

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Influence of Restricted Rotation on the Absorption Spectra of Aryl Substituted Aromatic Hydrocarbons

BY R. NORMAN JONES

The ultraviolet absorption spectra of alkyl derivatives of aromatic hydrocarbons usually resemble the spectrum of the unsubstituted hydrocarbon, the only differences being a shift of the spectrum to longer wave lengths and, occasionally, a loss of resolution in the fine structure bands.^{1,2,3}

Pickett, Walter and France⁴ have shown, however, that the absorption spectrum of bimesityl (I) differs considerably from that of biphenyl and resembles the spectrum of mesitylene much more closely. Pestemer and Mayer-Pitsch⁵ and O'Shaughnessy and Rodebush⁶ have measured the spectra of several ortho-substituted biphenyl derivatives in which rotation of the aromatic rings may be restricted, and it appears that the biphenyl spectrum is destroyed in those derivatives which are prevented from taking up a planar configuration. Unless the aromatic rings are coplanar, polarization across the bond joining the two rings does not occur under the influence of the electric vector of the light wave and the two halves of the molecule behave as independent resonators. X-Ray diffraction measurements⁷ indicate a length of 1.48 Å. in biphenyl for the bond joining the two rings, which may be compared with 1.54 Å. for a purely aliphatic bond and 1.38 Å. for an ethylenic bond. This indicates that the linkage has some double bond character which may be a requirement for its polarizability.

Co-planar Biphenyl Derivatives.—The absorption spectra of 9,10-dihydrophenanthrene (II)⁸ and 4,5-methylene-9,10-dihydrophenanthrene (III)⁹ have been measured in this Laboratory by Dr. D. M. Bowen. These measurements have an interesting bearing on this problem, since

(1) Jones, *THIS JOURNAL*, **62**, 148 (1940) (1,2-benzanthracene series).

(2) Morton and de Gouveia, *J. Chem. Soc.*, 916 (1934) (naphthalene series).

(3) Askew, *ibid.*, 509 (1935) (phenanthrene series).

(4) Pickett, Walter and France, *THIS JOURNAL*, **58**, 2296 (1936).

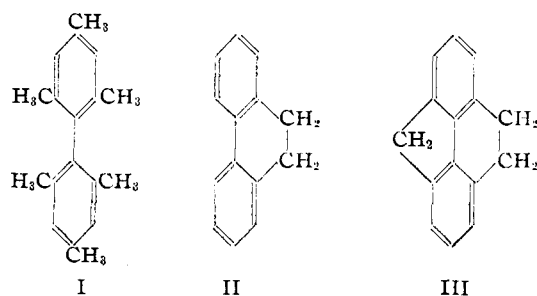
(5) Pestemer and Mayer-Pitsch, *Monatsh.*, **70**, 104 (1937).

(6) O'Shaughnessy and Rodebush, *THIS JOURNAL*, **62**, 2906 (1940).

(7) Dhar, *Indian J. Phys.*, **16**, 43 (1932).

(8) For preparation, see Fieser and Johnson, *THIS JOURNAL*, **61**, 168 (1939).

(9) For preparation, see Fieser and Cason (with Clapp), *ibid.*, **62**, 1293 (1940).



the compounds are biphenyl derivatives in which free rotation of the rings is restricted severely in such a manner as to hold the phenyl groups close to a planar configuration. Assuming an aliphatic bond length (1.54 Å.) for the co-annular linkage and normal bond angles and lengths in the remainder of the molecule,⁶ the dimethylene bridge can be accommodated with the minimum strain if the aromatic rings are rotated through an angle of 15° 2' about the common axis. The absorption spectrum of 9,10-dihydrophenanthrene (Fig. 1) agrees in shape and intensity with the biphenyl curve, allowance being made for the bathochromic effect of the alicyclic bridge. A secondary maximum is present on the long wave length side of the main maximum and may be compared with similar maxima in the spectra of 3,3'-dimethyl- and 4,4'-dimethylbiphenyl.⁶ Either the bond angles are deformed sufficiently to bring the rings into the same plane, or a small rotation of this order does not affect the polarizability of the bond.

