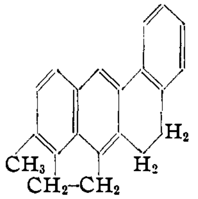
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

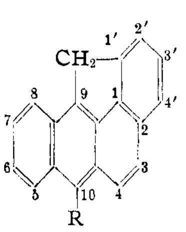
Further Observations on the Absorption Spectra of Derivatives of 1,2-Benzanthracene

BY R. NORMAN JONES

The ultraviolet absorption spectra of polynuclear aromatic hydrocarbons are characteristic of the unsaturated ring system present in the molecule[1] and in the case of unsubstituted hydrocarbons and their alkyl derivatives such spectra have proved a valuable aid to the identification of the particular ring structure present. Thus, for example, Fieser and Hershberg[2] identified a dihydro-20-methylcholanthrene as the 6,7-dihydro derivative (I) by the similarity of its spectrum to that of β-phenylnaphthalene.



(I)



(II)

In this Laboratory a large number of derivatives of 1,2-benzanthracene have been synthesized in connection with work on carcinogenesis and the availability of these compounds affords an opportunity to determine the extent to which various substituent groups may modify the spectrum of the hydrocarbon. The use of absorption spectrophotometry as an aid to structure determination would be greatly enhanced if one could predict the effect of a given substituent at a given position on the spectrum of the hydrocarbon. A theoretical approach to this problem is not possible at present but from the collection of empirical data of this kind some generalizations may be forthcoming.

In an earlier paper[3] the spectra of twelve alkyl derivatives of 1,2-benzanthracene were recorded and it was observed that with one exception the curves were all of a similar shape, differing only in the amount of the fine structure which could be resolved and in the shift of the whole spectrum to longer wave lengths. This bathochromic effect produced by alkylation has long been known.[4,5] The magnitude of the shift was found to vary greatly with the position of substitution, being greatest for derivatives with alkyl substituents at the reactive *meso* positions (9, 10), and to show a rough parallelism with the carcinogenic activity of the hydrocarbons.

1′,9-Methylene-1,2-benzanthracene (II, R = H) is an exception to this rule, the spectrum differing in several respects. Considerably more fine structure is present than in other disubstituted 1,2-benzanthracene hydrocarbons and is accompanied by a change in the character of the spectrum in the region of highest intensity. In the present paper the spectra of twenty-one further derivatives of 1,2-benzanthracene are published, including several containing functional as well as alkyl substituents.

Results.—The intensities and positions of the maxima of the compounds are summarized in Table I and Figs. 1–5. Purely on empirical grounds the spectra have been divided into three groups. Group I contains the compounds whose spectra closely resemble that of 1,2-benzanthracene itself. In this group the maxima have been distinguished by the letters A. . .K as has been done in previous papers.[3,6]

Group II contains two compounds whose spectra show more fine structure, particularly in the region of high intensity between 2700 and 3100 Å. and resemble that of 1′,9-methylene-1,2-benzanthracene. Group III contains the remaining compounds which cannot be included in the above categories. The experimental technique has previously been described.[3]

Discussion.—Examination of Table I shows that with the exception of the 1′,9-methylene derivatives all the hydrocarbons possess spectra of normal character. The intensities of the more prominent maxima (A, B, C, D, G, H, I) are approximately constant although differences are observed in the intensities of the other maxima particularly E and J; the latter is missing en-

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(1) Mayneord and Roe, *Proc. Roy Soc.* (London), **A152**, 299 (1935); **A158**, 634 (1937).

(2) Fieser and Hershberg, THIS JOURNAL, **60**, 940 (1938). For other examples see Fieser and Johnson, *ibid.*, **61**, 1647 (1939); Fieser and Hershberg, *ibid.*, **62**, 49 (1940).

(3) Jones, *ibid.*, **62**, 148 (1940). This paper includes curves of the spectra of 1,2-benzanthracene and 1,9-methylene-1,2-benzanthracene.

(4) Klingstedt, *Compt. rend.*, **175**, 1056 (1921).

(5) De Laszlo, *Z. physik. Chem.*, **118**, 369 (1929).

