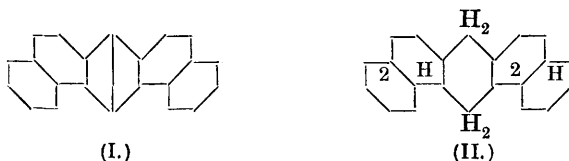


XCVII.—*The Absorption Spectra of Dinaphthanthracene and its Hydro-derivative Compared with the Absorption Spectra of its Isomerides.*

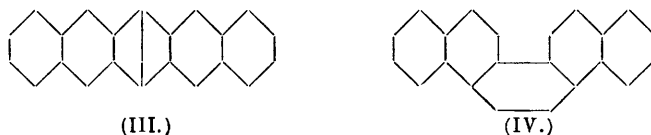
By ANNIE HOMER and JOHN EDWARD PURVIS.

A SPECTROSCOPIC examination of the hydrocarbon, $C_{22}H_{14}$, melting at $267\cdot5^{\circ}$, considered to be $\alpha\beta\alpha'/\beta'$ -dinaphthanthracene (I), together



with its hydride melting at $178\cdot5^{\circ}$ (II), which may be either the hexahydride, $C_{22}H_{20}$, or the octahydride, $C_{22}H_{22}$, described in the preceding paper, should furnish additional evidence as to the presence of an anthracene linking in the parent substance. The destruction of an anthracene cross-linking caused by the reduction of the hydrocarbon, $C_{22}H_{14}$, to a hexa- or octa-hydro-compound should be evidenced by some distinctive differences in the absorption spectra.

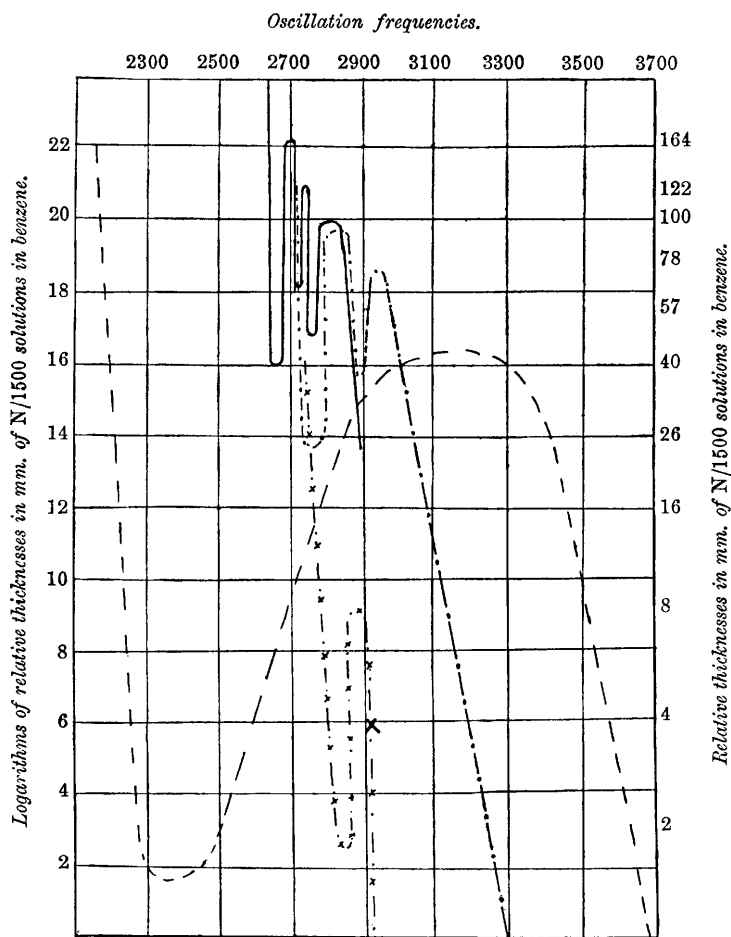
At the same time a comparison of the absorption spectra of Hartenstein's compound, which, from its method of formation, must have the $\beta\beta'\beta'$ -configuration, and of the $\alpha\beta\alpha'/\beta'$ -dinaphthanthracene (m. p. $267\cdot5^{\circ}$) and of its hydride (m. p. $178\cdot5^{\circ}$) might indicate whether his substance is a dinaphthanthracene, or, as has been suggested, a dihydrodinaphthanthracene, presumably a derivative in which the anthracene cross-linking no longer exists. The configuration of Hartenstein's compound, if a dinaphthanthracene, would be expressed by (III). Further, the absorption curves



of these substances were also compared with those of picene, for the latter substance is characterised by the absence of an anthracene linking, its constitutional formula being represented by (IV).

