

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

The Dipole Moment of *ms*-Tetraphenylporphine

BY W. D. KUMLER

The configuration of the porphine ring system is of much interest because of its presence in chlorophyll and hemoglobin. A dipole moment study of a compound such as *ms*-tetraphenylporphine appeared to offer a way to tell whether the compound and, hence, the ring system was symmetrical or unsymmetrical.

The *ms*-tetraphenylporphine used in these studies was the more abundant isomer with a hydrochloric acid number of 13.5.¹ The compound is highly colored and absorbs appreciably in the yellow, hence, the usual method of determining the electronic polarization by measuring the refractive index with the D sodium line could not be used. However, it appeared if light were used of a wave length that was not absorbed by the compound the refractive index might be measured despite the fact that the compound is highly colored. The orange 6143 line in a neon tube was found to be a suitable source. Abnormalities in the refractive index, which might have been expected had the wave length of light used been too near an absorption band, were not observed.

Results

The results are given in Table I.

TABLE I
MEASUREMENTS IN BENZENE AT 25°

ω_2	ϵ_{12}	ν_{12}			
0.002010	2.2777	1.1454			
.004458	2.2807	1.1447			
.005595	2.2816	1.1442			
.006762	2.2834	1.1436			
.007916	2.2851	1.1435			
ϵ_1	ν_1	α	$-\beta$	P_{20}	$P_{E_{20}}$
2.2742	1.1460	1.355	0.311	310	293

The P_{20} value was calculated by using the equations

$$P_{20} = \frac{3\alpha\nu_1}{(\epsilon_1 + 2)^2} + (\nu_1 + \beta) \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

$$P_{E_{20}} = P_{20}M_2$$

where the symbols have the same significance as in the previous paper.²

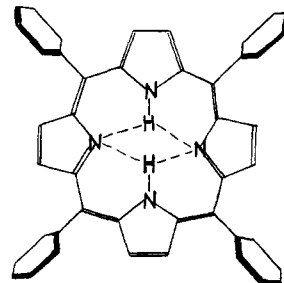
The values of α , β , ν_1 , and ϵ_1 were determined graphically. A combination of three factors, namely, the large size of the molecule, its low solubility, and the fact that its moment is small or

zero, result in a very small difference in the dielectric constant of the various solutions. As a result the experimental error in both P_{20} and $P_{E_{20}}$ is probably about 7 cc.

The value of 310 for P_{20} and 293 for $P_{E_{20}}$ indicates that the compound has a small or zero moment. The experimental error is of such magnitude that a moment of a few tenths cannot be distinguished from a moment of zero. It is probable that this large highly resonating molecule has a comparatively large atomic polarization of the order of the difference between P_{20} and $P_{E_{20}}$.

The polarization of the compound was also determined at 5° intervals between 25° and 45° but no decrease in polarization with increasing temperature was observed which likewise indicates the compound has zero moment.

With zero moment the molecule must be arranged in some symmetrical fashion. A symmetrical structure might exist with the giant ring either puckered or flat. The giant ring is, however, a highly resonating system and the atoms must get into such a position that the alternate single and double bonds can shift their position without involving an appreciable movement of the atoms. This demands a flat structure with the giant ring, the pyrrole rings and the 1 and 4 carbon atoms of each benzene ring all in one plane. The two hydrogen atoms in the center can conceivably be arranged symmetrically in a number of ways. First, on opposite nitrogen atoms with one hydrogen above and one below the plane of the main ring. Second, as above but forming hydrogen bonds to one of the adjacent nitrogen atoms. Third, in the plane of the main ring and forming a bifurcated hydrogen bond with both adjacent nitrogen atoms (as in the figure). Fourth, the same as in the second case except the covalence to each hydrogen shifts (resonates), being attached first to one and then to the other nitrogen atom. Fifth, the same as in the third case except the covalence to



ms-Tetraphenylporphine.

(1) Rothemund and Menotti, *THIS JOURNAL*, **63**, 267 (1941).

