

Summary

The Raman spectrum of O-methyl isourea hydrochloride in water has been determined. The observed spectrum is essentially that of the cation

(conjugate acid) of O-methyl isourea. The structure of this ion is briefly discussed, and its similarity to the methylguanidinium ion is pointed out.

BOSTON, MASS.

RECEIVED JUNE 4, 1943

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF QUEEN'S UNIVERSITY]

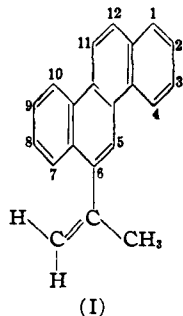
The Ultraviolet Absorption Spectra of Some Derivatives of Chrysene

By R. NORMAN JONES

The ultraviolet absorption spectra of numerous alkyl derivatives of polynuclear aromatic hydrocarbons have been recorded,¹ including those of several alkyl chrysenes.^{2,3} Comparatively little is known, however, regarding the modifications which are produced in the spectra of polynuclear aromatic hydrocarbons by the introduction of substituents containing functional groups.

The absorption spectra of some derivatives of chrysene, synthesized by Bergmann and Eschinazi,⁴ have recently been determined in this Laboratory and are recorded in Figs. 1-3 and Tables I and II.

6-Isopropenylchrysene.—The spectrum of 6-isopropenylchrysene (I) is illustrated in Curve A of Fig. 1 and, in Table I, the positions and intensities of the maxima are compared with similar data for 6-methylchrysene.³ It is apparent that



the introduction of the ethylenic group into the side chain makes practically no difference in the spectrum, although the ethylenic double bond is in a position indicative of conjugation with the aromatic ring system.

The introduction of a vinyl group into benzene causes a profound alteration of the absorption, as exemplified by styrene,⁵ and the spectrum of

- (1) Jones, *Chem. Rev.*, **33**, 1 (1943).
- (2) Jones, *THIS JOURNAL*, **63**, 313 (1941).
- (3) Brode and Patterson, *ibid.*, **63**, 3252 (1941).
- (4) Bergmann and Eschinazi, *ibid.*, **65**, in press (1943).
- (5) Arends, *Ber.*, **64**, 1936 (1931).

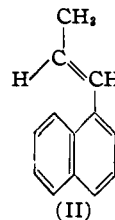
TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF 6-ISOPROPENYLCHRYSENE AND 6-METHYLCHRYSENE, COMPARISON OF THE WAVE LENGTHS AND INTENSITIES OF THE MAXIMA (SOLVENT ETHANOL)

6-Isopropenylchrysene		6-Methylchrysene ³	
Wave length, Å.	Intensity, log E_{molar}	Wave length, Å.	Intensity, log E_{molar}
2220	4.45
2430	4.30
2600	4.80	2600	4.90
2695	5.09	2695	5.18
2850	4.02	2850	4.02
2980	4.02	2970	4.08
3100	4.11	3095	4.15
3235	4.13	3230	4.13
(3450) ^a	3.06	3460	3.03
(3530) ^a	2.75	3530	2.63
3630	2.88	3620	3.03

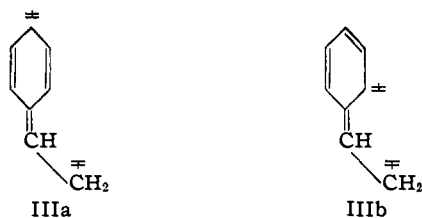
^a Infection only.

1-propenyl-naphthalene⁶ (II) shows a complete loss of fine structure and a bathochromic shift of about 200 Å. compared with 1-methylnaphthalene.⁷



If a vinyl substituent is to modify the electronic activation of a polynuclear aromatic hydrocarbon, it must do so by altering the nature and the relative contributions of the several canonical forms which participate in the ground and activated electronic states. Presumably, in the case of styrene, this will involve principally dipolar quinonoid structures such as IIIa and IIIb. Similar quinonoid structures may be written for the vinyl derivatives of complex polynuclear

- (6) Pestemer and Willigut, *Monatsh.*, **66**, 119 (1935).
- (7) de Laszlo, *Z. physik. Chem.*, **118**, 369 (1925).



aromatic hydrocarbons, but the extent to which such forms will contribute toward the structure of the molecule will depend upon the energies associated with the "normal" and the quinonoid forms. If these energies should differ very considerably interaction may be slight.

