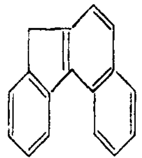
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND QUEEN'S UNIVERSITY]

The Spectrographic Characterization of a Hydrocarbon Synthesized by Bergmann and Eschinazi

BY R. NORMAN JONES

Selenium dehydrogenation of the cyclized condensation product of cyclohexenylcyclohexanone with α-naphthylmagnesium bromide yields a product which Bergmann and Eschinazi[1] believed to possess either structure IV or V as shown in their article.

The ultraviolet absorption spectrum provides a method of distinguishing between these two structures, since IV[1] is an alicyclic derivative of



A

3,4-benzphenanthrene and (V)[1] is an alicyclic derivative of chrysene. It is known that alicyclic rings do not alter significantly the spectrum characteristic of the polynuclear aromatic hydrocarbon to which they are attached.[2] The spectrum of (IV)[1] should resemble closely that of 3,4-benzphenanthrene, and the spectrum of (V)[1] should be similar to the spectrum of chrysene.

The spectrum of Bergmann and Eschinazi's hydrocarbon is compared with the spectra of chrysene[3] and 3,4-benzphenanthrene[4] in Fig. 1; but the resemblance to either of these spectra is so slight as to cast considerable doubt on the close relation of the compound to either hydrocarbon.

In Fig. 2 the spectrum of Bergmann and Eschinazi's hydrocarbon is compared with the spectrum of 3,4-benzfluorene[4] (A) which it resembles closely in the region from 2200 to 3600 Å. The low intensity structure between 3800 and 4600 Å., not observed in the spectrum of 3,4-benzfluorene, may be due to a trace of impurity. Assuming an intensity of log $E_{\text{molar}} = 4.0$–4.5 for a hypothetical component responsible for the 4360 Å. maximum, this would indicate a concentration of about 0.1% of impurity. Structure in this region of the spectrum was observed in early determinations of the spectrum of fluorene, but was later shown to be due to impurities.[5] It is also possible that corresponding low intensity structure might be present in the spectrum of 3,4-benzfluorene, but was not recorded by Mayneord and Roe,[4] whose measurements did not extend below log $E_{\text{molar}} = 1.6$. This explanation would seem more reasonable, as Bergmann and Eschinazi purified their compound through the picrate.

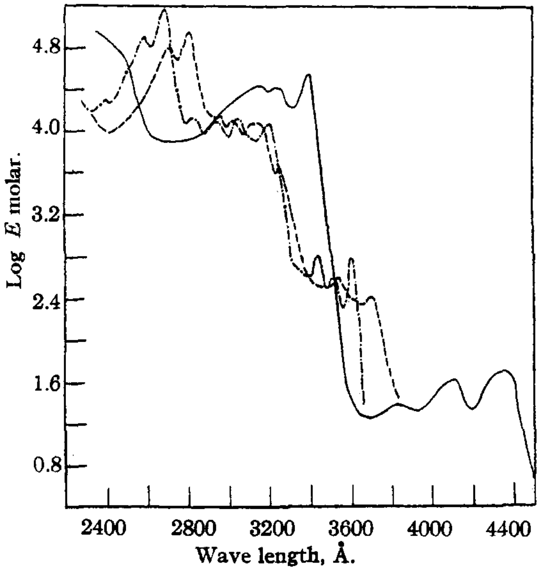


Fig. 1.———, Absorption spectrum of Bergmann and Eschinazi's hydrocarbon; —·—·—·, spectrum of chrysene; ------, spectrum of 3,4-benzphenanthrene.

Over the region from 2400 to 3400 Å. the absorption of Bergmann and Eschinazi's hydrocarbon is everywhere more intense than that of 3,4-

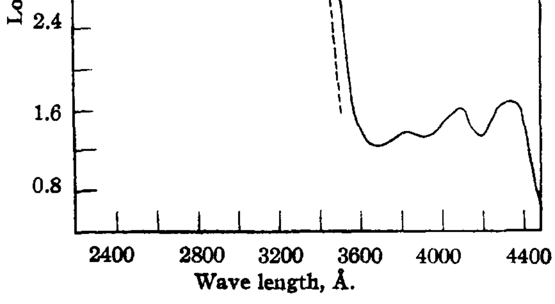


Fig. 2.———, Absorption spectrum of Bergmann and Eschinazi's hydrocarbon; ------, spectrum of 3,4-benzfluorene.

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[1] Bergmann and Eschinazi, THIS JOURNAL, 66, 183 (1944). With the exception of structure (A), reference should be made to this paper for structural formulas discussed in the current article.

[2] Jones, *Chem. Rev.*, **32**, 1 (1943).

