CXVIII.—*The Absorption Spectra of Anthracene Derivatives. Part I.*

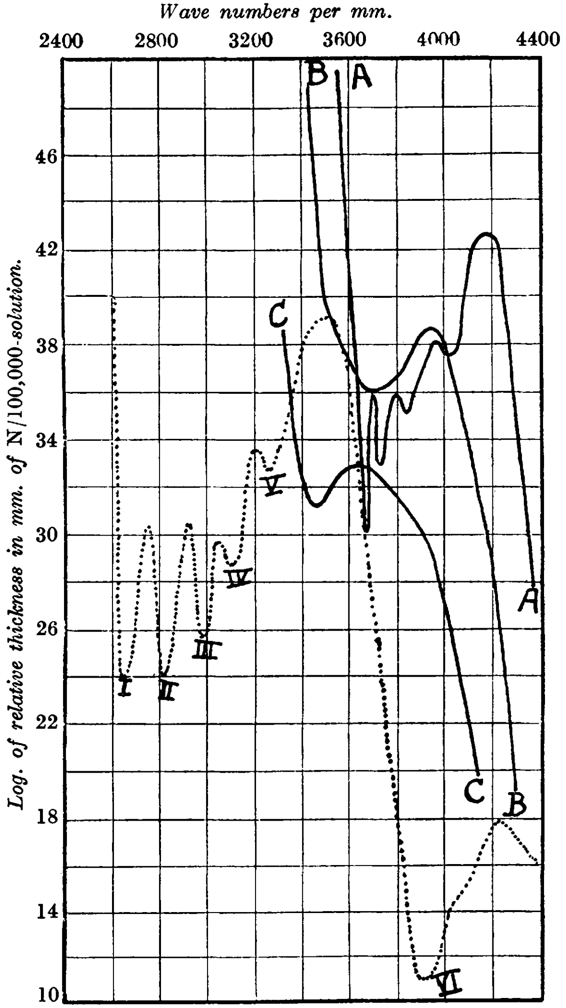
By Edward de Barry Barnett, James Wilfred Cook, and Thomas Eric Ellison.

The study of the valency problem presented by the *meso*-carbon atoms of anthracene has led to the discovery of many apparently anomalous reactions, the interpretation of which by purely chemical methods is difficult. It is proposed, therefore, to consider the evidence afforded by spectrophotography; and in the first place the effect produced on the spectrum by certain modifications of the molecule will be discussed.

Anthracene itself has been examined by numerous investigators. The absorption spectrum of the alcoholic solution, as obtained by the Hartley method, shows six bands (Fig. 1), each subdivisible by more refined methods into two or more components (Capper and Marsh, J., 1926, 724); for ease of reference these are numbered I to VI in the figure and in the table. There is an approximately constant frequency difference between each of the bands I to V. As long as the so-called " bridge " bond is present, the introduction of other groups into the *meso*-positions of anthracene has remarkably little effect on the spectrum. The mass of the substituent has an almost negligible influence on the amount of the displacement, one alkyl, alkyloxy, phenyl or benzyl group moving the spectrum as a whole 60—80 units of frequency towards the visible region, the position of band VI always being altered less than the positions of bands I to V. Thus the band heads of 9-methyl- and 9-benzylanthracene are at the same frequencies. In these *meso*-substituted derivatives band II is slightly more persistent than band I, the reverse being the rule elsewhere. The introduction of a second substituent causes a further shift of about 70 units towards the visible region, corresponding bands of anthracene and 9-methyl-

10-phenylanthracene, for example, having a frequency difference of about 140 units. In these 9 : 10-disubstituted anthracenes band V ceases to be detectable.

FIG. 1.