(6) Creech and Jones, THIS JOURNAL, **62**, 1970 (1940). This paper includes curves of the spectra of 1,2-benzanthryl-3-carbamidoacetic acid, 1,2-benzanthryl-10-carbamidoacetic acid, and ε-(1,2-benzanthryl-3-carbamido)-caproic acid.

TABLE I

WAVE LENGTHS (Å.) OF THE MAXIMA AND CORRESPONDING INTENSITIES (LOG E_{molar}) IN THE ULTRAVIOLET ABSORPTION SPECTRA OF DERIVATIVES OF 1,2-BENZANTHRACENE

Group I. Derivatives possessing spectra resembling that of 1,2-benzanthracene

Compound	Solvent	Absorption data A	B	C	D	E	F	G	H	I	I′	J	K
10-Methyl-3′-isopropyl-1,2-benzanthracene[a]	Ethanol	2615 (4.60)	2720 (4.63)	2830 (4.88)	2940 (4.99)	3035 (4.09)	3210 (3.66)	3370 (3.85)	3530 (3.93)	3725 (3.79)	..	..	3900 (2.61)
6-Methylcholanthrene[b,i]	Ethanol	2615 (4.63)	2755 (4.64)	2863 (4.83)	2975 (4.87)	3032 (4.45)	3238 (3.71)	3415 (3.89)	3598 (3.97)	3782 (3.83)	..	..	3945 (3.45)
6,20-Dimethylcholanthrene[b,i]	Ethanol	2610 (4.65)	2768 (4.65)	2868 (4.89)	2983 (4.98)	3044 (4.52)	3255 (3.69)	3430 (3.85)	3605 (3.92)	3800 (3.82)	..	..	3953 (3.51)
6,22-Dimethylcholanthrene[b,i]	Ethanol	2635 (4.64)	2780 (4.63)	2882 (4.78)	2985 (4.82)	3050 (4.43)	3310 (3.69)	3445 (3.80)	3600 (3.84)	3750 (3.75)	..	..	3970 (3.44)
1,2-Benzanthryl-10-isocyanate[c]	Hexane	2595 (4.56)	2720 (4.64)	2825 (4.89)	2940 (5.01)	..	3250 (3.66)	3430 (3.92)	3610 (4.02)	3805 (3.99)	..	..	3930 (3.45)
1,2-Benzanthryl-10-carbamidoacetic acid[c]	Aq. buffer *p*H 8	2600 (4.47)	2690 (4.58)	2800 (4.80)	2900 (4.90)	..	(3225) (3.55)	3360 (3.77)	3520 (3.82)	3675 (3.77)	..	..	..
9-Methyl-10-ethoxymethyl-1,2-benzanthracene[d]	Ethanol	2630 (4.56)	2715 (4.59)	2830 (4.85)	2940 (4.93)	..	(3250) (3.55)	3420 (3.83)	3600 (3.94)	3755 (3.84)	..	..	3960 (3.12)
10-Amino-1,2-benzanthracene hydrochloride[c,m]	2 *N* HCl in 50% aq. EtOH	2550 (4.40)	2700 (4.51)	2790 (4.70)	2895 (4.80)	3010 (3.97)	..	3350 (3.83)	3515 (3.89)	3655 (3.67)	3700 (3.74)	..	..
sym-Bis-(1,2-benzanthryl-10)-methyl disulfide[e,l]	Chloroform	[k]	2750 (4.56)	2855 (4.78)	2975 (4.82)	..	3300 (3.61)	3450 (3.84)	3625 (3.95)	3825 (3.88)	..	..	3935 (3.58)
7-Cholanthroic acid[f]	Hexane	2650 (4.65)		2850 (4.69)	2975 (4.75)	..	(3275) (3.82)	3440 (3.78)	3625 (3.89)	3810 (3.78)	..	..	3940 (3.52)
10-Nitro-1,2-benzanthracene	Ethanol	2645 (4.53)	2675 (4.65)	2770 (4.76)	2885 (4.78)	..	..	3350 (3.73)	3500 (3.76)	3680 (3.66)	..	..	3880 (3.44)

Group II. Derivatives possessing spectra similar to that of 1′,9-methylene-1,2-benzanthracene