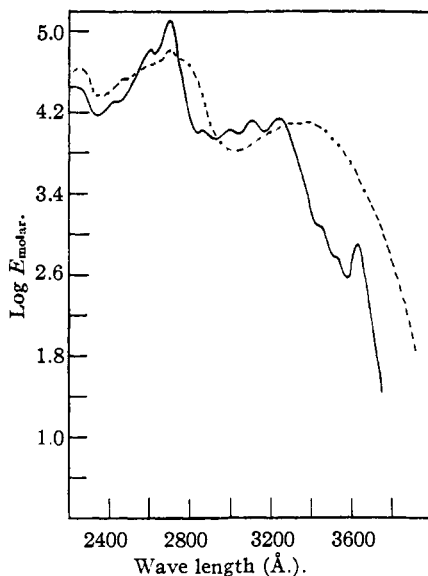
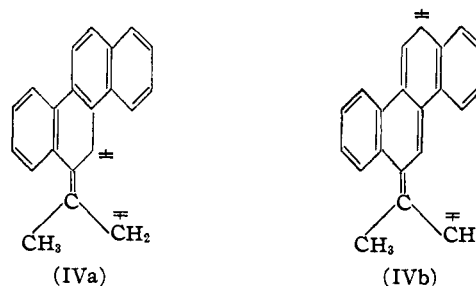


Fig. 1.—Curve A, ——— 6-isopropenylchrysene; Curve B, - - - - 6-acetylchrysene.

The two factors which will largely determine the energy associated with such dipolar quinonoid forms are, in the first place, the possibility of accommodating the α - and the β -hydrogen atoms or other substituents of the ethylenic group in the same plane as the aromatic ring structure and, secondly, the stability of the resultant quinonoid arrangement within the aromatic ring system. In the case of 6-isopropenylchrysene, the quinonoid ring structures of IVa and IVb should possess considerable stability, since they occur in 5,6- and 6,12-chrysenequinone, the normal reduction potentials of which are comparatively low⁸ (0.465 and 0.392 volt at 25° in alcoholic solution). The steric requirements for conjugation, however, are very unfavorable, as it is evident from Fig. 4

that the considerable interference between the β -hydrogen atom and the hydrogen atom at 7 can be relieved only by a rotation of the vinyl group about the bond attaching it to the chrysene ring system. It has been well established¹ that such rotation inhibits conjugation with the aromatic ring system.



In styrene, where a planar configuration is permitted, the conjugation effect on the spectrum is very large; a strainless planar structure is also possible for 1-propenylnaphthylene.

6-Acetylchrysene.—The spectrum of this compound is recorded in Curve B of Fig. 1. It is apparent from the spectrum that the interaction between the double bond of the carbonyl group and the chrysene ring system is much greater than that which occurs with the vinyl group of the isopropenyl derivative, although it would seem from Fig. 5 that in this case also there are steric factors present which oppose a planar structure. The interference diameters used in Figs. 4 and 5 are the van der Waals radii commonly employed⁹ and the structures represent the substituent group in the planar configuration which offers a minimum of overlap. Less favorable planar configurations also exist in which the side chains are rotated through 180°. If the molecules of 6-isopropenyl- and 6-acetylchrysene are constructed with Fisher-Hirshfelder models the interference in the case of the acetyl derivative is much less apparent than Fig. 5 would suggest, and the acetyl group can be rotated into a form co-planar with the chrysene ring system with very little strain. The discrepancy between the models and the diagram is due to the fact that the models are to a scalar of 0.8 of the van der Waals radii. This example serves to emphasize the fact that, while such models and diagrams serve a useful purpose, deductions from them should be treated with reserve in border-line cases.

(8) Fieser and Dietz, *THIS JOURNAL*, **53**, 1128 (1931).

(9) See for instance O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940); Kadesch and Weller, *ibid.*, **63**, 1310 (1941).

