116. *Absorption Spectra of Polycyclic Hydrocarbons. Part II. Partially Reduced Derivatives of Phenanthrene, etc.*

By F. A. Askew.

THE ultra-violet absorption spectra of compounds of this series were measured with the object of elucidating the relationship between the absorption spectra and the positions of double bonds in compounds of the sterol group.

The compounds measured include 9 : 10-dihydrophenanthrene, tetrahydrophenanthrene, and two isomeric octahydrophenanthrenes, together with *cis*- and *trans*-hexahydrochrysene, 7 : 8-dihydrophenalyl-7-*spirocyclo*pentane, and fluorene. Relationships between the spectra of these compounds and those described in Part I (preceding paper) are discussed below, together with the bearing of some of the results on Clar's theory (*Ber.*, 1932, **65**, 503, 846, 1411) regarding the correlation between certain parts of the spectrum and the " diyl " state.

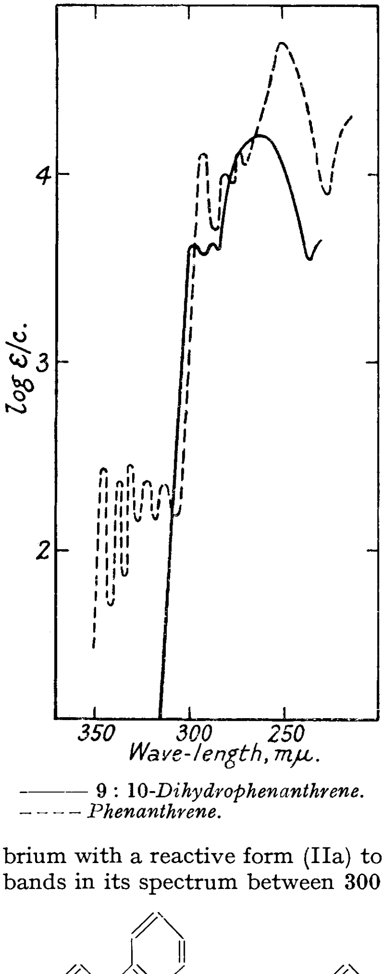
The methods and units employed were as described in Part I.

9 : 10-*Dihydrophenanthrene* (I).—A specimen of this compound, prepared from phenanthrene by catalytic reduction (Schroeter, Müller, and Huang, *Ber.*, 1929, **62**, 645), m. p. 35°, gave the absorption spectrum reproduced in Fig. 1. Comparison with that of phenanthrene (II and IIa) (Clar, *loc. cit.*, p. 846) shows that saturation of the 9 : 10 double bond is accompanied by considerable changes; the series of sharp bands between 300 and 350 mμ has entirely disappeared, the

bands about 290 mμ have become less marked, and the main band has been displaced towards the longer wave-lengths.

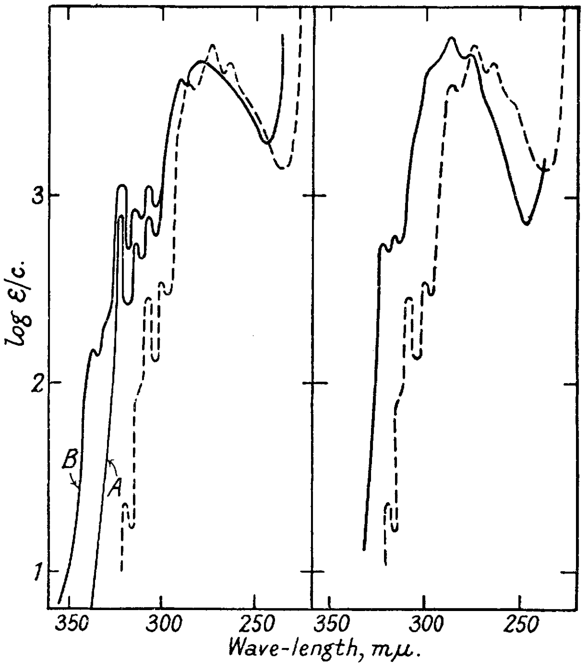
This observation, together with others (p. 516), accords well with Clar's hypothesis regarding the connexion between absorption spectra and the reactive "diyl" state of condensed polynuclear hydrocarbons. According to his views, phenanthrene (II), for example, exists in equilibrium with a reactive form (IIa) to which many of its properties are due, and the series of sharp bands in its spectrum between 300 and 350 mμ is due to the presence of such a reactive form.

FIG. 1.