····· *Anthracene.* B 1 : 5-*Dichloro*-9 : 10-*dihydroanthraquinol.*
A 9 : 10-*Dihydroanthracene.* C 1 : 5 : 9 : 10-*Tetrachloro*-9 : 10-*dihydroanthracene.*

1 : 5-Dichloroanthracene and a few of its mono- and di-substitution products have also been examined. The effect of the chlorine atoms is to move the whole spectrum towards the visible region, bands I to V being moved 90—95 units and band VI about

30 units in accordance with the above-mentioned rule that the position of band VI is invariably less affected by substitution than are the other five. No other alteration of the spectrum is observed, despite the profound influence of α-chlorine atoms on the chemical behaviour of the *meso*-carbon atoms. The effects of further substitution on the spectrum of 1 : 5-dichloroanthracene are similar to those found with anthracene itself.

9 : 10-Dihydroanthracene has been examined by Baly and Tuck (J., 1908, **93**, 1902), but the evident impurity of their specimen has made a re-examination desirable, and it has now been found that the spectrum resembles that of an alkyl derivative of benzene, four major band heads being detectable at 3660, 3730, 3830, and 4020 (Fig. 1). The effect of reduction on the fluorescence and absorption of anthracene is therefore analogous to that found in the acridine series (Dobbie and Tinkler, J., 1905, **87**, 269). In the allied substances 1 : 5 : 9 : 10-tetrachloro-9 : 10-dihydroanthracene and 1 : 5-dichloro-9 : 10-dihydroanthraquinol, the complex band system of the more symmetrical dihydroanthracene is fused into a single broad band, which on account of the mass of the substituents is nearer to the visible region than are the bands of dihydroanthracene itself. Evidently the curve of this class of derivative has no detail in common with that of anthracene.

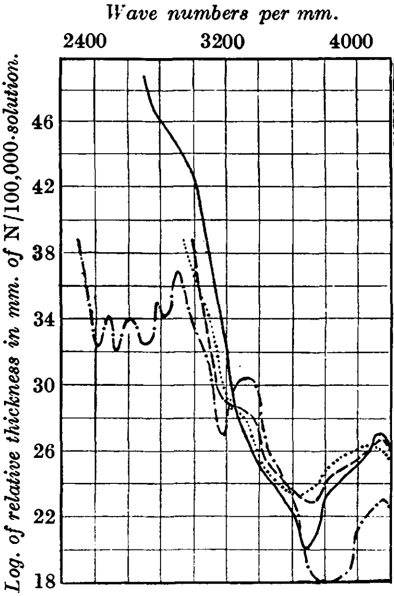
The anthrones present a third type of derivative and a few of these have been examined. Anthrone itself, being in tautomeric equilibrium with anthranol, may be expected to possess a complex spectrum, but where, by replacement of the methylene hydrogen atoms by non-mobile groups, the possibility of such tautomeric change is excluded, a characteristic curve containing one broad, indefinite and shallow band is obtained. The spectra of 9 : 9-dimethyl-, 9 : 9-diphenyl-, and 9 : 9-dibenzyl-anthrone are shown in Fig. 2.

The Mechanism of Bromination of meso-*Alkylanthracenes.*—The facile formation of ω-bromo-derivatives of 9-alkyl- and 9 : 10-dialkyl-anthracenes has been discussed elsewhere (Barnett, Cook, and Matthews, *Ber.*, 1926, **59**, 1429, 2863; 1927, **60**, 2353, 2366), and an explanation suggested based on the possible transannular tautomerism according to the scheme :

$$C_6H_4<\overset{C\cdot CH_3}{\underset{CH}{|}}>C_6H_4 \rightleftharpoons C_6H_4<\overset{C{:}CH_2}{\underset{CH_2}{}}>C_6H_4$$

