The Photochemistry of Benz[*de*]anthracen-7-ones. Part II.[1] Flash Photolysis

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The primary photochemical processes following light absorption by benz[*de*]anthracen-7-one and some of its 3-, 4-, 6-, and 8-substituted derivatives have been studied by laser ns and conventional μs flash photolysis. The transients observed on laser flash photolysis of benz[*de*]anthracen-7-one and its 4-anilino-, 6-hydroxy-, and 6-amino-derivatives in benzene are the lowest triplet excited states. The rate constants for triplet quenching by oxygen have been determined. The 6-hydroxy- and 6-amino-benz[*de*]anthracen-7-ones behave rather like benz[*de*]anthracen-7-one itself whereas the 8-hydroxy- and 8-amino-derivatives show no transient absorption or dye fading on μs flash photolysis and show only weak transient absorption on laser photolysis. These observations are discussed in relation to the overall light stability of the benz[*de*]anthracen-7-ones.

IN Part I[1] we reported on the electronic absorption and emission spectroscopy of benz[*de*]anthracen-7-ones (benzanthrones) (I). Earlier work[2] has shown that slight structural differences in 6-substituted benzanthrones

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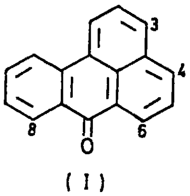
[1] Part I, P. Bentley, J. F. McKellar, and G. O. Phillips, *J.C.S. Perkin II*, 1974, 523.

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

markedly affect their photochemistry and recently[3] we found a remarkable difference between the photostability of 6- and 8-hydroxybenzanthrone. Here we



(I)

report on the flash photolysis of these interesting compounds in a variety of solvents.

EXPERIMENTAL

Laser Flash Photolysis.[4]—The ruby laser was Q-switched by means of a Pockels cell and after frequency doubling produced *ca.* 50 mJ pulses of 347 nm light with a half-peak width of *ca.* 20 ns. The photolysis cell was a quartz cylinder (10 mm long × 10 mm diam.). The monitoring beam was passed through the optically flat end windows of the photolysis cell and was arranged at right angles to the laser beam. The analysing light was produced by a pulsed 250 W high pressure xenon arc lamp and was focused through the cell and on to a small orifice in the cell housing. After refocusing, the light transmitted by a small Bausch and Lomb monochromator was received by either an RCA 931-A photomultiplier or an EMI SPD1 photodiode. The signals from the photodetector were observed on a Tektronix 585A oscilloscope and recorded on polaroid film.

Solutions were deoxygenated by saturating with nitrogen in an upright 20 cm^3 syringe fitted with a ground glass joint. After expelling excess of nitrogen, the solution was pumped into the cell against a slight pressure of nitrogen. Oxygen-saturated solutions were prepared in another syringe in a similar manner. Solutions containing any required concentration of oxygen could be prepared by transferring the appropriate amount of solution from one 20 cm^3 syringe to the other by means of a 2 or 5 cm^3 microsyringe fitted with a fine needle. Mixing was achieved by inverting the syringe and causing a thin washer to stir the solution. The solubility of oxygen in benzene[5] was assumed to be 9.12×10^{-3} mol dm^{-3}. Plots of the pseudo-first-order rate constant for transient decay against oxygen concentration were linear and gave the rate constant for oxygen quencing.

The solutions were normally prepared with an absorbance of *ca.* 1.8 at 347 nm for a 10 mm path and were in the concentration range 10^{-4}—10^{-3} mol dm^{-3}.

Conventional Flash Photolysis.—The conventional flash photolysis apparatus is similar to that described by Allen and McKellar.[6] The photolysis cells were 200 mm long and had optically flat end windows. Transient absorption was recorded on Ilford HP3 plates which are light sensitive up to *ca.* 600 nm. Plate densitometry was performed on a Loebel–Joyce double beam microdensitometer. The solutions of the benzanthrones were in the concentration range 5×10^{-6}—10^{-5} mol dm^{-3}. Deoxygenation was performed by bubbling the solutions with nitrogen containing <5 p.p.m. oxygen.

Materials.—The benzanthrones were obtained as before.[1] However, in addition to the benzanthrone used earlier, further samples were obtained from three commercial sources. The commercial samples were purified by chromatography on an alumina column using toluene as eluant followed by several successive crystallizations from hexane. Some experiments were performed on samples which had also been sublimed under reduced pressure. Purified benzanthrone had m.p. 170—171° (lit.,[7] 170—171°).

1,1,2-Trichlorotrifluoroethane was passed down an alumina column and fractionated. Hexane was treated with three successive portions of silica gel and then fractionated under nitrogen. Methanol and propan-2-ol were refluxed with acidified 2,4-dinitrophenylhydrazine in a stream of nitrogen for 3 h and then fractionated under nitrogen. Benzene was of AnalaR quality and used without further purification. Water was de-ionized and distilled from alkaline permanganate.