In 4,5-methylene-9,10-dihydrophenanthrene (III), the introduction of the methylene bridge affects the geometry of the molecule in a manner which cannot be predicted exactly. Fluorene (2,2'-methylenebiphenyl) can have no strainless structure in which the normal bond lengths and angles are conserved. Evidence from dipole moments¹⁰ favors an approximately planar structure in which the phenyl groups are not symmetrical about an axis through the 4,4'-positions. In crystalline fluorene the X-ray data¹¹ favor a non-planar structure. In 4,5-

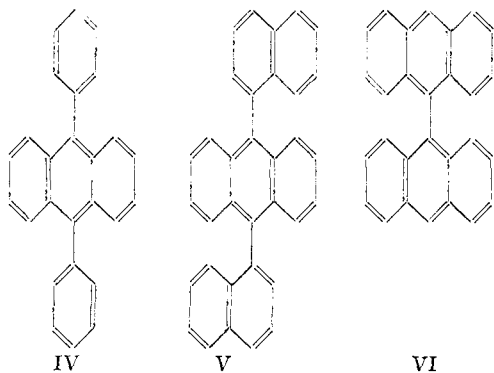
(10) Hughes, Le Fèvre and Le Fèvre, *Chemistry and Industry*, **55**, 545 (1936); see also *J. Chem. Soc.*, 202 (1937).

(11) Iball, *Z. Krist.*, **94**, 397 (1936); Cook and Iball, *Chemistry and Industry*, **55**, 467 (1936).

methylene-9,10-dihydrophenanthrene the conflicting steric requirements of the two bridges would appear to be most favorably compromised in an approximately planar configuration, and the absorption spectrum is in agreement with this. The spectrum resembles that of biphenyl fairly closely, although the intensity of the secondary maximum is enhanced. In the spectrum of fluorene¹² this secondary maximum develops into a system containing considerable fine structure and is in agreement with the observed effect of a methylene bridge on other polynuclear aromatic ring systems.^{1,13}

meso-Aryl-anthracenes.—There is no reason to suppose that hindrance of this kind operates only in the biphenyl series. O'Shaughnessy and Rodebush⁶ give evidence of its influence on the spectra of ortho-substituted acetophenones, and several cases of anomalous absorption spectra in the literature may be explained satisfactorily if it be assumed that conjugated aromatic chromophores contribute additively to the total absorption when prevented from acquiring a coplanar configuration.

The absorption spectra of 9-phenylanthracene,¹⁴ 9,10-diphenylanthracene (IV),¹⁵ 9,10-di(α -naphthyl)-anthracene (V)¹⁶ and 9,9'-dianthryl (VI)¹⁷ are almost identical with the spectrum of anthracene. The aryl group at the *meso* position



produces only a bathochromic shift and a slight increase in the intensity of absorption.¹⁸ In 9,9'-dianthryl the molecular extinction coefficient is approximately twice that of anthracene and is

(12) Mayneord and Roe, *Proc. Roy. Soc. (London)*, **A158**, 634 (1937).

(13) Jones, *THIS JOURNAL*, **63**, 313 (1941).

(14) Capper and Marsh, *J. Chem. Soc.*, 724 (1926).

(15) Radulescu and Ostrogovich, *Ber.*, **64**, 2233 (1931).

(16) Clar and Guzzi, *ibid.*, **65**, 1521 (1932).

(17) Clar, *ibid.*, **65**, 503 (1932).

(18) This is particularly well illustrated for 9,10-diphenylanthracene in Fig. 9 in the paper by Radulescu and Ostrogovich quoted above.

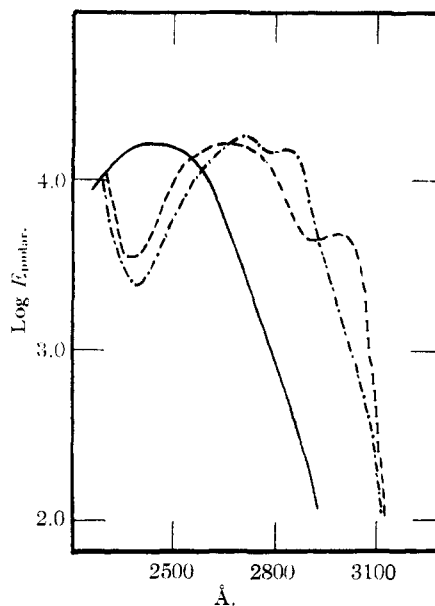


Fig. 1.— — Biphenyl (Pickett, Walter and France); - - - 9,10-dihydrophenanthrene; - · - · 4,5-methylene-9,10-dihydrophenanthrene (solvent ethanol).

consistent with the two anthracene resonators contributing independently to the total absorption.

In the absence of hindrance, one would anticipate that considerable interaction would occur between the resonating systems of the *meso*-aryl groups and the anthracene ring system in these compounds and that the bond joining the aryl substituents to the *meso* carbon atoms would have considerable double bond character. Examination of Stuart models shows that even with the normal aliphatic bond length it is impossible to rotate the *meso*-aryl groups into the plane of the anthracene rings on account of interference between the ortho-hydrogen atoms and those at the 1 and 8 positions. Shortening of the bond under the influence of resonance effects would further increase this hindrance. The spectra and steric considerations in these substances are thus in agreement in indicating that the *meso*-aryl groups must be inclined to the plane of the anthracene ring system. In the naphthacene series Dufraisse and Horclois¹⁹ have observed that the (visible) spectrum of rubrene (5,6,11,12-tetra-phenylnaphthacene) resembles the naphthacene spectrum closely and here also the same conditions obtain.