The experimental conditions of the investigation were the same as those employed in the investigation of the absorption spectra of

picene, tetramethylpicene, and Hartenstein's compound (Homer and Purvis, *Trans.*, 1908, **93**, 1319). Solutions in benzene of *N*/1500-strength of the hydrocarbons were used. The resulting absorption



Full curve : *N*/1500-solution of picene in benzene.
 Dash curve : *N*/1500-solution of $C_{22}H_{14}$ (*m. p.* 267·5°) in benzene.
 Dot and dash curve : *N*/1500-solution of $C_{22}H_{20}$ in benzene.
 Dot, cross, and dash curve : *N*/1500-solution of Hartenstein's $C_{22}H_{14}$ in benzene.

spectra have been plotted in the accompanying curves, so that the abscissæ represent the oscillation frequencies, and the ordinates the logarithms of the relative thicknesses of the solutions.

It will be noticed that the supposed $\alpha\beta\alpha'\beta'$ -dinaphthanthracene

exhibits one large persistent band, which commences about 2360 (oscillation frequency). The absorption band at all thicknesses includes that portion of the visible spectrum commencing between the green and blue solar lines F and G, and this accounts for the persistent yellow colour of the hydrocarbon. Solutions of the hydrocarbon have a green fluorescence.

The hydride of $C_{22}H_{14}$ has a different type of curve from that of the parent substance. It is characterised by two bands in the ultra-violet region of the spectrum, which commence about 2760 and 2880 (oscillation frequencies).

These results strengthen the supposition that the process of reduction has produced some fundamental change, such as the suggested elimination of an anthracene cross-linking, for the mere addition of six or eight hydrogen atoms to the molecule could hardly cause so complete a change in the character of the curve. The types of the two absorption curves of the reduced compound are not unlike two of those of picene where the anthracene linking is absent, whilst the angular linking or space configuration is possibly the origin of the two bands as compared with the three bands of picene where the linking of the rings is more symmetrical.

That Hartenstein's compound contains an anthracene linking is indicated by the fact that the absorption curve is marked by one persistent band, such as is shown by $\alpha\beta\alpha'/\beta'$ -dinaphthanthracene, and not by the two or three bands, which are the features of the hydro-dinaphthanthracene and picene curves respectively.

It is interesting to notice that the position and persistency of the band exhibited by the curves for the isomeric dinaphthanthracenes differ so markedly. The band of the coloured $\alpha\beta\alpha'/\beta'$ -compound is much more persistent and nearer the red end of the spectrum than that of Hartenstein's colourless compound. It seems as though the space configuration, or, to express it another way, the angular linking of the dinaphthanthracene, is such that the vibrations of the atoms within the molecule have a greater amplitude than those in the molecule of the isomeric compound of Hartenstein's. The latter compound is marked by a linear linking of the rings, whilst the former is more angular.

These results strengthen the supposition that Hartenstein's compound and the hydrocarbon formed by the action of *s*-tetrabromoethane on naphthalene in the presence of aluminium chloride are isomeric dinaphthanthracenes.

It is also of considerable importance to note that the isomeric dinaphthanthracenes show one absorption band, that the hydro-derivative of the $\alpha\beta\alpha'/\beta'$ -compound shows two bands, and that picene shows three bands. The two bands of the hydride of $C_{22}H_{14}$

probably correspond with the two less refrangible bands of picene. The bands of picene are nearer the red end of the spectrum than the corresponding bands of the hydride, and they are also much more persistent. The origin of these differences may be sought for in differences in the space configurations or the angular linkings of the rings of the two compounds. The linkings of the rings of picene are symmetrically arranged as compared with those of the hydrodinaphthanthracene compound.

Results.

The results of the preceding investigation are that:

1. The spectroscopic evidence supports the proposition that the hydrocarbon $C_{22}H_{14}$, melting at 267.5° , is a dinaphthanthracene compound, and that its hydride, $C_{22}H_{20}$, no longer contains an anthracene linking.

2. Hartenstein's substance is not a dihydrodinaphthanthracene, but a dinaphthanthracene isomeric with the dinaphthanthracene compound, melting at 267.5° , and with picene. The absorption curves indicate similarity in the type of configuration of Hartenstein's compound and the $C_{22}H_{14}$, melting at 267.5° , which differs markedly from that of the isomeric picene.

3. The origin of the differences in the absorption bands of the above four compounds may be explained by a consideration of differences in the anthracene linkings and in the angular or linear linkings of the rings.

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