(2) Halverstadt and Kumler, *ibid.*, **64**, 2988 (1942).

each hydrogen shifts among three nitrogen atoms. Case one is unlikely because it appears highly probable that hydrogen bonds are present.^{3,4,5} If the actual situation is that of case four or five, which does not appear at all unlikely, there would be no isomerism due to the position of the hydrogen atoms.

It appears from a study of the Fisher models that a flat giant ring of this type can be constructed without undue strain. However, there is much interference between the pyrrole rings and the benzene rings if an attempt is made to place the latter in the same plane as the rest of the molecule. This suggests that the benzene rings do not have free rotation and are probably oscillating about a position perpendicular to the plane of the main ring. The general shape of the molecule would then be that of a flat disc with the four benzene rings cutting it at about right angles. If the benzene rings do not have free rotation then derivatives of *ms*-tetraphenylporphine having ortho or meta substituents should exist in a number of stereoisometric forms depending on whether the substituents are above or below the plane of the giant ring.

Experimental

The dielectric constant measurements were carried out with the same apparatus and in the same manner as described previously.⁶ The refractive indices were measured with a Pulfrich

(3) Corwin and Quattlebaum, *THIS JOURNAL*, **58**, 1081 (1936).

(4) Vestling and Downing, *ibid.*, **61**, 3511 (1939).

(5) Aronoff and Weast, *J. Org. Chem.*, **6**, 550 (1941).

(6) Kumler, *THIS JOURNAL*, **62**, 3292 (1940).

refractometer using a neon Geissler tube as a light source.

The *ms*-tetraphenylporphine was recrystallized twice from benzene.

Acknowledgment.—We are indebted to Dr. O. L. Inman and Dr. Paul Rothemund of the C. F. Kettering Foundation at Antioch College for the sample of *ms*-tetraphenylporphine.

Summary

The more abundant isomer of *ms*-tetraphenylporphine was found to have a polarization of 310 and an electronic polarization of 297. Measurement of polarizations at different temperatures gave no evidence of a decrease of polarizations with increasing temperatures. Both methods indicate the compound has zero moment although the data do not enable one to distinguish between a moment of a few tenths and a zero moment.

The electronic polarization of the compound was obtained by measuring the refractive index of the solutions although they were highly colored. This was accomplished by using the orange line of a neon tube. This light had a wave length that was not absorbed by the solution.

The zero moment indicates the compound is symmetrical. The resonance demands that the giant ring and the pyrrole rings be in one plane. A study of the Fisher models suggests the benzene rings do not have free rotation and are perpendicular to this plane. With ortho or meta substituents on the benzene rings this hindered rotation will give rise to a number of stereoisomers.

SAN FRANCISCO, CALIF. RECEIVED SEPTEMBER 24, 1942

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 885]

The Serological Properties of Simple Substances. I. Precipitation Reactions between Antibodies and Substances Containing Two or More Haptenic Groups

BY LINUS PAULING, DAVID PRESSMAN, DAN H. CAMPBELL, CAROL IKEDA, AND MIYOSHI IKAWA

The study of serological precipitation reactions is complicated by the fact that ordinarily these reactions involve two proteins, the antigen and the antibody. The understanding of these reactions was greatly advanced by the introduction into their study of precise microanalytical methods and a further simplification involving the use of a nitrogen-free multivalent hapten of pneumococcus polysaccharide.¹ A few years ago it was reported

by Landsteiner and van der Scheer^{2a} that the precipitin reaction and anaphylaxis could be produced by simple substances formed by coupling two haptenic groups with resorcinol or tyrosine, in place of the azoprotein (containing the same haptenic group) which has been used as the antibody-producing antigen. Landsteiner^{2b} suggested that "the ready precipitability of these

(1) M. Heidelberger and F. E. Kendall, *J. Exptl. Med.*, **50**, 809 (1929); **61**, 559, 563 (1935).

(2) (a) K. Landsteiner and J. van der Scheer, *Proc. Soc. Exptl. Biol. Med.*, **29**, 747 (1932); *J. Exptl. Med.*, **56**, 399 (1932); **57**, 633 (1933); **67**, 79 (1938). (b) K. Landsteiner, "The Specificity of Serological Reactions," Charles C Thomas, Baltimore, Md., 1936, p. 120.