Calculation of Theoretical Curves.—If the above argument is correct, it should be possible

(19) Dufraisse and Horclois, *Bull. soc. chim.*, [5] **3**, 1880 (1936). See also *Ann. Reports Chem. Soc.*, **34**, 389 (1937).

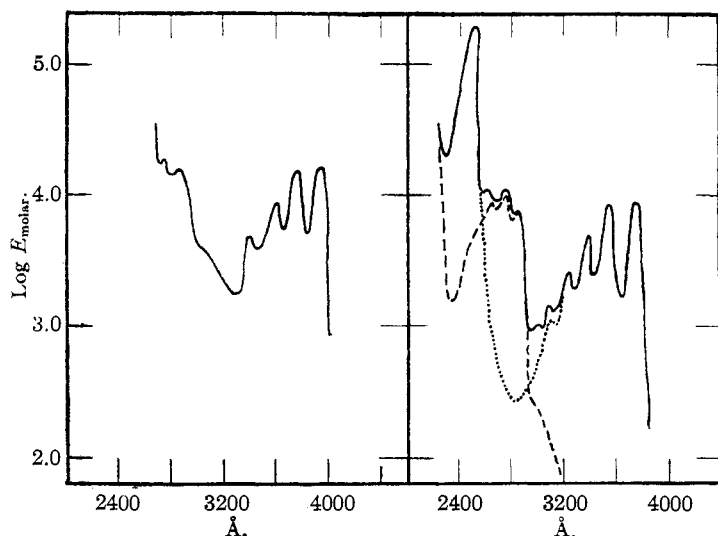
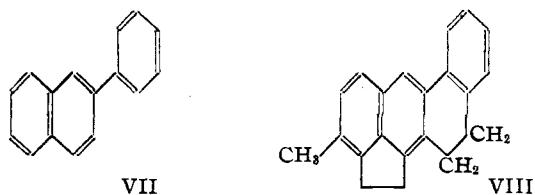


Fig. 2A.— 9,10-Di-(α -naphthyl)-anthracene (Clar and Guzzi).

Fig. 2B.— — Anthracene + 2 \times naphthalene; . . . anthracene; - - - 2 \times naphthalene.

to calculate these spectra approximately by adding that of the *meso* substituents to the anthracene spectrum. In the case of 9-phenylanthracene and 9,10-diphenylanthracene, the contribution of the phenyl groups (assumed identical with that of benzene) is negligible at all wave lengths. For 9,10-di-(α -naphthyl)-anthracene, there is a region between 2700–2900 \AA . in which the naphthalene contribution is dominant, and it will be observed in Fig. 2 that the spectrum of this compound shows some evidence of this effect.

Non-Hindered Aryl Derivatives of Aromatic Hydrocarbons.—If these explanations are valid, aryl substituted polynuclear aromatic hydrocarbons in which the aryl group is not hindered should have spectra which deviate considerably from this additivity rule. A substance of this type is β -phenylnaphthalene (VII), the spectrum²⁰ of which is compared with that calculated for a mixture of one mole of naphthalene and one mole of benzene in Fig. 3. Considerable differences are observed: the shape of the curve is fundamentally changed and the intensity of the ab-



(20) Fieser and Hershberg, *THIS JOURNAL*, **60**, 940 (1938).

sorption in the region of the maxima is increased tenfold and is comparable with the increase in intensity of the biphenyl spectrum over that of benzene. Included in Fig. 3 is the closely similar spectrum²⁰ of 6,7-dihydro-20-methylcholanthrene (VIII), a derivative of β -phenylnaphthalene in which the rings are restricted in an approximately coplanar position by a dimethylene bridge. This evidence may not be strictly acceptable, since the similarity of this spectrum to that of β -phenylnaphthalene was used as evidence in assigning the constitution of VIII.²⁰

Porphine Derivatives.—A further example of a compound in which the introduction of phenyl substituents does not significantly alter the spectrum is provided by the *meso*-tetraphenylporphines. The absorption spectra of *meso*-tetraphenylporphine and *meso*-tetravanillinporphine have been measured by Knorr and Albers,²¹ who observed that the spectra of these aryl derivatives differ little from those of alkyl derivatives except that the bathochromic shift is slightly greater; similar effects are observed in the isoporphine series. In these compounds, again, steric factors are operative in inhibiting a coplanar structure.