[3] Redrawn from the data of Mayneord and Roe, *Proc. Roy. Soc.* (London), **A152**, 299 (1935).

[4] Redrawn from the data of Mayneord and Roe, *ibid.*, **A158**, 634 (1937).

[5] Askew, *J. Chem. Soc.*, 512 (1935).

benzfluorene. This is unusual, but a similar effect has been recorded by Bachmann and Carmack,[6] who compared the spectra of 3,4-benzpyrene and its 4′,5-dimethylene derivative.

The formulation of Bergmann and Eschinazi's hydrocarbon as a derivative of 3,4-benzfluorene requires the postulation of a five-membered ring closure, the product being 9,9-spirocyclohexanyl-3,4-benzfluorene, (VI)[1] in their article. The presence of the spirane ring should not affect the spectrum,[7] and the failure of this compound to hydrogenate further[1] also supports this formulation.

The spectrum of the quinone derived from (VI)[1] by oxidation, which has a probable structure (VII),[1] is recorded in Fig. 3; but in the absence of comparative data, this is of no value for the further characterization of the ring system.

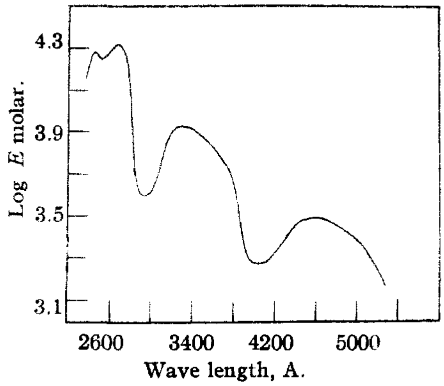

Fig. 3.———, Absorption spectrum of quinone (probably VII[1]).

TABLE I

POSITION AND INTENSITY OF ABSORPTION MAXIMA

Wave length, Å.	Intensity (log E_{molar})
(a) Hydrocarbon (VI)[1] (solvent ethanol)	
3150	4.45
3250	4.43
3395	4.55
3845	1.38
4105	1.61
4360	1.69
(b) Quinone (VII)[1] (solvent ethanol)	
2470	4.28
2680	4.32
3330	3.94
4600	3.49

In Table I data for the position and intensity of the maxima of the spectra of compounds (VI)[1] and (VII)[1] are recorded. The spectrographic methods employed have been reported previously.[8]

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Summary

Comparison of the ultraviolet absorption spectrum of a hydrocarbon synthesized recently by Bergmann and Eschinazi, with the spectra of chrysene, 3,4-benzphenanthrene and 3,4-benzfluorene suggests that the new hydrocarbon is 9,9-spirocyclohexanyl-3,4-benzfluorene.

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[6] Bachmann and Carmack, THIS JOURNAL, 63, 1685 (1941).

[7] Compare the spectra of 7,8-dihydrophenalyl-7-spirocyclopentane and naphthalene, in reference 5.

[8] Jones, THIS JOURNAL, 62, 148 (1940).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 939]

A Spectroscopic Study in the Stereoisomeric Capsanthin Set. *cis*-Peak Effect and Configuration

BY A. POLGÁR AND L. ZECHMEISTER

Recent experiments with some carotenoid hydrocarbons and alcohols have shown that the bending of the molecule by *trans* → *cis* rearrangements which modify the entire extinction curve produces a particularly characteristic change in a certain ultraviolet region of the spectrum.[1] This change which results in a new maximum, the "*cis*-peak," between 320 and 380 mμ has recently been given a theoretical interpretation.[2]

After a chromatographic separation of the main stereoisomers which are present in a mixture formed by iodine catalysis, the height of the *cis*-peak can be determined for each stereoisomer.[1,2,3] This procedure has been used recently to assign tentative configurations to the main observed members of the stereoisomeric sets of α-carotene, β-carotene, lycopene and lutein.[2,3]

In order to provide data for compounds of another type a carotenoid ketone, capsanthin, $C_{40}H_{58}O_3$, which is the main pigment of the red pepper (*Capsicum annuum*) has been investigated. Capsanthin was one of the first C_{40}-carotenoids in which stereochemical effects in the form of spontaneous isomerization were observed by Cholnoky and one of the authors.[4] This was

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[1] L. Zechmeister and A. Polgár, THIS JOURNAL, 65, 1522 (1943).

[2] L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár and L. Pauling, *ibid.*, 65, 1940 (1943).

[3] L. Zechmeister and A. Polgár, *ibid.*, 65, 137 (1943).

[4] L. Zechmeister and L. Cholnoky, *Ann.*, 530, 291 (1937).