

## CI.—*Absorption Spectra of Condensed Nuclear Hydrocarbons.*

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It was shown recently that visible absorption bands attributed to anthracene were due to an impurity, chrysogen (*J. Amer. Chem. Soc.*, 1925, **47**, 2847). It has now been found that other coal-tar hydrocarbons have been insufficiently purified for spectroscopic examination. Thus the four chief hydrocarbons boiling between 275° and 360° cannot be separated by crystallisation, as they appear to form mixed crystals. In particular, fluorene and phenanthrene retain traces of anthracene, which can be detected by its intense ultra-violet absorption. The absorption bands of the purified substances exhibit constant frequency differences, which have been attributed to the double carbon bond in the aromatic series (Marsh, *Phil. Mag.*, 1925, **49**, 971, 1206). Other synthetic hydrocarbons also have been examined.

*Purification of Phenanthrene and Fluorene from Anthracene.*—A good commercial phenanthrene showed anthracene bands of an intensity corresponding with a content of about 16%, and this was not greatly reduced by fractional crystallisation. The melting point gives no trustworthy information as to the purity. In the fluorene used, the anthracene content was not more than 1 or 2%.

Purification of both substances was effected by refluxing a strong xylene solution by the heat from a silica mercury vapour lamp. The light caused the anthracene present to polymerise, even in glass vessels. Owing to its very slight solubility, the dianthracene produced was readily separated, but since anthracene and dianthracene attain to an equilibrium repeated light treatments and separations were necessary. About 1% of anthracene was thus eliminated from Kahlbaum's "purest reagent" phenanthrene. The spectra of the purified products examined in concentrated chloroform solutions indicated an anthracene content of about 0.01% in the phenanthrene and 0.001% in the fluorene. The melting point of the fluorene was 114—114.5°, a value higher than that commonly accepted. The phenanthrene melted at 98°. The higher values usually quoted probably result from the eutectic mixture with anthracene containing very nearly 100% of phenanthrene. The purified material in both cases lost its visible fluorescence, even in strong actinic light, or in the case of phenanthrene at most only a slight trace remained.

*The absorption spectra* were studied with a Hilger spectrophotometer and condensed copper spark. Little description will be

necessary if the absorption curves, the photographic reproductions, and the table of band positions are examined.

*Phenanthrene*.—Previous spectroscopists have used specimens containing from 0.3% (Baly and Tuck, J., 1908, **93**, 1902) to upwards of 10% of anthracene, masking completely the true spectrum, which in the region above 3000 Å. is some 25 times weaker than that of anthracene. Probably the small narrow band recorded at about  $1/\lambda 4000$  is due to the remaining trace of anthracene, and a very faint band at  $1/\lambda 3120$  to acenaphthene.

*Fluorene*.—A band found at  $1/\lambda 3117$  may be ascribable to the presence of 1% of acenaphthene.

*Anthracene, 9-phenylanthracene, and 1:2-benzanthracene* have very similar spectra. Relatively to those of anthracene, 9-phenylanthracene has its bands shifted about 60 units towards the visible spectrum, and they are not so distinct. In 1:2-benzanthracene, the weaker member of each pair appears on the red side of the strong band, but the first pair is very weak. In the middle ultra-violet, bands corresponding to those found in phenanthrene are seen. The structure may be regarded as 2:3-benzphenanthrene.

On examining anthracene vapour (20 cm.) at 50° to 120°, both of the strongest bands were seen to have a weak neighbour on each side, and there was also a faint band midway between the two strong ones. The bands were shifted almost 100 units with respect to their solution positions.

*Octahydroanthracene* lacks entirely the set of bands above  $\lambda 3000$  found in anthracene, but has several at about  $1/\lambda 3500$  to 3700, *i.e.*, in the same region as those in other alkyl derivatives of benzene.

*Bisdiphenylene-ethylene*,  $(C_6H_4)_2C:C(C_6H_4)_2$ , showed only a broad band in the blue region, an undeveloped one at about  $1/\lambda 3600$ , and another at about 4100.

*Chrysofen*.—This substance of unknown structure occurring in small quantities—probably less than 0.1%—in most samples of anthracene has an anthracene nucleus, since it is capable of polymerising similarly to anthracene itself. Its spectrum is distinctly of the polynuclear hydrocarbon type. In fused anthracene the band positions are 60—80 Å. nearer the red end of the spectrum.