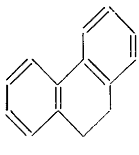
——— 9 : 10-*Dihydrophenanthrene*.
– – – – *Phenanthrene*.

FIG. 2a. FIG. 2b.

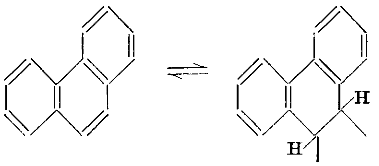


——— 1 : 2 : 3 : 4-*Tetrahydrophenanthrene* (*Two samples*, A *and* B).
– – – – *Naphthalene*.

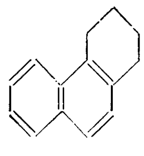
7 : 8-*Dihydrophenalyl*-7-spirocyclo*pentane*.



(I.)



(II.) (IIa.)



(III.)

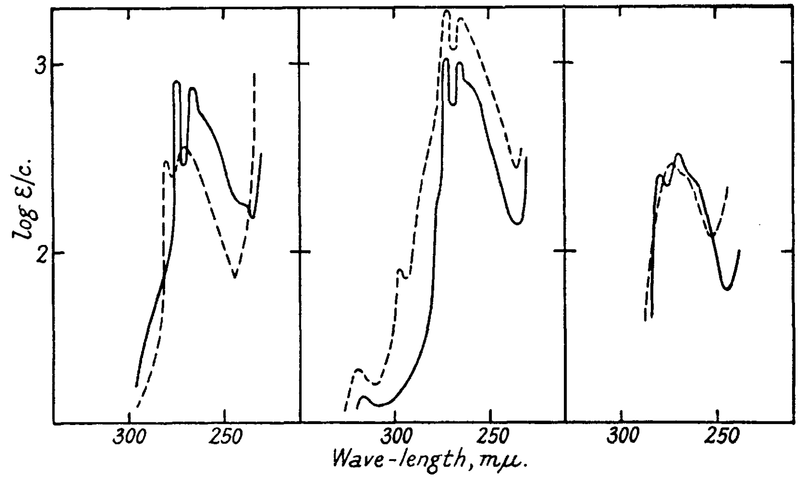
The fact that the bands attributed to the "diyl" state have completely disappeared in 9 : 10-dihydrophenanthrene affords experimental confirmation of Clar's correlation between these bands and such 9 : 10-reactivity.

1 : 2 : 3 : 4-*Tetrahydrophenanthrene* (III).—The spectra of two specimens from different sources are shown in Fig. 2a. One specimen (A) was prepared by catalytic reduction of phenanthrene (Schroeter, Müller and Huang, *loc. cit.*), the other (B) by Clemmensen reduction of 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene. The spectra practically coincide over the region 250—300 mμ, and the bands at 307, 313, and 321 mμ are similar in form and wave-length, but differ in height, and specimen B shows an extra band at 336 mμ. This difference suggests the presence of an impurity absorbing at these wave-lengths. Since specimens A and B were prepared by different methods,

it seems possible that this impurity is a product of decomposition (both specimens rapidly turned yellow on keeping) and that, in general form, the spectrum is that of tetrahydrophenanthrene.

7 : 8-*Dihydrophenalyl*-7-spiro*cyclo*pentane (IV).—A specimen of this compound, prepared by the method of Cook and Hewett (J., 1933, 1098; 1934, 365), gave the spectrum shown in Fig. 2b. Comparison of the spectra of (III) and (IV) with that of naphthalene (reproduced from Clar and Lombardi, *loc. cit.*) shows a considerable resemblance between these three compounds. The curves are of similar form, but that of tetrahydrophenanthrene is displaced from that of naphthalene towards the longer wave-lengths by about 7 mμ, while that of the *spiro*-compound (IV) is displaced by about 15 mμ. The maxima of both these compounds are less well marked than those of naphthalene. These effects are in accordance with the structures of these compounds, since they can both be regarded, from the point of view of absorption spectra, as alkyl-substituted naphthalenes, which exhibit similar displacements and smoothing-out of maxima (de Laszlo, *Z. physikal. Chem.*, 1925, **118**, 369).

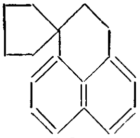
Fig. 3a. Fig. 3b. Fig. 3c.

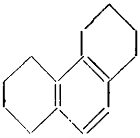


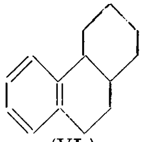
——— 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenanthrene.*
- - - - - - - 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*Octahydrophenanthrene.*

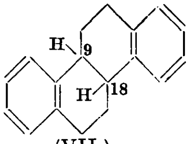
——— cis- } 1 : 2 : 9 : 10 : 11 : 18-*Hexahydrochrysene.*
- - - - trans- }

——— *Dodecahydrochrysene.*
- - - - *Dodecahydrotriphenylene.*

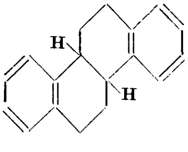

(IV.)