	Max.	Intensity	Max.	Intensity
10-Methyl-1′,9-methylene-1,2-benzanthracene,[g] solvent ethanol	2590	4.56	3455	3.77
	2850	4.69	3575	3.91
	2920	4.72	3655	3.73
	2985	4.61	3735	3.79
	3100	3.84	3780	3.80
	3400	3.77	3940	3.70
1,2-Benzanthryl-3-isocyanate,[e] solvent hexane	2555	4.65	3170	3.77
	2760	4.67	3305	3.88
	2865	4.85	3460	3.94
	2970	4.85	3650	3.79
	3020	4.78		

Group III. Other derivatives

	Max.	Intensity	Max.	Intensity
1,2-Benzanthryl-3-carbamidoacetic acid,[c] aq. buffer soln., *p*H 8.3 + ethanol	2555	4.57	3290	3.82
	(2800)	4.58	3435	3.88
	2920	4.70	3615	3.81
	(3075)	4.33		
ε-(1,2-Benzanthryl-3-carbamido)-caproic acid,[c] aq. buffer soln., *p*H 8.3 + ethanol	2555	4.62	3290	3.82
	(2800)	4.65	3435	3.92
	2900	4.71	3625	3.84
	(3050)	4.43		
3-Amino-1,2-benzanthracene,[c] ethanol	2555	4.53	3460	3.92
	(2830)	4.59	3650	3.93
	2925	4.62	(4150)	3.36
	(3050)	4.42		
3-Amino-1,2-benzanthryl hydrochloride,[m] 2 *N* HCl in 50% aqueous ethanol	2550	4.59	(3145)	3.96
	2685	4.58	3275	3.77
	2780	4.76	3440	3.80
	2895	4.86	3540	3.67
	3005	4.17		
10-Amino-1,2-benzanthracene,[c] ethanol	2595	4.54	3025	4.64
	2900	4.60	4050	3.92
Hexane	2595	4.54	(3660)	3.70
	2900	4.64	3830	3.93
	3025	4.68	4050	3.96
	(3150)	3.70		
3-Hydroxy-1,2-benzanthracene,[h] ethanol	2550	4.57	3380	3.94
	2800	4.71	3550	3.89
	2880	4.73	3850	3.31
	3045	4.45	4070	3.33
	3235	3.87		

TABLE I (*Concluded*)

Compound	Max.	Intensity	Max.	Intensity
3-Methoxy-1,2-benzanthracene,[h] ethanol	2550	4.60	3200	3.85
	2770	4.74	3345	3.90
	2850	4.82	3505	3.74
	2955	4.56	3740	3.32
	3015	4.46	3950	3.34
3-Methoxy-10-methyl-1,2-benzanthracene,[j] ethanol	2585	4.60	3280	3.80
	2780	4.73	3430	3.88
	2900	4.80	3600	3.90
	3050	4.48	3780	3.42
			4020	3.35

Wave lengths in parentheses refer to points of inflection.

[a] Fieser and Clapp, THIS JOURNAL, in press. [b] Fieser and Bowen, *ibid.*, **62**, 2103 (1940). [c] Fieser and Creech, *ibid.*, **61**, 3502 (1939); Creech and Jones, *ibid.*, **62**, 1970 (1940). [d] Sandin and Fieser, *ibid.*, **62**, 3098 (1940). [e] Wood and Fieser, *ibid.*, **62**, 2674 (1940). [f] Fieser and Kilmer, *ibid.*, **62**, 1354 (1940). This paper includes a curve of the spectrum of 7-cholanthroic acid. [g] Fieser and Cason, *ibid.*, **62**, 432 (1940). [h] Prepared by Dr. H. J. Creech by method due to Fieser and Dietz, *ibid.*, **51**, 3141 (1929). [i] I am indebted to Dr. D. M. Bowen for permission to include his measurements on these compounds. [j] Prepared by Dr. H. J. Creech by method due to Fieser and Hershberg, *ibid.*, **59**, 1028 (1937). [k] Not measured due to the absorption of the solvent. [l] Calculated on a semi-molecular weight basis. [m] Calculated as ion.