*Other Polynuclear Hydrocarbons*.—In the substances examined, except fluorene and octahydroanthracene, every carbon atom has an unsatisfied valency, and except for bisdiphenylene-ethylene the unsaturation is entirely aromatic in character. Leaving aside these three, the chief feature of the spectra is a series of rather narrow bands between  $\lambda 3000$  and 4000, which show a constant frequency difference of about 142 waves/mm. Previous workers have examined other hydrocarbons which come into the same

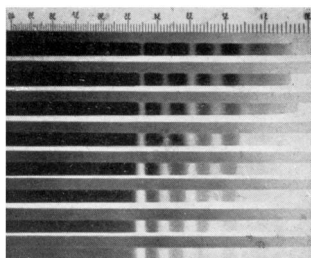
category. These substances also exhibit narrow bands, although the interval may vary. The absorption bands of benzene vapour are spaced 92.4 units apart (Henri, *J. Phys. Radium*, 1922, **3**, 181) and the emission bands at 98.7 unit intervals (J., 1923, **123**, 642). Naphthalene vapour shows a long series of bands, both absorption (Henri and László, *Proc. Roy. Soc.*, 1924, *A*, **105**, 662) and emission (Dickson, *Z. wiss. Photochem.*, 1912, **10**, 166), at 47.4 unit intervals. The emission spectrum shows every third band stronger than its neighbours, making an interval of 142 as in anthracene, etc. Baly and Tuck found in chrysene (J., 1908, **93**, 1902) four bands as nearly as can be determined at 140 unit intervals. A partial examination of picene, 2 : 3 : 6 : 7-dibenzanthracene, and  $\beta\beta$ -dinaphthyl was made by Homer and Purvis (J., 1908, **93**, 1319).

## TABLE OF BANDS.

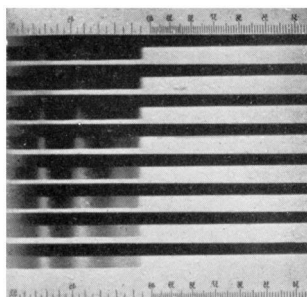
The figures are oscillation frequencies, and in italics are the frequency intervals. Small bands detected but difficult to locate accurately have been omitted.

Anthracene.	2661	2701 <i>143</i>	2804	2844 <i>143</i>	2947	2994 <i>143</i>	3090
		<i>103</i>		<i>103</i>		<i>96</i>	
	3133 <i>141</i>	3231	3231	3373 <i>142</i>	3960 <i>6 \times 98</i>	4058 <i>98</i>	
		<i>98</i>					
Vapour.	2725	2759	2797	2830	2864	2899	2934
	(2759 and 2899 correspond to solution bands 2666 and 2804.)						
Phenanthrene.		2895	2958 <i>138</i>	3033	3100 <i>138</i>	3171 <i>142</i>	3243 <i>140</i>
		3415 <i>140</i>	3555 <i>99</i>	3654	3787	3990 <i>2 \times 101</i>	4132 <i>142</i>
9-Phenylanthracene.	2603 <i>140</i>	2743 <i>140</i>	2883 <i>140</i>	3024 <i>141</i>	3917		
1 : 2-Benzanthracene.	2599	2670 <i>140</i>	2740	2787	2826 <i>143</i>		
	2930 <i>140</i>	3070	3339	3479 <i>140</i>			
Chrysogen.	2105 <i>142</i>	2247 <i>142</i>	2389				
Fluorene.	3117 ?	3333	3426	3820			
Octahydroanthracene.	3268	3333	3506	3580	3629	3686	
Bisdiphenylene-ethylene.	2190	3610	4130	(All broad and indefinite)			

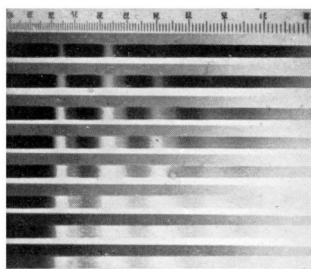
Benzene and the other eight condensed nuclear hydrocarbons all have the same type of multiple narrow-banded spectra, the main intervals being generally 142 units in the heavier molecules, 142 or 142/3 in naphthalene, and  $142 \times \frac{2}{3}$  in benzene. The simple methyl and other derivatives may also give spectra consisting of



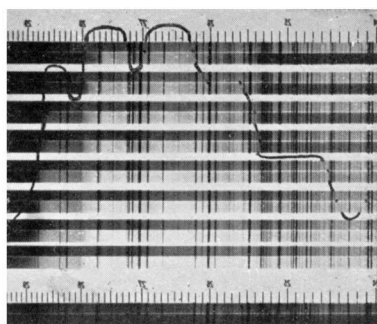
Phenanthrene. 1 cm.  $M/200$ .