RESULTS AND DISCUSSION

Benzanthrone.—On laser flash photolysis of benzanthrone a strong transient with a broad maximum centred at 490 nm (Figure) is formed within the duration of the flash. It is quenched by oxygen at *ca.* 10% of diffusion controlled rate (Table 1) but the initial yield is unaffected. The behaviour of the transient is relatively independent of solvent (Table 1; Figure), and in alcohol–water mixtures the lifetime is not significantly affected by the pH of the solution. The same spectrum is observed on conventional flash photolysis of benzanthrone in benzene (10^{-5} mol dm^{-3}). As the transient decays the benzanthrone is regenerated with very low overall decomposition.

TABLE 1

First half-life of decay in nitrogen saturated solution and rate constant for oxygen quenching in benzene, K_Q, of transients formed on laser flash photolysis of benzanthrones

	$t_{\frac{1}{2}}/\mu s$		$K_Q/10^9$
	Benzene	Methanol	dm^{-3} mol^{-1} s^{-1}
Benzanthrone[a]	1.0 ± 0.1	1.8 ± 0.1	1.2 ± 0.2
3-Methoxy	2.4 ± 0.2	10.0 ± 0.5	1.3 ± 0.3
4-Anilino	*ca.* 0.28 *ca.* 9.3	*ca.* 6	1.7 ± 0.3
6-Hydroxy	1.0 ± 0.2	2.4 ± 0.4[b]	1.2 ± 0.2
6-Amino	2.3 ± 0.1	3.7 ± 0.2[b]	1.2 ± 0.2
6-Anilino	N.o.	N.o.	
8-Hydroxy	3.0 ± 0.5	3.0 ± 0.5	
8-Amino	*ca.* 6	*ca.* 10	

[a] In 1,1,2-trichlorotrifluoroethane, $t_{\frac{1}{2}} = 1.0 \pm 0.1$ μs. [b] In propan-2-ol.

It is clear from these observations that this transient

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

[4] D. L. Wheat, Ph.D. Thesis, University of Salford, 1974.

[5] J. L. R. Morgan and H. R. Pyne, *J. Phys. Chem.*, 1930, **34**, 2045; J. Horiuti, *Sci. Paper Inst. Phys. Chem. Res., Tokyo*, 1931, **17**, 125; P. Schläpfer, T. Audykowski, and A. Bukowiecki, *Schweizer Arch. Angew. Wiss. Tech.*, 1949, **15**, 299; N. K. Naumenko, N. N. Mukhin, and V. B. Aleskovskii, *Zhur. Priklady Khim.*, 1969, **42**, 2522.

[6] J. H. Allen and J. F. McKellar, *Lab. Pract.*, 1967, **16**, 991.

[7] L. C. MacLeod and C. F. H. Allen, *Org. Synth.*, 1950, Coll. Vol. 2, p. 62.