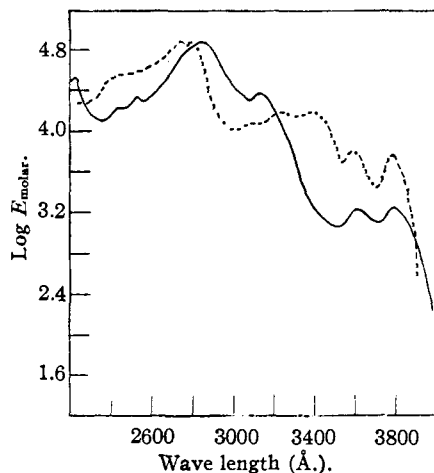


Fig. 2.—Curve A, ——— monoacetylchrysenes (position of substitution uncertain); Curve B, - - - - diacetylchrysenes (positions of substitution uncertain).

Curves A and B of Fig. 2 are the spectra of an isomeric monoacetylchrysenes and a diacetylchrysenes in which the positions of the substituents are not known. In both of these cases the resolution of structure in the spectra is better than in the spectrum of 6-acetylchrysenes and would suggest that in these compounds conjugation between the carbonyl group and the ring structure is very slight. This may be due to the substituent being attached at a position which offers much opposition to a planar configuration, or, more probably, the groups are attached at positions which do not permit of low energy quinonoid configurations within the ring system.

Curve A of Fig. 3 is the spectrum of a substance believed by Bergmann and Eschinazi⁴ to have the

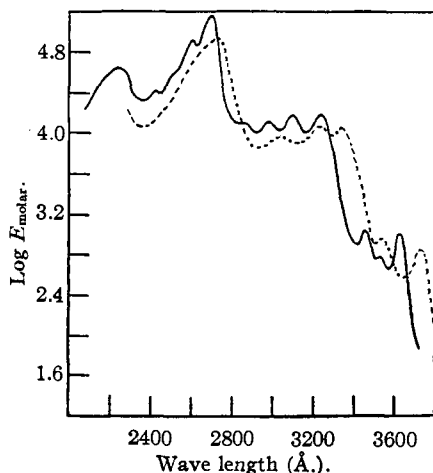


Fig. 3.—Curve A, ——— alicyclic derivative of chrysenes; Curve B, - - - - 5,6-dimethylchrysenes.

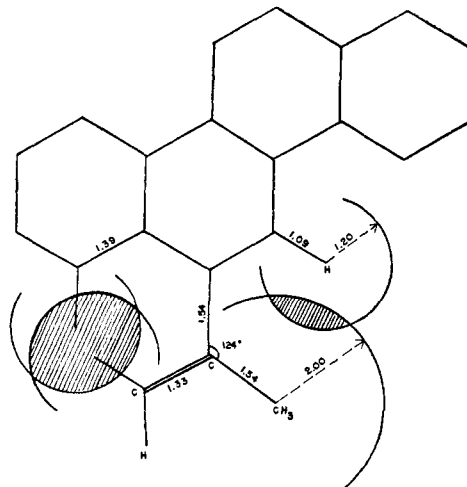


Fig. 4.—6-Isopropenylchrysenes, planar configuration with minimum interference.

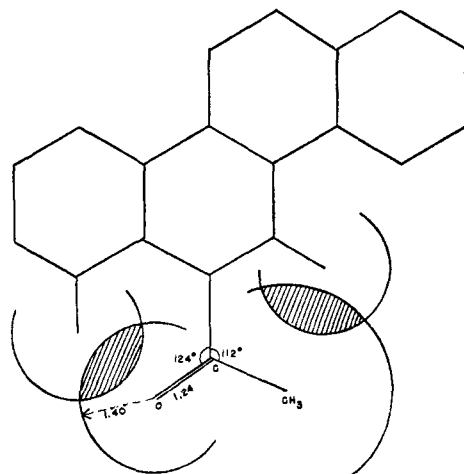
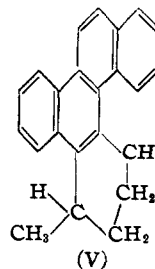


Fig. 5.—6-Acetylchrysenes, planar configuration with minimum interference.

structure V. Data for the maxima are given in Table II, and curve B of Fig. 3 is the spectrum of 5,6-dimethylchrysenes.² It has been observed previously¹ that derivatives of polynuclear aromatic hydrocarbons which contain alicyclic rings frequently exhibit more highly developed fine structure than do derivatives with alkyl



groups at the same positions. This is illustrated in the simplest case, by the spectra of *o*-xylene and hydrindene.^{1,10} While the spectrum of V does not confirm the structure attributed to this

compound by Bergmann and Eschinazi, it is quite consistent with it.