(V.)

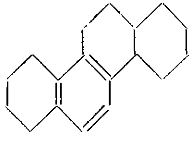

(VI.)

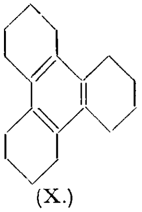


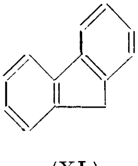
(VII.)



(VIII.)


(IX.)


(X.)

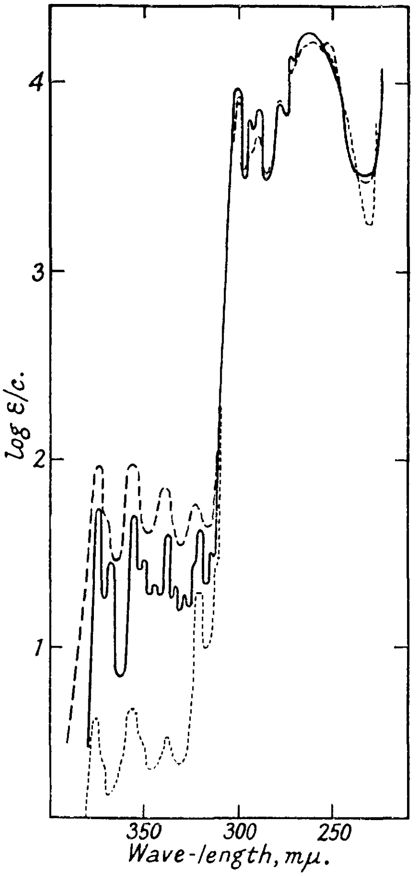

(XI.)

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8- *and* 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenanthrene* (V and VI).—A specimen of the symmetrical compound (V), prepared by catalytic reduction of phenanthrene (Schroeter, Hulle and Müller, *Ber.*, 1924, **57**, 2025), gave the spectrum reproduced in Fig. 3a, *viz.*, a main band having a maximum at 269 mμ and a second smaller maximum at 279 mμ.

The compound (VI), prepared by cyclisation at — 5° of 1-β-phenylethyl*cyclo*hexanol (Cook and Hewett, *loc. cit.*), gave the spectrum also reproduced in Fig. 3a. A measurement of another specimen, prepared by cyclisation at 100° of 1-β-phenylethyl*cyclo*hexene (*idem, ibid.*), revealed the presence of a considerable proportion of tetrahydrophenanthrene, the formation of which is easily explained by the simultaneous dehydrogenation ensuing when the cyclisation is carried out at 100° (Dr. Cook, private communication). The presence of this impurity caused little change in the chemical properties, but produced a profound alteration in the spectrum.

The spectra of both the octahydrophenanthrenes are of the general type shown by benzene and its alkyl derivatives, as would be expected from the fact that each contains one substituted benzene ring. The spectra, however, differ considerably both in the wave-lengths of the maxima and in the relative heights of the maxima and minima; these differences are discussed below.

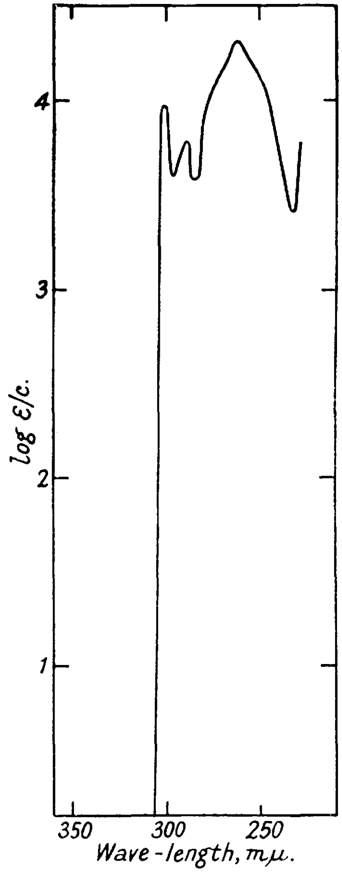
FIG. 4.



Fluorene.

——— *Menczel.*
– – – – – *"Pure" fluorene, Spec.* A.
- - - - - - ,, ,, ,, B.

FIG. 5.



