are added, and a colorless bromination product is obtained.

4. Di-(9-phenanthryl)-carbinol (XIII) is very easily converted into tetra-(9-phenanthryl)-ethylene (XIV), but neither compound could be cyclized to tetrabenzfluorene. Oxidation of the carbinol (XIII) with chromic acid gave the normal di-(9-phenanthryl) ketone (XV), but the ethylene (XIV) yielded an anomalous product, which contains one mole of acetic acid and is tentatively formulated as a derivative of tetrabenzfluorenone (XVI). Bromination of XIV gave a black perbromide (tetrabromide).

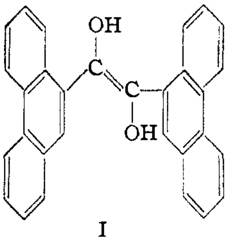
REHOVOTH, PALESTINE RECEIVED JUNE 2, 1944

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

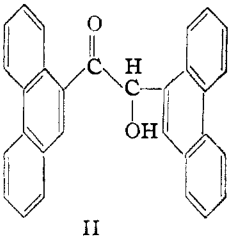
The Ultraviolet Absorption Spectrum of 9,9'-Phenanthroin

BY R. NORMAN JONES

Bergmann and Israelashwili[1] have recently reported the synthesis of 9,9'-phenanthroin by the benzoin condensation of phenanthrene-9-aldehyde, but have attributed to this compound the enediol structure I, instead of the normal carbonyl structure II.



I

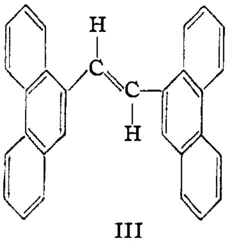


II

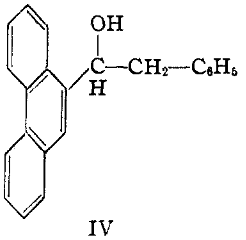
A comparison of the ultraviolet absorption spectrum of 9,9'-phenanthroin with the spectra of certain related phenanthrene derivatives provides supporting evidence for the enediol structure.

In a previous publication,[2] the spectrum of tetra-(9-phenanthryl)-ethylene has been recorded, and it has been pointed out that the spectrum of this compound may be divided into two main regions; between 2500 and 3000 Å. the absorption shows a general resemblance to that of phenanthrene but at longer wave lengths (3100–4000 Å.) a broad, high intensity band occurs, which has no counterpart in the phenanthrene spectrum. It has been suggested that the absorption bands in the shorter wave length region are associated with electronic excitations centered within the phenanthrene ring system, while the absorption at longer wave lengths involves electronic excitations in which both the phenanthrene ring systems and the ethylenic bond participate. Further studies of an extensives series of phenanthrene derivatives which have since been carried out[3] substantiate this interpretation.

Should 9,9'-phenanthroin possess the carbonyl arrangement II, its spectrum should show no evidence of structure involving conjugation between the phenanthrene ring systems, but some modification of the phenanthrene spectrum would be anticipated as a result of the conjugation with the carbonyl group.[4] The spectrum of a compound with structure II should approximate to that of an equimolar mixture of 9-acetophenanthrene and 9-methylphenanthrene. In the enediol structure I, the possibility exists for conjugation between the phenanthrene ring systems, and the spectrum should show a resemblance to that of symmetrical 9,9'-diphenanthrylethylene (III).



III



IV

The spectra of 9,9'-phenanthroin, 9,9'-diphenanthrylethylene, 9-acetophenanthrene, 9-methylphenanthrene, and benzyl-(9-phenanthryl)-carbinol (IV) are shown in Figs. 1 and 2. In the spectrum of 9,9'-phenanthroin the long wave length absorption band with maximum at 3300 Å. is well developed, and the spectrum of this compound approximates much more closely to that predicted for structure I than to the spectrum calculated for an equimolar mixture of 9-aceto- and 9-methyl-phenanthrene (Fig. 2, curve a). This supports the enediol structure. The shift of the absorption maximum from 3420 Å. in the spectrum of 9,9'-diphenanthrylethylene to 3300 Å. in the spectrum of the enediol I may be attributed to partial suppression of conjugation through steric inhibition of resonance, induced by the substitution of the hydroxyl groups for the hydrogen atoms on the ethylenic bond. This may be compared with the hypsochromic shift observed on the introduction of methyl groups on the ethylenic bond of stilbene.[2,5]

In 9-acetophenanthrene, the absorption maxi-

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[1] Bergmann and Israelashwili, THIS JOURNAL, **67**, 1951 (1945).

[2] Jones, *ibid.*, **65**, 1818 (1943).

[3] Unpublished observations from this Laboratory.

[4] This assumes a more or less planar configuration for the phenanthroyl part of the molecule.

[5] Arends, *Ber.*, **64**, 1936 (1931).