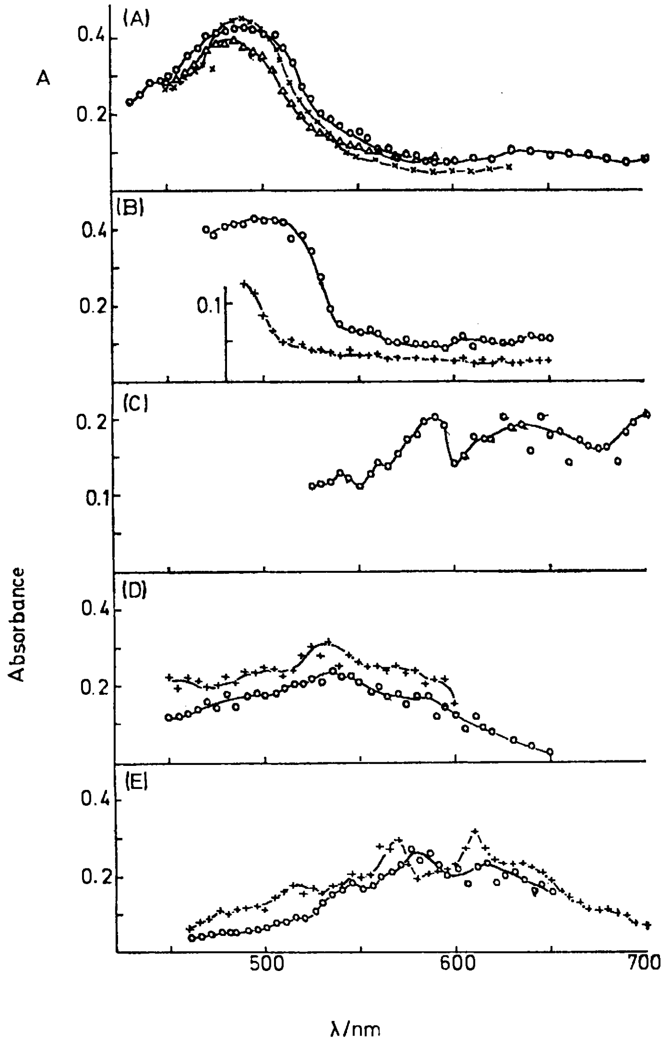
TABLE 2

Wavelength maxima (nm) of transients (± 5 nm) and approximate percentage conversion to products on conventional flash photolysis of benzanthrones. N.o. = no transient absorption observed

	Hexane	Benzene	Methanol	Methanol–0.1M aqueous NaOH (3 : 2)
Benzanthrone	365, 435 (20%)	370, 500 (2%)	360, 435 (60%)	365, 475 (50%)
3-Methoxy	370, 490 (5%)	370, 490 (2%)	345, 445(30%)	370, 460 (40%)
4-Anilino	500—600 (30%)	500—600 (2%) [a]	N.o. (0%)	
6-Hydroxy	550 (20%)	490—540 (0%)	350, 435, 500, 550 (50%)	
6-Amino	500—600 (0%)	490—600 (0%)	500—600 (3%)	340, 500—600 (5%)
6-Anilino	N.o. (0%)	N.o. (0%) [a]	N.o. (0%)	
8-Hydroxy	N.o. (0%)		N.o. (0%)	
8-Amino			N.o. (0%)	

[a] In toluene.

must be benzanthrone in its lowest triplet excited state. However the precise mode of its decay is less certain. For example, the transient decays with predominantly second-order, rather than first-order, kinetics and its lifetime depends upon the initial yield formed at the end of the laser pulse, either when the total benzanthrone concentration is varied or when the light intensity of the laser pulse is varied. These observations thus suggest that in addition to unimolecular triplet decay, a triplet–triplet annihilation process [8] is also important.



Absorption spectra of the transients observed at the end of the pulse on laser flash photolysis of: benzanthrone (A); 3-methoxybenzanthrone (B); 4-anilinobenzanthrone (C); 6-hydroxybenzanthrone (D); and 6-aminobenzanthrone (E): in benzene ○; 1,1,2-trichlorotrifluoroethane Δ; methanol ×; or propan-2-ol +

The behaviour of benzanthrone on conventional flash photolysis in hydrogen atom donating solvents is markedly different from that observed on laser flash photolysis. Flash photolysis of 5×10^{-5} mol dm^{-3} solutions of benzanthrone in nitrogen-saturated alcoholic solvents results in the formation of strong transient absorption at 360 and 435 nm. The transient decays over a period of *ca.* 100 μs and no regeneration of benzanthrone is observed. One 500 J flash is sufficient to convert *ca.* 60% of the benzanthrone into permanent product. No transient absorption or product formation was observed in oxygen saturated solutions. On flashing solutions of benzanthrone at high pH, transient absorption occurs to longer wavelengths (Table 2) and decays over *ca.* 200 μs. Again a permanent product is formed. In this case the product is spectrally similar to its transient precursor.

The present observations are consistant with the suggestion [2] that photoexcited benzanthrone abstracts a hydrogen atom from alcohol to form a ketyl radical which is converted to its anion at high pH. The behaviour is, however, surprising in view of the $\pi\pi^*$ nature of both the lowest singlet and triplet states of benzanthrone.[9] Indeed, the behaviour of benzanthrone on laser flash photolysis and on continuous photolysis [10] of alcoholic solutions (10^{-4} mol dm^{-3}) using light of 365 nm ($\phi_{\text{disappearance}}$ *ca.* 10^{-3}) is exactly as expected from the nature of the lowest excited states.

3-Methoxybenzanthrone.—The behaviour of 3-methoxybenzanthrone in benzene on both laser and conventional flash photolysis is similar to that of benzanthrone (Tables 1 and 2; Figure) and the transient observed in benzene is again likely to be the triplet. Transient absorption on laser flash photolysis in propan-2-ol is significantly weaker than in benzene. This is no doubt

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[8] A. A. Lamola, ' Technique of Organic Chemistry,' eds. P. A. Leermakers and A. Weissberger, Wiley, New York, 1969, vol. XIV, ch. II.