tirely in several cases. In addition to the hydrocarbons, Group I includes 10-amino-1,2-benzanthracene hydrochloride while 3-amino-1,2-benzanthracene hydrochloride, although placed in Group III due to some differences in the region between 2950 and 3200 Å., is essentially similar; in marked contrast are the spectra of the un-ionized bases (Figs. 3, 4). The inclusion of 1,2-benzanthryl-10-isocyanate in Group I should also be noticed. If it is assumed that the deviations from the hydrocarbon type spectrum are due to interaction between the electrons of the substituent group with those of the ring structure this suggests that there can be little such interaction in this case in spite of the unsaturated nature of the isocyanate group.

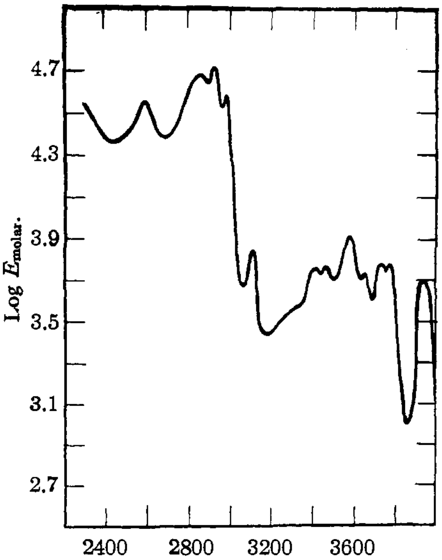
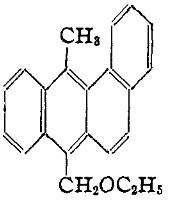
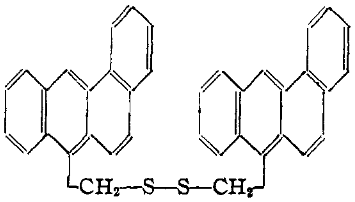


Fig. 1.—10-Methyl-1',9-methylene-1,2-benzanthracene.

Of the other compounds in Group I, the spectra of 9-methyl-10-ethoxymethyl-1,2-benzanthracene (III) and the disulfide (IV) are in accordance with expectation. In both these compounds the conjugated system of the benzanthryl group is separated from the ethereal oxygen atom or the disulfide group by a methylene group which is sufficient to inhibit any interaction effects,[7] so that any change in the spectrum due to the presence of the ethereal oxygen or the disulfide linkage will only be an additive one. The ether group has no chromophoric character (diethyl ether is trans-



III



IV

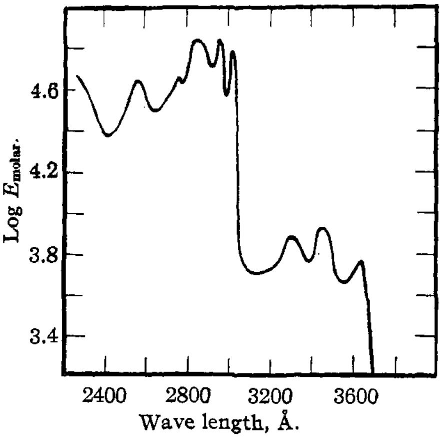


Fig. 2.—1,2-Benzanthryl-3-isocyanate.

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[7] Ramart-Lucas, *Bull. soc. chim.*, **51**, 289 (1932).

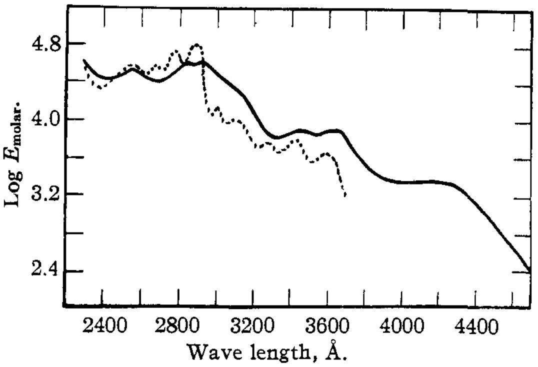

Fig. 3.— ———, 3-Amino-1,2-benzanthracene; - - - -, 3-amino-1,2-benzanthracene hydrochloride.