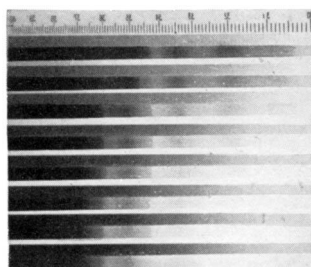
Chrysogen in 4 cm. of  
 $M/10$ -anthracene.



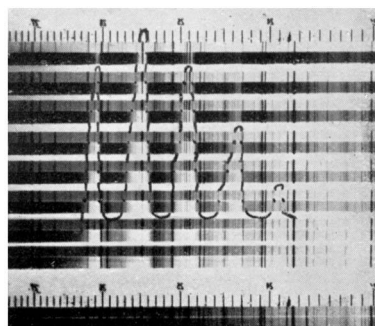
Anthracene. 1 cm.  $M/5000$ .



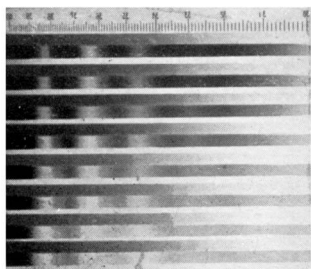
Naphthalene. 1 cm.  $M/5000$ .



1 : 2-Benzanthracene.  
1 cm.  $M/5000$ .



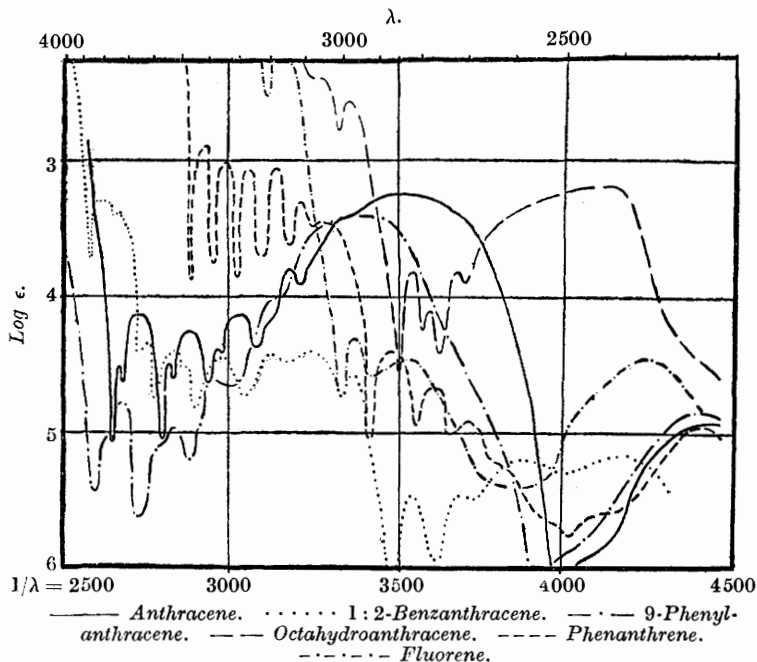
Benzene. 1 cm.  $M/200$ .



9-Phenylanthracene.  
1 cm.  $M/5000$ .

a number of narrow bands, but the regularity and sharpness are usually less marked, *e.g.*, László (*Z. physikal. Chem.*, 1925, **118**, 369) finds band series at the intervals 154, 142.5, 147, and 138, for 1-methyl-, 2-methyl-, 2:7-dimethyl-, and 2:6-dimethylnaphthalene, respectively. In phenanthrene alternate bands are similar and show the interval 142, the intermediate ones being not quite centrally situated.

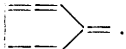
FIG. 1.



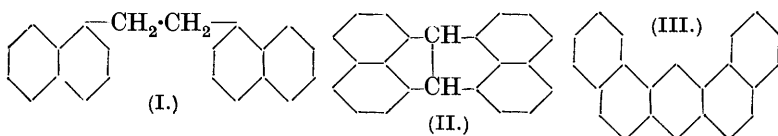
Besides the series of five or six bands already mentioned, most of the substances give other bands farther in the ultra-violet and of greater intensity. There is usually one well marked, with, on the more refrangible side, other less distinct bands, again at intervals of 142 units. Phenanthrene and 2:3-benzphenanthrene (1:2-benzanthracene) have also a third intermediate region.

#### *Discussion of Results.*

By removing all anthracene from phenanthrene and fluorene, entirely new absorption curves for these two substances have been found. Fluorene now gives a spectrum similar to that of *o*-xylene or other simple substituted benzene derivative. Phen-

anthrene presents a spectrum differing from that of anthracene in strength, band position, and arrangement. Hyatt (*Physical Rev.*, 1922, **19**, 391), employing the same methods as ours, measured 16 bands for anthracene. Three of these not now observed were possibly due to phenanthrene. We do not find that the remainder can be divided into a series at intervals of 147 and another at 142. Both our series run at intervals of 142. The spectral type of bis-diphenylene-ethylene differs completely from that of the other polynuclear hydrocarbons. The strong red colour is associated with the ethylenic bond, disappearing on its reduction, and it constitutes with its neighbours the characteristic system of the visibly coloured fulvenes, .