[9] D. N. Shigorin, N. A. Shcheglova, and N. S. Dokunikhin, *Doklady Akad. Nayk S.S.S.R.*, 1960, **137**, 1416; N. S. Proskuryakova and R. N. Nurmuknametov, *Optika i Spectrosk.*, 1969, **27**, 224.

due to the greater fluorescence efficiency in propan-2-ol [10] leading to a lower quantum yield of triplet formation.

4- *and* 6-*Anilinobenzanthrone*.—On laser flash photolysis of 4-anilinobenzanthrone in benzene transient decay consists of strong, short-lived and weak, relatively long lived components (Table 1). Only the short lived component is observed in solutions containing $>$*ca.* 10^{-3} mol dm^{-3} oxygen. It seems probable that the short-lived component is the triplet state. It cannot be the singlet since the fluorescence lifetime is less than the duration of the laser flash. On conventional flash photolysis of 4-anilinobenzanthrone in toluene strong transient absorption is also observed. As the transient decays, 4-anilinobenzanthrone is regenerated almost quantitatively.

The behaviour of 4-anilinobenzanthrone in methanol differs markedly from that in aromatic solvents. The intensity of transient absorption on laser flash photolysis is more than an order of magnitude less than that in benzene. On conventional flash photolysis neither transient absorption nor fading of 4-anilinobenzanthrone was observed. These results are of particular interest in relation to the observation that the quantum yield of fluorescence of 4-anilinobenzanthrone decreases by a factor of >50 on changing from an aromatic to a polar solvent.[10] Thus, the laser flash photolysis studies indicate that the decrease in fluorescence with increasing solvent polarity cannot be due to enhanced intersystem crossing, but is due to an increased rate of internal conversion, $S_1 \longrightarrow S_0$.

The rapid de-activation of the lowest excited singlet state of 4-anilinobenzanthrone in methanol is also of interest with respect to the remarkable behaviour of 6-anilinobenzanthrone. In agreement with an earlier report,[2] no transient absorption or dye photolysis was observed on conventional flash photolysis of 6-anilinobenzanthrone. In the present work we were also unable to observe any transient absorption on laser flash photolysis of 6-anilinobenzanthrone in either benzene or methanol. Both the ' window ' in 6-anilinobenzanthrone ground state absorption at 390—410 nm and the region from 500 to 800 nm were examined. This observation must mean that photoexcited 6-anilinobenzanthrone is deactivated in $<$ *ca.* 10 ns and strongly supports the hypothesis that deactivation occurs by some rapid process within the singlet manifold.[2]

6- *and* 8-*Hydroxy- and Amino-benzanthrones*.—In marked contrast to 6-anilinobenzanthrone, the behaviour of 6-amino- and 6-hydroxy-benzanthrone resembles that of benzanthrone itself. Thus on laser flash photolysis relatively strong transients are formed whose absorption spectra (Figure) and rates of decay, although non-exponential, are relatively independent of solvent (Table 1). The rate of quenching by oxygen is similar to that of the benzanthrone triplet. Again, spectrally similar transients are formed on conventional flash photolysis in benzene and as the transients decay the ground states are regenerated. We therefore attribute these transient species to the lowest triplet states of 6-hydroxy- and 6-amino-benzanthrone.

The transient formed on conventional flash photolysis of 6-hydroxybenzanthrone in methanol is spectrally different from that in benzene. In this case as the transient decays, the 6-hydroxybenzanthrone is not regenerated. This transient is probably the ketyl radical. 6-Aminobenzanthrone is more stable to flash photolysis. It shows very little overall decay even on flashing in methanol and the transient observed is spectrally similar to that observed in non-polar solvents or at high pH (Table 2).

The behaviour of 8-hydroxy- and 8-amino-benzanthrone is markedly different from that of their 6-substituted analogues. As in the case of 6-anilinobenzanthrone, no transient absorption or dye fading is observed on conventional flash photolysis of the 8-hydroxy- and 8-amino-derivatives.

On laser flash photolysis of 8-hydroxy- and 8-aminobenzanthrone, transient absorption is weaker by more than an order of magnitude than that observed in the case of the corresponding 6-substituted derivatives.

These observations clearly indicate that triplet formation is more efficient in the case of the 6-amino- and 6-hydroxy derivatives. Indeed, earlier [1] we found that whereas the 6-hydroxy- and 6-amino-benzanthrones showed phosphorescence emission at 77 K, no such emission was observed from the 8-substituted benzanthrones. Furthermore, this difference in the efficiency of triplet formation provides support for our view [3] that the relatively poor light stability of 6-hydroxybenzanthrone compared to the 8-hydroxy-derivative is due to the inefficiency of the rapid deactivating process which occurs within the singlet manifold of 8-hydroxybenzanthrone.

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[10] P. Bentley, J. F. McKellar, and G. O. Phillips, unpublished data.