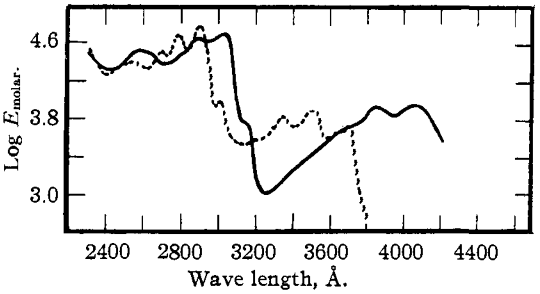

Fig. 4.— ———, 10-Amino-1,2-benzanthracene; - - - -, 10-amino-1,2-benzanthracene hydrochloride.

parent to 2200 Å.). The disulfide group in diethyl disulfide[8] has a maximum near 2500 Å. with an intensity log $E_{\text{molar}} = 2.6$. However, as the intensity in the 2500 Å. region due to the absorption of the benzanthryl group is of the order of log $E = 4$, the increase due to the additive effect of the disulfide group will be negligible. Furthermore, the relative contributions of the benzanthryl and the disulfide chromophores are in the ratio of 2:1.

The spectrum of 10-methyl-1′,9-methylene-1,2-benzanthracene (II, R = CH_3), Fig. 1, resembles the spectrum of 1′,9-methylene-1,2-benzanthracene as might be expected, but the somewhat similar spectrum of 1,2-benzanthryl-3-isocyanate, (Fig. 2) also showing abnormal structure in the 2700–3100 Å. region is surprising. The appearance of these spectra suggests that the D maximum has been split into two. In the 1′,9-methylene compounds this apparent splitting of the maxima extends to the longer wave length region but not with the 3-isocyanate.

The remaining compounds in Group III for the most part contain substituents at the 3-position. In the case of 1,2-benzanthryl-3-carbamidoacetic acid,[6] and ε-(1,2-benzanthryl-3-carbamido)-caproic acid[6] the spectra are normal at longer wave lengths but in the short wave length region there is a fall in intensity and loss of fine structure. This diminished intensity in the 2500–2900 Å. region is not common to all 3-substituted derivatives of 1,2-benzanthracene as the 6-methylcholanthrenes (which are 3-methyl derivatives in the 1,2-benzanthracene system of ring numbering) behave normally.

The 3-amino and 10-amino compounds differ considerably from the other derivatives. There is much less structure in the spectra and a broad band of low intensity extends well into the visible region, producing the yellow color.

The spectrum of 3-hydroxy-1,2-benzanthracene (Fig. 5) also shows some interesting differences. The resolution in the neighborhood of the two intense maxima (C and D) is diminished. A new prominent band (E ?) is present and at the long wave length end of the spectrum are two broad bands which may possibly be related to the J and K maxima of the hydrocarbon spectrum. The spectrum of 3-methoxy-1,2-benzanthracene is similar to that of the hydroxy compound except that the maxima lie at shorter wave lengths and more structure is resolved. The introduction of a 10-methyl group has the same effect on the 3-methoxy derivative as on the hydrocarbon causing a bathochromic shift and some loss of resolution.

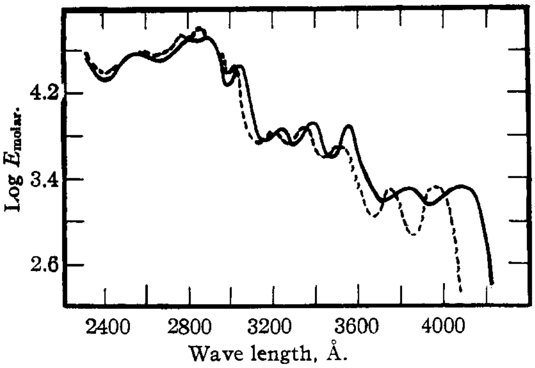

Fig. 5.— ———, 3-Hydroxy-1,2-benzanthracene; - - - -, 3-methoxy-1,2-benzanthracene.