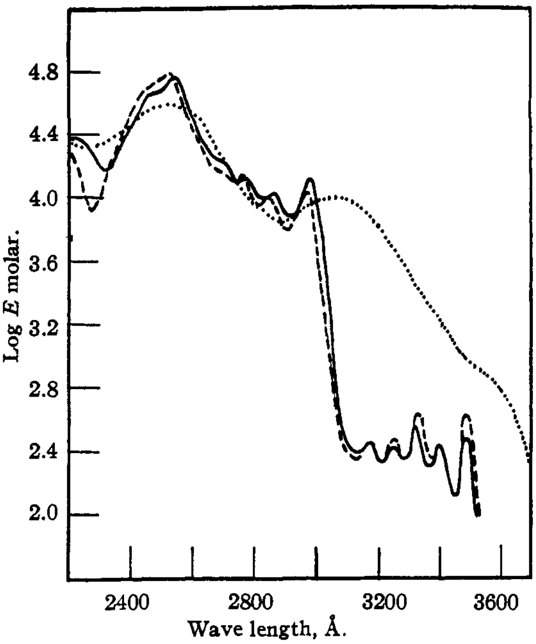
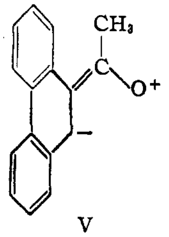


Fig. 1.—Ultraviolet absorption spectra: Curve a, ———, benzyl-(9-phenanthryl)-carbinol (solvent *n*-heptane); curve b, – – – – – –, 9-methylphenanthrene (solvent ethanol); Curve c, ..., 9-acetophenanthrene (solvent ethanol).

mum at 3050 Å. is probably a consequence of electronic activations involving the significant contribution of structures such as V to the excited state, and it may be argued that substitution of the phenanthrylcarbinol group of IV for the methyl group of the acetyl derivative might account for a bathochromic shift of the maximum to 3300 Å. in 9,9'-phenanthroin. However, there are valid reasons for considering this to be improbable; in benzyl-(9-phenanthryl)-carbinol, the α-hydroxyl group produces no significant change in the phenanthrene absorption (Fig. 1, curve a), and, indeed, it would seem more probable that replacement of the methyl group of 9-acetophenanthrene by a more bulky group would tend to produce a hypsochromic shift in the "conjugation band" as a result of the increased possibility of steric inhibition of resonance.



V

The small maximum at 2880 Å. in the spectrum of 9,9'-phenanthroin suggests the presence of a non-conjugated phenanthrene chromophore in the molecule. This is more readily reconciled with the carbonyl than the enediol structure, and introduces an element of uncertainty in the allocation of structure to 9,9'-phenanthroin. It is possible that in the dioxane solution in which the spectra were determined both the enediol and the carbonyl tautomers were present, with the equilibrium favoring a higher concentration of the enediol form.

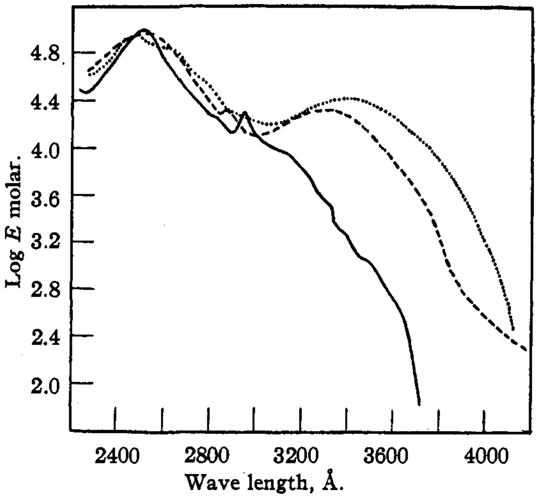


Fig. 2.—Ultraviolet absorption spectra: Curve a, ———, calculated summation curve for equimolar mixture of 9-methyl- and 9-acetophenanthrene; Curve b, – – – – – –, 9,9'-phenanthroin (solvent dioxane); Curve c, ..., 9,9'-diphenanthrylethylene (solvent dioxane).

Experimental

The compounds used in this investigation were supplied by Dr. F. Bergmann, with the exception of 9-acetophenanthrene, which was synthesized by Mr. G. D. Thorn. The spectra were determined on a Beckman ultraviolet spectrophotometer using a constant band width of 10 Å.

Acknowledgments.—Thanks are due to Mrs. G. D. Thorn, for technical assistance in the determination of the spectra, and to the Penrose Fund of The American Philosophical Society for financial support.

Summary

A comparison of the ultraviolet absorption spectrum of 9,9'-phenanthroin with the spectra of 9,9'-diphenanthrylethylene, 9-methylphenanthrene, and 9-acetophenanthrene favors an enediol structure for 9,9'-phenanthroin, but does not exclude the possibility that the normal carbonyl form may be present also in solution.

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