Experimental

All the spectra were determined on a Beckman ultraviolet spectrophotometer in solution in ethanol; the diacetylchrysene was dissolved in ethanol containing not more than 10% of dioxane.

Acknowledgment.—The author wishes to express his thanks to Dr. Bergmann who supplied the compounds, and his appreciation of the opportunity to cooperate with him. He also wishes to thank the International Cancer Research Foundation for financial assistance.

Summary

The similarity between the ultraviolet absorption spectra of 6-isopropenylchrysene and 6-methylchrysene is attributed to the action of steric hindrance which prevents the ethylenic group from acquiring a configuration co-planar with the chrysene ring system. In the absence of such a planar structure interaction between the aromatic ring system and the ethylenic bond of the side chain does not occur.

The spectra of certain acetylchrysenes and of a chrysene derivative containing an alicyclic ring attached at the 5,6-positions are also recorded and discussed.

TABLE II
ABSORPTION SPECTRA OF CHRYSENE DERIVATIVES, WAVE LENGTHS AND INTENSITIES OF THE MAXIMA

Wave lengths, Å.	Intensity, log E_{molar}	Wave lengths, Å.	Intensity, log E_{molar}
A. 6-Acetylchrysene		B. Isomeric acetylchrysene	
2250	4.63	2220	4.52
(2470) ^a	4.52	(2430) ^a	4.21
(2630) ^a	4.68	2530	4.32
2700	4.82	2850	4.89
(2780) ^a	4.68	3130	4.36
3350	4.10	3610	3.24
		3790	3.24
C. Diacetylchrysene		D. Substance V	
2240	4.28	2230	4.64
(2320) ^a	4.30	2420	4.42
(2440) ^a	4.55	(2520) ^a	4.60
2740	4.89	2600	4.92
2780	4.88	2690	5.16
3100	4.07	(2860) ^a	4.10
3240	4.18	2980	4.12
3390	4.19	3100	4.20
3580	3.80	3240	4.20
3780	3.76	3450	3.04
		3530	2.76
		3620	3.03

^a Inflection only.

(10) Ramart-Lucas and Hoch, *Bull. soc. chim.*, [5] 2, 327 (1935).

KINGSTON, CANADA

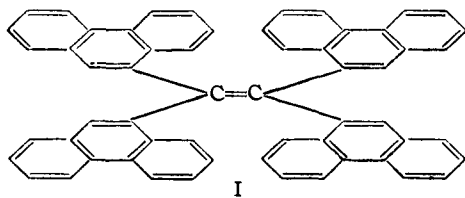
RECEIVED MAY 20, 1943

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF QUEEN'S UNIVERSITY]

The Ultraviolet Absorption Spectra of Arylethylenes

By R. NORMAN JONES

Tetra-(9-phenanthryl)-ethylene (I) has been synthesized recently by F. Bergmann,¹ and the ultraviolet absorption spectrum of a sample of this substance, kindly supplied by Professor



Bergmann, is shown in curve A of Fig. 1; data for the position and intensities of the maxima are

given in Table I. Comparison of this curve with the spectrum of a four molar solution of phenanthrene² (Curve B of Fig. 1) suggests that the tetra-(9-phenanthryl)-ethylene spectrum may be divided into three distinct parts: (a) a region in the neighborhood of 2500 to 2600 Å. in which the two curves are similar in shape and intensity; (b) a region between 2800 and 3000 Å. in which fine structure, characteristic of the phenanthrene chromophore, is present, but in which the intensity is enhanced; (c) a region of high intensity absorption between 3300 and 4000 Å.

(1) Bergmann, private communication.

(2) Calculated from the data of Mayneord and Roe, *Proc. Roy. Soc. (London)*, **A183**, 299 (1935).