115. *Absorption Spectra of Polycyclic Hydrocarbons. Part I. Alkyl-substituted Phenanthrenes.*

By F. A. Askew.

The ultra-violet absorption spectra of a number of compounds related to phenanthrene have been determined, in view of their bearing on the structure of the sterols, and, more directly, on the " Diels hydrocarbon " $C_{18}H_{16}$. The absorption spectra of this compound and of synthetic 1 : 2-*cyclo*pentenophenanthrene and its 3′-methyl derivative have already been reported (Harper, Kon, and Ruzicka, J., 1934, 124; see also Cook and Hewett, J., 1933, 1103), and those of a series of 18 alkyl-substituted phenanthrenes are now described, and their relationships to the *cyclo*-compounds discussed. Further data on partly reduced compounds of this series are in the following paper.

Methods and Units.—Alcoholic solutions of the substances were photographed in a quartz cell, a hydrogen-discharge tube being used as a source of continuous ultra-violet radiation. The technique and apparatus used in the spectrography and in measuring the extinction coefficients were as described by Philpot and Schuster (Medical Research Council, Spec. Report Series, No. 177).

The figures are plotted with wave-lengths as abscissæ and values of log ε/c as ordinates, where ε is the extinction coefficient and c the concentration in g.-mols. per litre. The latter units have been used in order to render the results more easily comparable with those of other workers, although in previous papers from this laboratory, concentrations have been expressed in g. per litre.

The table gives the values for log ε/*c* for the maxima and minima of the bands observed in the series of alkyl-substituted phenanthrenes, together with the values for phenanthrene (Clar, *Ber.*, 1932, **65**, 846). The full curves for 1 : 2-dimethyl- and 1 : 2 : 8-trimethylphenanthrene and 1 : 2-*cyclo*pentenophenanthrene are given in the fig.

(In each case, the upper row gives λ, in mμ, and the lower log ε/*c*.)

	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max
Phenanthrene.	345	342	337	334	329	326	322	319	314	308	293	287	282	278	275	271	251
	2·44	1·70	2·36	1·80	2·46	2·16	2·34	2·15	2·32	2·19	4·10	3·66	3·99	3·97	4·10	4·07	4·70
9-Methyl	349	344	340	337	331	330	325	322	317	314	297	290	284	281	277	273	252
	2·64	2·15	2·41	2·32	2·63	2·37	2·45	2·38	2·49	2·44	4·07	3·77	3·99	3·98	4·13	4·14	4·79
1-Ethyl	349	346	341	337	333	330	326	322	318	314	300	293	288	283	277	273	256
	2·46	2·04	2·32	2·23	2·52	2·30	2·36	2·28	2·42	2·35	4·12	3·75	4·01	3·86	4·03	3·96	4·70
1 : 2-Dimethyl	350	348	343	340	335	330	328	324	320	314	300	295	288	285	279	274	258
	2·43	2·08	2·29	2·26	2·58	2·36	2·37	2·35	2·49	2·38	4·11	3·79	4·02	3·84	4·20	4·14	4·81
1 : 3 ,,	350	348	344	340	335	330	329	324	320	317	303	297	290	286	279	277	258
	2·66	2·20	2·40	2·34	2·67	2·40	2·44	2·37	2·56	2·52	4·10	3·83	4·02	3·86	4·03	3·99	4·69
1 : 7 ,,	351	348	341	339	335	330	326	324	320	314	301	295	289	286	280	276	259
	2·30	2·09	2·34	2·32	2·55	2·38	2·40	2·35	2·51	2·42	4·16	3·75	4·04	3·96	4·14	4·07	4·84
1 : 8 ,,	351	348	344	340	335	331	330	~	~	~	306	298	292	288	281	278	259
	2·35	2·14	2·40	2·37	2·54	2·46	2·51				4·23	3·84	4·14	3·86	4·04	3·94	4·76
1 : 9 ,,	351	348	344	340	335	331	328	326	320	316	303	296	290	286	280	275	258
	2·68	2·24	2·40	2·39	2·69	2·42	2·45	2·43	2·58	2·55	4·17	3·92	4·13	4·03	4·17	4·11	4·76
2 : 3 ,,	349	347	340	337	332	330	326	321	317	313	297	292	285	~	279	276	254
	2·23	2·04	2·27	2·23	2·41	2·33	2·56	2·36	2·45	2·44	4·00	3·60	3·95		4·06	4·03	4·68
2 : 5 ,,	350	346	344	~	333	~	328	324	319	314	298	292	287	283	277	273	253
	2·19	2·02	2·20		2·45		2·31	2·28	2·35	2·30	4·05	3·73	3·95	3·88	4·05	3·99	4·83
4 : 9 ,,	350	345	~	~	334	~	~	326	320	317	299	294	289	283	277	273	253
	2·74	2·43			2·74			2·47	2·56	2·54	4·06	3·90	4·00	3·93	4·03	4·01	4·84
7-Methyl-1-ethyl	349	347	~	~	334	329	326	323	319	314	300	295	287	284	279	274	258
	2·19	1·98			2·48	2·30	2·33	2·31	2·47	2·38	4·29	3·77	4·05	3·99	4·15	4·10	4·82
1 : 2 : 7-Trimethyl	353	348	~	~	337	~	~	326	322	317	302	298	291	288	283	278	260
	2·60	2·26			2·71			2·42	2·60	2·46	4·10	3·74	4·08	4·06	4·18	4·14	4·82
1 : 3 : 7 ,,	352	349	344	340	337	333	330	326	319	317	304	297	290	288	281	278	260
	2·21	2·09	2·31	2·30	2·49	2·36	2·40	2·34	2·55	2·54	4·13	3·82	4·02	3·96	4·14	4·11	4·78
1 : 4 : 7 ,,	354	349	~	~	337	334	332	329	323	~	307	300	295	288	282	279	257
	2·53	2·34			2·64	2·51	2·53	2·51	~		4·14	3·94	4·06	3·90	4·00	3·98	4·82
1 : 6 : 7 ,,	351	348	343	340	335	~	~	324	320	315	302	295	290	286	281	278	258
	2·73	2·53	2·63	2·60	2·78			2·52	2·66	2·56	4·17	3·77	4·02	3·93	4·12	4·06	4·83
1 : 2 : 8 ,,	354	351	347	~	339	332	–	–	323	320	307	301	295	290	283	280	261
	2·18	2·15	2·30		2·54	2·41			2·62	2·61	4·19	3·84	4·08	3·89	4·07	3·99	4·77
1-Methyl-7-*iso*-propyl	351	348	344	~	334	330	~	~	318	314	301	294	288	285	279	275	259
	2·36	2·18			2·58	2·46			2·80	2·75	4·19	3·88	4·11	4·04	4·20	4·11	4·85
1-Ethyl-7-*iso*-propyl	350	~	340	~	333	330	328	323	318	314	300	297	288	286	280	276	258
	2·05		2·30		2·51	2·33	2·36	2·32	2·47	2·41	4·16	3·65	4·06	4·02	4·18	4·15	4·83