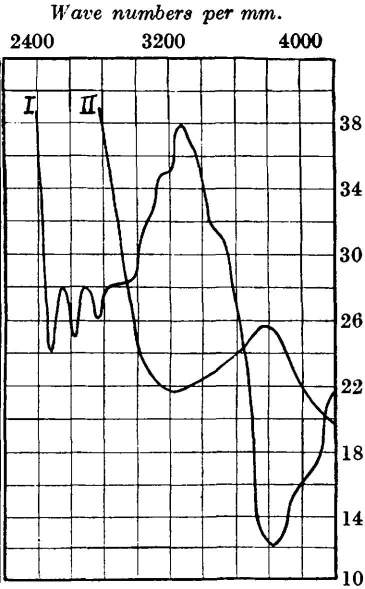
The presence of the methylene phase would readily account for the side-chain bromination by addition of bromine to the double bond and elimination of hydrogen bromide across the ring. More definite evidence of this type of tautomerism has been sought in a study of the spectra of the *meso*-alkylanthracenes, since a tautomeric change of this type might be indicated spectroscopically in two ways, *viz.*, the curve might show bands characteristic of both the extreme phases of the oscillation, and it might show modifications due to the actual oscillation itself. The point may be illustrated by

FIG. 2.



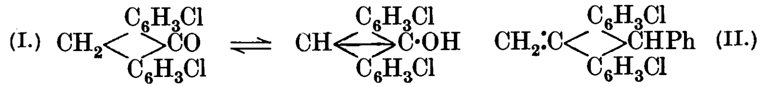
——— 9 : 9-*Dimethylanthrone.*
· · · · · 9 : 9-*Diphenylanthrone.*
— — — 9 : 9-*Dibenzylanthrone.*
— · — · — 1 : 5-*Dichloroanthrone.*

FIG. 3.



I *Yellow derivatives of* 1 : 5-*dichloro*-9-*benzylanthracene* (*formula V*).
II *Colourless derivatives of* 1 : 5-*dichloro*-9-*benzylanthracene* (*formula III or IV*).

reference to 1 : 5-dichloroanthrone (I), the curve of which is shown in Fig. 2.

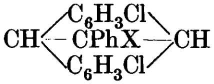


$$\text{(I.)}\ CH_2\!<\!\begin{matrix}C_6H_3Cl\\ \\ C_6H_3Cl\end{matrix}\!>\!CO \rightleftharpoons CH\!\lessgtr\!\begin{matrix}C_6H_3Cl\\ \\ C_6H_3Cl\end{matrix}\!\gtrless\!C{\cdot}OH \qquad CH_2{:}C\!<\!\begin{matrix}C_6H_3Cl\\ \\ C_6H_3Cl\end{matrix}\!>\!CHPh\ \text{(II.)}$$

In this the anthracene bands are well marked, although less persistent than usual. The band with head at 3850 is of distinctly anthrone type, whereas the band with head at 3190 is possibly due to the tautomeric change.

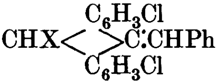
The spectra of the alkylanthracenes which possess the property of easy side-chain bromination have been examined along with those of certain other *meso*-substituted anthracenes such as 9-methoxy- and 9-acetoxy-anthracene for the purposes of comparison, but a deviation from the normal the occurrence of which would support the hypothesis of transannular tautomerism has not been detected. The spectra have also been examined in the presence both of hydrochloric acid and of sodium ethoxide, but neither acid nor alkali produces any observable effect. The very nature of the method, however, makes it impossible to say that tautomerism does not occur, particularly as selective absorption can scarcely be detected in 1 : 5-dichloro-10-phenyl-9-methylene - 9 : 10 - dihydroanthracene (II), the only compound known definitely to have the methylene structure which has been examined up to the present.

Derivatives of 1 : 5-*Dichloro*-9-*benzylanthracene.*—It has been shown (Barnett, Cook, and Matthews, *loc. cit.*) that 1 : 5-dichloro-9-benzylanthracene yields two series of isomeric derivatives, *viz.*, a colourless series obtained by direct replacement of the bromine atom in the bromo-compound (of which only one isomeride is known) and a yellow series obtained from the colourless compounds by isomeric change. An examination of the absorption spectra of the bromo-compound and of the colourless hydroxy- and methoxy-compounds (curve II, Fig. 3) has shown that the curves are indistinguishable from one another in the region examined (solutions of the bromo-compound could not be examined in higher concentration than $M/10{,}000$ on account of its instability and slight solubility). This is in agreement with the view already expressed, that the bromo-compound has a structure corresponding to that of the colourless series. The absorption curve, however, does not lead to a decision between the alternative structures (III and IV) suggested for these colourless compounds, as reference compounds of the two types are not available at present :