The spectrum of stilbene, the simplest example of a substance containing an ethylenic bond between benzene nuclei, consists of a single broad band at about  $\lambda 3300$ : in phenanthrene this double bond becomes aromatic, and half-a-dozen narrow bands occupy the same region. Thus the effect of an ethylenic bond is to cause the fusion of the aromatic bands. Another substance having an absorption curve very similar to those of bisdiphenylene-ethylene and stilbene and in a position intermediate between them was examined by Purvis and Homer (J., 1909, **97**, 1155). It was a product of the reaction between tetrabromoethane and naphthalene. They concluded, largely on spectroscopic evidence, that it was 1:2:7:8-dibenzanthracene. Its spectrum, however, is entirely different from what we have found for 1:2-benzanthracene and would be the only deviation from the type characteristic of the class of substances to which their formula would relegate it. Ethylene dibromide and naphthalene were considered to give rise to *s*-di- $\alpha$ -naphthylethane (I), which then broke down to picene. Tetrabromoethane and naphthalene might therefore give rise to the substance (II), and this would be much more likely to give a spectrum with broad bands than would a substance having the suggested formula (III).



*Relationship to Infra-red Spectra.*—It does not seem possible to offer any detailed explanation of the differences which make all these closely related spectra individually characteristic, but the cause of the similarity constituting the spectral type found in this

group of hydrocarbons must be some common factor, and therefore one or more of the following: (a) a benzene ring, (b) a C=C linking, (c) a CH<sub>2</sub> group. These possibilities will be considered with reference to the known features of the infra-red spectra of these or similar substances. Coblenz (*Carnegie Inst. Publication*, No. 35, 1905), from a study of some thirty hydrocarbons, concluded that characteristic absorption maxima due to methyl and methylene groups are found at 3.43, 6.86, 13.6—13.8, and 14  $\mu$ . Weniger (*Physical Rev.*, 1910, **31**, 388) gives also a band at 7.3  $\mu$ . In the aromatic series, Coblenz gives the following bands as characteristic of benzene: 3.25, 6.75, 8.68, 9.8, 11.8, and 12.95  $\mu$ . The first two and the last are identifiable with bands in hydrocarbons of the aliphatic series, but, owing to the unsaturation of the carbon atom of the CH<sub>2</sub> group, their frequency is increased somewhat. Thus the 3  $\mu$  band has the value 3.08 for acetylene, 3.25 for benzene, 3.28 for ethylene, and 3.39 for ethane.

The strongest bands of ethylene are:

$\lambda$ .....	( 21 )	10.5	6.98	5.3	3.28
$1/\lambda$ .....	( 47.6 )	95.24	143.3	188.9	304.9
Diff. ....		47.6	48.1	45.6	—

Except the last, these are evidently multiples of a band which should occur at  $1/\lambda 47.6$ , and may be considered as due to C:C. In benzene vapour, is a series of bands at intervals of 15.9, *i.e.*,  $47.6/3$ ; in naphthalene, the series interval is 47.4 and in the heavier hydrocarbons 142, *i.e.*,  $47.4 \times 3$ . The ethylene band 6.98  $\mu$  occupies also the position of a CH<sub>2</sub>-band. The fifteen aliphatic hydrocarbons examined by Coblenz show, as consistently the most prominent in their spectrum, two bands at about 6.86 and 7.33  $\mu$ . The frequencies (145.8—136.4 waves/mm.) are just what are found to be the intervals between the ultra-violet bands of the polynuclear hydrocarbons. Experimental difficulties have prevented thorough investigation of the infra-red spectra of the solid aromatic hydrocarbons. Stang (*Physical Rev.*, 1917, **9**, 342), however, has examined naphthalene and several of its derivatives and finds a band at 7.19  $\mu$  ( $1/\lambda 139.1$ ) to be among the strongest in the spectrum. It remains therefore an open question as to whether this common frequency difference is due to CH<sub>2</sub> or C:C, but probably it is a frequency to which both can resonate and for this cause it dominates the infra-red and ultra-violet spectra. Indeed, if any sort of harmonic motion is to be preserved in the molecule, it is necessary that different oscillations should be in tune with one another, and that the relative frequencies must be expressible as whole numbers.

We are much indebted to Mr. E. de B. Barnett for supplying very pure samples of the three anthracene derivatives examined.

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