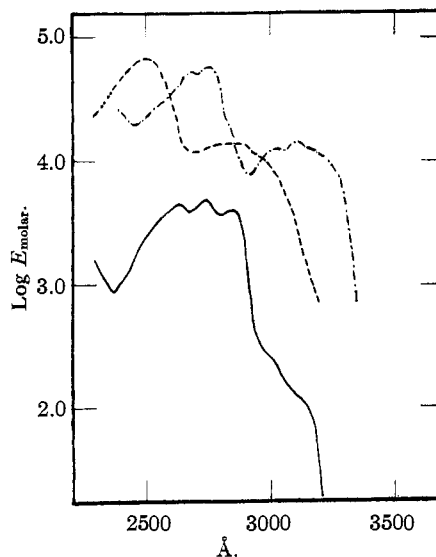


Fig. 3.— — Naphthalene + benzene; - - - β -phenylnaphthalene; . . . 6,7-dihydro-20-methylcholanthrene (broken curves by Fieser and Hershberg, solvent ethanol).

(21) Knorr and Albers, *J. Chem. Phys.*, **9**, 197 (1941); Albers and Knorr, *ibid.*, **4**, 422 (1936).

Conclusions.—The examples discussed suggest that geometrical factors may play a greater part in determining the absorption spectra of substances containing aryl substituents than has been realized heretofore. In solution, the molecules are oriented randomly toward the electric vector of the light wave and the study of absorption spectra of oriented layers of molecules would help considerably to clarify this subject if suitable methods of measurement could be devised.

Acknowledgments.—The author wishes to express his appreciation of the encouragement given by Professor L. F. Fieser, and to thank the International Cancer Research Foundation for financial support. Thanks are also due to Dr. D. M. Bowen who measured the spectra of the dihydrophenanthrene compounds and to Dr. R. B. Woodward who has checked the calculations of the 9,10-dihydrophenanthrene rotation.

Summary

Ultraviolet absorption spectra measurements on derivatives of biphenyl in which the rings are constrained in a coplanar form by alicyclic bridge linkages between the 2,2' and 6,6' positions support the argument that a coplanar structure is necessary for the development of the typical biphenyl spectrum. From this it may be inferred that conjugated aromatic chromophores contribute additively to the total absorption when prevented from acquiring a coplanar configuration.

On the basis of this assumption, several examples of anomalous absorption spectra in the *meso*-arylanthracene series can be explained satisfactorily.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conjugation of Horse Serum Albumin with Isocyanates of Certain Polynuclear Aromatic Hydrocarbons

BY HUGH J. CREECH AND R. NORMAN JONES

In an earlier paper,¹ a description was given of four conjugates prepared from horse serum albumin and 1,2-benzanthryl-3-isocyanate (I) and 1,2-benzanthryl-10-isocyanate (II). It was demonstrated that chemical combination of the components had occurred in an aqueous dioxane medium, and the extent of conjugation was determined by ultraviolet spectrophotometry. As prepared under the experimental conditions specified, the 1,2-benzanthryl-10-carbamido horse serum albumins contained twelve hydrocarbon prosthetic groups per molecule, and one preparation of the 1,2-benzanthryl-3-conjugate contained eighteen hydrocarbon groups per molecule. After preliminary removal of adsorbed isocyanate, the conjugates retained a constant benzanthryl content following repeated and different chemical treatments. By adding unreactive aminobenzanthracene to the albumin solution under the conditions used in the formation of the conjugates, it was shown that the methods of purification completely removed the adsorbed hydrocarbon derivative from the protein.

(1) Creech and Jones, *THIS JOURNAL*, **62**, 1970 (1940).

This work has been repeated and extended to the preparation of horse serum albumin conjugates formed from β -anthryl isocyanate (III),² 10-methyl-1,2-benzanthryl-3-isocyanate (IV),³ 1,2,5,6-dibenzanthryl-9-isocyanate (V)⁴ and 3,4-benzpyrenyl-5-isocyanate (VI).³ It appears that the extent of introduction of hydrocarbon radical into the protein molecule at a given pH is dependent upon the amount of dioxane used in the reaction mixture and the solubility of the particular hydrocarbon isocyanate in dioxane. Under practically identical conditions, it was found that the more soluble isocyanates I, II and IV were coupled with serum albumin to a greater extent than the less soluble isocyanates III, V and VI. It was also found that the process of conjugation under a given set of experimental conditions could be repeated readily without any appreciable variation in the degree of coupling. The conjugates are soluble in distilled water and the solutions usually are optically clear at a protein concentration of 2%. The conjugates, however, are

(2) Fieser and Creech, *ibid.*, **61**, 3502 (1939).

(3) Creech, *ibid.*, **63**, 576 (1941).

(4) Creech and Franks, *ibid.*, **60**, 127 (1938).