Fluorene
(*purified specimen*).

cis- *and* trans-1 : 2 : 9 : 10 : 11 : 18-*Hexahydrochrysene* (VII and VIII).—The spectra of specimens of these two compounds (Ramage and Robinson, J., 1933, 608), in which the *cis–trans*-isomerism is about the 9 : 18 bond, are shown in Fig. 3b. Apart from a difference in height, the two absorption spectra are similar. The reason for this may be that the important absorbing groups, the benzenoid rings, are some distance away from the centre of isomerism. In contrast to this similarity in spectra, Bernal (*Chem. and Ind.*, 1933, **52**, 287) found that the crystal structures of these two compounds were markedly different, the unit cell of the *cis*-form having 64 molecules, as against 2 for the *trans*-form. In Fig. 3c are shown the spectra of dodecahydrochrysene (Philpot, private communication) (IX) and dodecahydrotriphenylene (X) (Clar and Lombardi, *loc. cit.*).

Comparison of these spectra and the structures shows that those compounds with more than one reduced ring fused to the benzenoid ring (compounds V, IX, X) show spectra having a maximum near 270 mμ, with a shoulder or small maximum near 280 mμ. On the other hand, compounds in which the benzenoid rings are in the end positions (compounds VI, VII, VIII) have two much sharper maxima at about 265 and 275 mμ, with a pronounced minimum between them.

Fluorene (XI).—As has been seen above, in dihydrophenanthrene, where the 9 : 10 double bond is reduced, the bands in the spectrum of phenanthrene attributed by Clar to the "diyl" state are no longer present. This being so, one would not expect such bands to be present in the spectrum of fluorene (XI). In Fig. 4 is shown Menczel's curve (*Z. physikal. Chem.*, 1927, **125**, 161) for the absorption spectrum of fluorene; it possesses a number of prominent bands between 300 and 375 mμ, *i.e.*, in the "diyl" region. Measurement of the absorption of two commercial specimens (A and B) of "pure" fluorene gave the results also shown in Fig. 4. Although the three curves agree fairly closely over the region 240—300 mμ, there is considerable divergence over the region 300—375 mμ, and one of the specimens (B) has a considerably lower absorption (intensity about 1/12) over this region than Menczel's specimen. The simplest explanation of this discrepancy is that all three samples contained different amounts of an impurity with a large absorption between 300 and 375 mμ. Capper and Marsh (J., 1926, 724) drew a similar conclusion, but their paper appears to have been overlooked by Menczel; their purest fluorene had only one small band in this region, at 319 mμ, but they concluded that their sample still contained at least 1% of an absorbing impurity (acenaphthene ?).

It thus appeared possible that pure fluorene would be found not to have any absorption bands in the "diyl" region, a result which would be in agreement with the findings with dihydrophenanthrene. Attempts were therefore made to purify fluorene by recrystallisation from alcohol, but measurements made after five and after ten recrystallisations showed definite increases in the height of the bands between 375 and 300 mμ, indicating that the impurity was becoming more concentrated. The later samples were markedly fluorescent.

It was therefore decided to examine a specimen not obtained directly from coal-tar, but regenerated from a purified derivative. Through the courtesy of the Gesellschaft für Teerverwertung, Duisberg-Meiderich, a sample of fluorene was obtained from fluorenecarboxylic acid (prepared by the action of carbon dioxide on the sodium compound of fluorene; Weissgerber, *Ber.*, 1908, **41**, 2913); this had m. p. 116—117° and gave the spectrum reproduced in Fig. 5. No trace was observed of the bands between 375 and 300 mμ, though the specimen was photographed in concentrations up to 0·5%. The maximum observable at 251 mμ in some specimens had also entirely disappeared. It is considered that the absorption spectrum recorded in Fig. 5 is that of pure fluorene.

SUMMARY.

(1) The ultra-violet absorption spectra of the following reduced hydrocarbons related to the sterol nucleus have been measured: 9 : 10-dihydrophenanthrene, tetrahydrophenanthrene, two isomeric octahydrophenanthrenes, *cis*- and *trans*-hexahydrochrysenes, and 7 : 8-dihydrophenalyl-7-*spirocyclo*pentane.

(2) It has been shown that previous measurements of the absorption spectrum of fluorene have been made on impure materials, and the absorption of pure fluorene has now been measured.

(3) The data presented are consistent with the structures of these compounds. A relation is suggested between the type of spectrum and the position of the benzenoid nucleus in these compounds.

(4) The results obtained with fluorene and dihydrophenanthrene confirm Clar's theory concerning the relation between part of the spectrum and the reactive state of condensed polynuclear hydrocarbons.

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