Fluorescence.—Qualitative observations of the fluorescence of the majority of these compounds have been made, both in the solid state and in solution. The results are tabulated in Table II. The solids were exposed on microscope slides in a dark room the light source being a quartz mercury vapor lamp in conjunction with a Corex red-purple filter no. 986. The solutions

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(8) Ley and Arends, *Z. physik. chem.*, **B17**, 213 (1932).

TABLE II

FLUORESCENCE OF 1,2-BENZANTHRACENE DERIVATIVES

Compound	Solid	Solution (100 γ per ml. in ethanol)
10-Methyl-3′-isopropyl-1,2-benzanthracene	++ blue	+++ violet
10-Methyl-1′,9-methylene-1,2-benzanthracene	+ blue	++++ blue-violet
6-Methylcholanthrene	+++ pale blue	+++ violet
7-Cholanthroic acid	None	+++ green-yellow
1,2-Benzanthryl-10-isocyanate	None	None[a]
1,2-Benzanthryl-3-isocyanate	++ green-yellow	++ violet[a]
10-Amino-1,2-benzanthracene	++ green-yellow	+++ green-yellow
10-Amino-1,2-benzanthracene hydrochloride		+++ green-yellow[b]
3-Amino-1,2-benzanthracene	+++ green-yellow	++++ green-yellow
3-Amino-1,2-benzanthracene hydrochloride		++++ green-yellow[b]
10-Nitro-1,2-benzanthracene	None	None
1,2-Benzanthryl-10-carbamidoacetic acid	None	+++ blue-violet[c]
1,2-Benzanthryl-3-carbamidoacetic acid	None	++++ blue[d]
ε-(1,2-Benzanthryl-3-carbamido)-caproic acid	+++ blue	++++ blue[d]
3-Hydroxy-1,2-benzanthracene	None	++++ blue
3-Methoxy-1,2-benzanthracene	++ green-yellow	++++ blue
3-Methoxy-10-methyl-1,2-benzanthracene	++ green-yellow	++++ blue-violet
3-Hydroxy-1,2-benzanthracene (sodium salt)		++++ yellow
sym-Bis-(1,2-benzanthryl-10)-methyl disulfide	+ yellow	None[e]

[a] Solvent hexane. [b] Solvent 2 *N* HCl in 50% aqueous ethanol. [c] Solvent buffer *p*H 8.3. [d] Solvent buffer *p*H 8.3 + ethanol. [e] Solvent chloroform.

(concn. 100 γ per ml.) were exposed in quartz tubes. All the compounds showed fluorescence in solution with the exception of the 10-nitro, 10-isocyanate and the disulfide derivative; the 3-isocyanate fluoresced quite strongly. The fluorescence of the 3-amino compound was not distinguishable visually from that of the 3-amino hydrochloride nor was that of the 10-amine from that of the 10-amine hydrochloride. The fluorescence of the 3-hydroxy compound changed from blue to a pure yellow on adding aqueous sodium hydroxide solution.

Conclusions.—The presence of one or several alkyl substituents does not effect the spectrum of 1,2-benzanthracene apart from producing a bathochromic shift and some loss of fine structure. Derivatives with a 1′,9-methylene bridge are an exception to this rule and in view of this exception care should be exercised in the use of absorption spectra as a means of characterizing aromatic ring structures. However, even in these exceptional cases there still remains a considerable similarity which may be sufficient to suggest a preferred structure.

The introduction of functional groups may produce larger changes. Amino, hydroxy and methoxy groups cause appreciable modification of the spectrum, the isocyanate, nitro and carboxylic acid groups a lesser change. The spectrum of the positively charged amine ion resembles that of the hydrocarbon much more closely than does the spectrum of the un-ionized base. This effect is at present being examined in several other aromatic series and seems to be a general one.

Acknowledgment.—The author wishes to thank Prof. L. F. Fieser for his encouragement and advice during the progress of this work, the International Cancer Research Foundation for financial support and Mr. Lyon Southworth for micro-weighings.

Summary

The absorption spectra of twenty-one derivatives of 1,2-benzanthracene are recorded and classified according to their qualitative resemblance to the spectrum of the unsubstituted hydrocarbon. Qualitative observations on the fluorescence of the majority of the compounds are also included.

CONVERSE LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

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