All the curves showed the same general form as the spectrum of phenanthrene, *viz.*, a series of five bands between 300 and 355 mμ, a series of three bands of considerably greater intensity between 270 and 300 mμ, and a still more intense maximum at about 250 mμ.

In the table, similar bands are grouped in the same vertical column; in some cases no definite values could be ascribed to the maxima or minima, though a marked inflexion was apparent in the curve; such cases are denoted in the table by the sign ~.

Additional bands. Besides the maxima and minima tabulated, the following bands (in mμ) were observed :

1 : 7-Dimethylphenanthrene	381	371	359	
2 : 3-Dimethylphenanthrene	379		358	311
1 : 6 : 7-Trimethylphenanthrene	380		360	

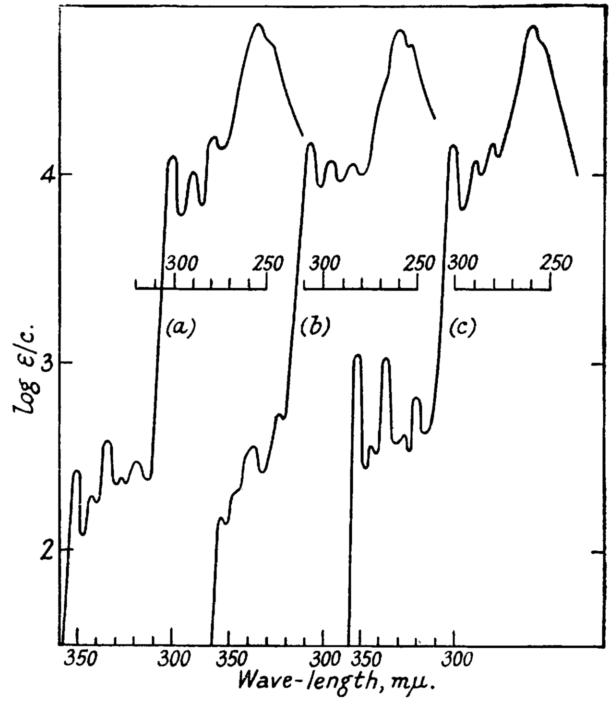
These bands do not appear to be due to the alkylphenanthrenes themselves, but rather to some absorbing impurity, since they were produced to varying extents by different specimens of the same compound. They were still obtained, however, with the purest available samples of these compounds. Again, if these bands were characteristic of some particular grouping (*e.g.*, 1 : 7, or 2 : 3 which is equivalent to 6 : 7), one would expect similar bands to be produced by analogous compounds such as 7-methyl-1-ethylphenanthrene; this does not occur. It does not appear that a common impurity was introduced by a common method of synthesis, since a specimen of 1 : 7-dimethylphenanthrene prepared from *d*-pimaric acid still showed the extra bands. It is more probable that these bands are due to products of decomposition. The spectra of these compounds are included in the table, since these extra bands mostly occurred in regions outside the ordinary phenanthrene spectrum, and variations in their height between different specimens did not greatly affect the other bands.

