\text{C}}\text{OH}$$
$$\text{BH}\cdot + \text{OH}^- \longrightarrow \text{B}^{\cdot-} + \text{H}_2\text{O}$$

---

[19] A. A. Lamola and L. J. Sharp, *J. Phys. Chem.*, 1966, **70**, 2634; O. Kysel, *Coll. Czech. Chem. Comm.*, 1974, **39**, 3256.

[20] E. Clar and D. G. Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235.

[21] D. N. Shigorin, N. A. Shcheglova, and N. S. Dokunikhin, *Doklady Akad. Nauk S.S.S.R.*, 1961, **137**, 1416.

but must be formed by electron abstraction by photoexcited benzanthrone

$$B^* + OH^- \longrightarrow B^{\cdot -} + OH\cdot$$

This pattern of behaviour is similar to that exhibited by 2-piperidinoanthraquinone on photolysis at high pH.[22]

Photolysis of benzanthrone derivatives. The quantum yield for the disappearance of benzanthrones on photolysis in de-oxygenated methanol tends to decrease with increasing rate of singlet deactivation, $k_i (= 1/\tau_s)$ as shown in Figure 3. The correlation probably arises as follows. Assuming no singlet reaction, the quantum yield of disappearance is given by

$$\phi_d = \alpha\phi_T = \frac{\alpha k_{isc}}{k_{isc} + k_{ic} + k_f} = \frac{\alpha k_{isc}}{k_i} \qquad (1)$$

where ϕ_T is the triplet quantum yield, α is the fraction of triplet molecules which undergo photolysis and k_{isc}, k_{ic}, and k_f are the rates of intersystem crossing ($S_1 \rightsquigarrow T_1$), internal conversion and fluorescence respectively. Now since the lowest-energy triplet states of the benzanthrones are all of the same configuration [14] and since the radiative lifetimes of the benzanthrones are similar (Table 2) then α and k_f are, to a first approximation, constant. Hence, an increase in the k_i might arise from either an increase in k_{isc} or an increase in k_{ic}. However, increasing k_{isc} would tend to increase ϕ_T, while the opposite is true as shown by the flash-photolysis results incorporated in Figure 3. It would appear, therefore, that the correlation shown in Figure 3 must arise beause the photostability of the compounds examined depends mainly on the rate of deactivation of their photoexcited states within the singlet manifold.[3]

An observation that may be of technological interest is that 3-methoxybenzanthrone (C.I. Disperse Yellow 13) [5] is an exception to the correlation since the quantum yield of disappearance is much less than its rate of singlet deactivation implies. An explanation for this is possibly that k_{ic} and k_{isc} are extremely slow for this compound. Hence the fluorescence quantum yield is high ($\phi_f = 0.76$) so that ϕ_T, and therefore ϕ_d, are relatively low. The possibility of slow intersystem crossing is discussed above.

We thank the S.R.C. for financial support to P. B.

[6/386 *Received, 25th February,* 1976]

---

[22] A. K. Davies, J. F. McKellar, and G. O. Phillips, *Proc. Roy. Soc.* 1970, *A*, **323**, 69.