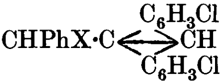
$$\mathrm{CH}\overset{\diagup\mathrm{C_6H_3Cl}\diagdown}{\underset{\diagdown\mathrm{C_6H_3Cl}\diagup}{-\mathrm{CPhX}-}}\mathrm{CH}$$

(III.)



$$\mathrm{CHX}<\overset{\mathrm{C_6H_3Cl}}{\underset{\mathrm{C_6H_3Cl}}{}}>\mathrm{C{:}CHPh}$$

(IV.)



$$\mathrm{CHPhX{\cdot}C}\overset{\mathrm{C_6H_3Cl}}{\underset{\mathrm{C_6H_3Cl}}{\Longleftrightarrow}}\mathrm{CH}$$

(V.)

The yellow hydroxy- and methoxy-compounds, on the other hand, give curves (curve I, Fig. 3) of the true " anthracene " type which are indistinguishable from that of 1 : 5-dichloro-9-benzylanthracene, and this is in harmony with the chemical evidence of the formula (V) already given to these compounds.

The indiscriminate manner in which special structures, especially quinonoid, are assigned to organic compounds for no other reason than the possession of visible colour makes it of interest to note that in all the " bridge " compounds dealt with in this communication the electronic structure of the anthracene complex remains the same although the visible colour ranges from colourless in the case of anthracene to greenish-yellow in the case of some of the derivatives of 1 : 5-dichloroanthracene.

The greatest care has been taken to obtain all the substances used as pure as possible, every sample having been repeatedly recrystallised after the melting point had become constant. All the spectra were taken in ethyl-alcoholic solution.

Table of Bands.

Substituents.				Oscillation frequencies.					
1	5	9	10	I.	II.	III.	IV.	V.	VI.
				2660	2810	2970	3100	3250	3930
		COPh		2610	2750	2890	—	3180	3910
		OAc		2600	2740	2890	3020	3170	3890
		Ph		2600	2730	2880	3000	3170	3860
		OMe		2580	2730	2870	3000	3160	3860
		Me		2580	2720	2850	2990	3160	3850
		CH_2Ph		2580	2720	2850	2990	3160	3850
		Pr^β		2580	2730	2870	2990	3140	3850
		iso-C_5H_{11}		2570	2720	2850	2990	3140	3850
Cl	Cl			2570	2720	2850	2990	3140	3900
		Me	Ph	2520	2670	2820	2980	—	3840
		Ph	Ph	2520	2670	2820	2980	—	3840
		iso-C_5H_{11}	Ph	2520	2660	2820	2970	—	3840
Cl	Cl	OAc		2510	2650	2790	2970	—	3890
Cl	Cl	Me		2490	2630	2760	—	—	3850
Cl	Cl	CH_2Ph		2490	2620	2760	—	—	3830
Cl	Cl	CH(OH)Ph		2490	2620	2760	—	—	3830
Cl	Cl	CH(OMe)Ph		2490	2620	2760	—	—	3830
Cl	Cl	CH_2Br		2430	2550	—	—	—	3790
Cl	Cl	Ph	CH_2Ph	2420	2530	2680	2830	?	3760
Cl	Cl	Anthrone *		2420	2530	2680	2820	—	—

* 1 : 5-Dichloroanthrone also has bands at 3190 and 3850.

The authors' thanks are due to Professor A. W. Stewart for the interest he has taken in this work.

THE SIR DONALD CURRIE LABORATORIES,
QUEEN'S UNIVERSITY, BELFAST.
SIR JOHN CASS TECHNICAL INSTITUTE,
JEWRY STREET, E.C. 3.

[*Received, January* 14*th*, 1928.]