The structure of 4 : 9-dimethylphenanthrene is less well established than those of the other compounds described.

The data given in the table lead to the following tentative conclusions :

(1) No additional complication appears to be introduced into the spectrum of phenanthrene when the symmetry of the molecule is destroyed by the introduction of alkyl groups: phenanthrene and its 1 : 8-dimethyl homologue are symmetrical, but have as many bands (or inflexions) as the others.

(2) Although the wave-lengths of the maxima vary from one compound to another, there is a general shift towards the longer wave-lengths as the number of substituent alkyl groups increases, and the distinctness of the maxima and minima tends to become less marked; many of the maxima and minima present in the simpler compounds merge into inflexions in the series of tri-substituted compounds (cf. 1 : 2-dimethyl- and 1 : 2 : 8-trimethylphenanthrenes). Both these effects are in accordance with observations of de Laszlo (*Z. physikal. Chem.*, 1925, **118**, 369) on mono- and di-methylnaphthalenes, and of Radulescu and Ostrogovitch on β-methylanthracene (*Ber.*, 1931, **64**, 2233).



(a) 1 : 2-*Dimethylphenanthrene.*
(b) 1 : 2 : 8-*Trimethylphenanthrene.*
(c) 1 : 2-cyclo*Pentenophenanthrene.*

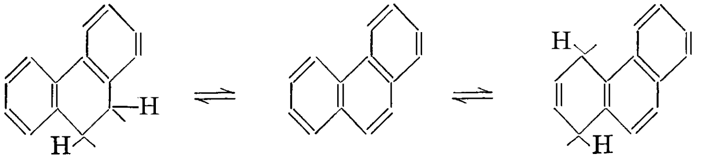
(3) The data in the table would seem to indicate that the wave-length shift depends on the number rather than on the size of the substituents.

(4) Within the series of dimethyl-substituted compounds, the maxima of those with a substituent in the 1-position tend to be at longer wave-lengths than those without.

(5) In contrast to the smoothing-out effect of increasing number of alkyl substituents, mentioned in (2) above, the effect of the fusion to the phenanthrene nucleus of a polymethylene or other saturated ring appears to be a marked increase in the heights of the first and the third maximum (at about 350 mμ and 335 mμ) compared with the corresponding dialkyl compound. This effect can be seen in the fig. (curves *a* and *c*). Similarly

high maxima are shown by 3′-methyl-1 : 2-*cyclo*pentenophenanthrene (Harper, Kon, and Ruzicka, *loc. cit.*), and a similar effect is to be seen by comparison of the curves of 6 : 7-*cyclo*penteno- and 6 : 7-dimethyl-1 : 2-benzanthracene (Rosenheim and King, *J. Soc. Chem. Ind.*, 1933, **52**, 299) and also in 1 : 10-trimethylenephenanthrene and in several other compounds containing a phenanthrene-ring system having a saturated ring fused on (see Clar, *Ber.*, 1933, **66**, 202, Figs. 3, 4, 5, 6).

(6) It will be seen from the table that the greatest variation in the heights of the maxima takes place in the region 300—350 mμ. According to Clar (*Ber.*, 1932, **65**, 1411), these bands in the phenanthrene spectrum are due to the " diyl " states of the molecule :



If these views are correct, the variations in these bands in the present series of compounds should be connected with the effect of substituents on the capacity of the molecule to assume the " diyl " state. Clar (*Ber.*, 1933, **66**, 202) has attempted to correlate the first, third, and fifth bands (at 345, 329, and 314 mμ in phenanthrene) with the 9 : 10- " diyl " state and the second and fourth (at 337 and 322 mμ) with the 1 : 4-" diyl " state.

From the table it may be seen that the compounds having a substituent in the 9 (or 10) position have considerably higher values of log ε/*c* for the first, third, and fifth maxima than have the other members of the series. On the other hand, there does not appear to be any direct correlation between the second and fourth maxima and the presence or absence of substituents on the 1 : 4 (or 5 : 8) carbon atoms.

The author's thanks are due to Dr. R. D. Haworth for kindly supplying purified samples of alkylphenanthrenes synthesised by him and his co-workers, to Dr. O. Rosenheim for helpful advice and criticism, to his colleagues Dr. R. K. Callow and Mr. J. St. L. Philpot, and also to Mr. E. H. Pitte, for assistance at various times with the measurements.

NATIONAL INSTITUTE FOR MEDICAL RESEARCH,
HAMPSTEAD, N.W. 3.

[*Received, March 2nd,* 1935.]