

etioporphyrin II-copper complex bands and no unreacted etioporphyrin II.

Exchange Reactions between Compound IV and Methene III.—(a) Using the same general procedure described in the competition reaction for copper, the copper complex of compound IV was formed first and then the methene was added to the solution. The reaction mixture was boiled for 5 minutes and, after cooling, the hand spectroscopy showed no formation of etioporphyrin II, compound IV. (b) Using the same procedure, the copper complex of methene III was formed and compound IV was then added to the solution. After boiling, the hand spectroscopy showed formation of the copper complex of compound IV.

Competition and Exchange Reactions between Compound V and Methene II for Copper.—The same general method was used for the competition and exchange reactions between compound V and methene III for copper as that described for compound IV and methene III.

Exchange Reaction between Compound IV and Methene II and Magnesium.—The procedure used for this exchange reaction is the same as that described for the exchange reactions of methene II and methene III and magnesium, using 4-methyl-1,3-dioxane as the solvent, 1.72 mg. of methene II, 1.2 mg. of compound IV and 1 drop of 1 *M* Grignard reagent.

Competition between Compound IV and Compound VI for Copper.—In 4 ml. of pyridine was dissolved 2.39 mg. of compound IV (0.5×10^{-5} mole), and 3.27 mg. of compound VI (0.5×10^{-5} mole) was dissolved in 5 ml. of pyridine. The two porphyrin solutions were mixed. One mg. of cupric acetate monohydrate (0.5×10^{-5} mole) was added to the porphyrin solution and the mixture heated to boiling and boiled 5 minutes. For spectra, the solution was diluted 1:10 and then 5:10 with pyridine:

(1)	ϵ_{620}	0.163	Etioporphyrin II	0.48×10^{-5} mole
(2)	ϵ_{620}	0.127	Etioporphyrin II	0.46×10^{-5} mole

Exchange Reactions with Copper between Compound IV and Compound VI.—The procedure used in the competition reaction was tried for an exchange reaction.

Competition and Exchange Reactions with Magnesium, Compound IV and Compound VI.—The procedure described for the methene-magnesium reactions was used for the reactions between these two porphyrins and magnesium.

Competition and Exchange Reactions between Compound V and Compound IV for Copper.—(a) 2.39 mg. of compound IV (0.5×10^{-5} mole) and 2.40 mg. of compound V (0.5×10^{-5} mole) were dissolved in 19 ml. of glacial acetic acid. One mg. of cupric acetate monohydrate (0.5×10^{-5} mole) dissolved in 1 ml. of glacial acetic acid was added to the solution at room temperature with stirring and in a hydrogen atmosphere. After 10 minutes the spectrum was taken and absorption bands appeared at 520, 560 and 620 $m\mu$. (b) Exchange reactions were performed using the same general procedure described for the competition reaction in a.

Competition and Exchange of Magnesium between Compound V and Compound IV.—The procedure used in the methene-magnesium competition and exchange reactions also were used for the chlorin-porphyrin reactions with magnesium.

Formation of Copper Mesoporphyrin in Pyridine and Pyridine-Water Mixture.—(a) To 1 ml. of a pyridine solution of mesoporphyrin 5×10^{-4} *M* was added 1 ml. of pyridine and 5 drops of a pyridine solution of cupric acetate monohydrate 0.012 *M*. (b) To 1 ml. of the same mesoporphyrin solution was added 1 ml. of distilled water and 5 drops of cupric acetate monohydrate in pyridine (0.012 *M*). Solutions a and b were placed in a water-bath at 50° for 20 minutes. The spectrum of the two solutions after that time was taken with a hand spectroscopy. Solution a showed no copper-mesoporphyrin spectrum, while b showed the formation of the copper complex of mesoporphyrin.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Dipole Moments of Phenylmercurials

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The dielectric constant of solid diphenylmercury has been found to be 2.87, showing that the atomic polarization is normal. Thus the observed polarization apparently is due to orientation, so that diphenylmercury is not linear. Also non-linearity in the C-Hg-X bond is confirmed by dipole moment studies of several substituted phenylmercuric halides. The included angle of these mercurial linkages seems to be 130–150°.

There is doubt about the valence angle which mercury assumes when it is bonded to carbon or to carbon and halogen. Smyth¹ and Oesper² assumed an angle of 180° in calculation of the electric moment of benzylmercuric chloride. This assumption is validated by evidence from Raman spectra,^{3–5} electron diffraction⁶ and X-ray diffraction⁷ that mercuric chloride is linear, at least in the vapor state. Indeed the valence electrons of mercury (II), occupying 6s² orbitals might be expected in compound formation to assume sp orbitals which, from symmetry considerations, are diametrically opposed.

However other studies have indicated that the C-Hg-X bond in organomercurials is angular.

(1) C. P. Smyth, *J. Org. Chem.*, **6**, 421 (1941).

(2) P. F. Oesper and C. P. Smyth, *THIS JOURNAL*, **64**, 173 (1942).

(3) K. W. F. Kohlrausch, "Der Smekal-Raman Effekt," Verlag von Julius Springer, Berlin, 1931, pp. 182–184.

(4) P. Krishnamurti, *Ind. J. Phys.*, **5**, 113 (1930).

(5) H. Braune and G. Engelbrecht, *Z. physik. Chem.*, **10B**, 1 (1930); **11B**, 409 (1931).

(6) H. Braune and S. Knoke, *ibid.*, **23B**, 163 (1933).

(7) H. Braune and R. Linke, *ibid.*, **31B**, 12 (1935).

Curran⁸ assigned a non-linear bonding in the arylmercuric bromides to explain the moments of 3.06, 3.39 and 1.57 *D* obtained, respectively, from phenyl-, *p*-tolyl- and *p*-chlorophenylmercuric bromides. This angularity cannot be ascribed to coordination with the solvent, dioxane, because the moments determined in benzene solution are about the same.⁹ Curran assumed the C-Hg moment to be about zero, the over-all H-C₆H₅-Hg moment to be 0.3, the *p*-CH₃-C₆H₄ moment to be 0.4 and the -HgBr moment to be 2.75. Then if the difference between the C-Cl and C-H dipoles is 1.6 Curran's calculation shows that the C-Hg-Br angle varies with the aryl group; it is 140° for the *p*-tolylmercurial and 167° for the *p*-chlorophenylmercurial. However these results should be regarded only qualitatively since a difference of 0.1 *D* in these highly degenerate *para*-substituted benzenes would vitiate the calculated differences.

Earlier Hampson¹⁰ had presented evidence for

(8) B. C. Curran, *THIS JOURNAL*, **64**, 830 (1942).

(9) B. C. Curran, *ibid.*, **57**, 2162 (1935).

(10) G. C. Hampson, *Trans. Faraday Soc.*, **30**, 877 (1934).

the angularity of the C-Hg-C linkage when he found for diphenylmercury a moment of 0.44 D at 25° and 0.54 D at 142° in decalin, also 0.41 D in benzene at 25°. Furthermore this significant deviation from the zero moment expected of a linear C-Hg-C linkage was substantiated by moments of 0.74, 0.87, 0.92 and 1.15 D found in decalin at 142° for diphenylmercury substituted in the *para* positions, respectively, by methyl, fluoro, bromo and chloro groups. These values correspond with C-Hg-C angles of 151, 165, 165 and 157°, respectively, for a $\overset{\oplus}{\text{C}}-\overset{\ominus}{\text{Hg}}$ moment of about 0.5 D .

Hampson considered these moments to be caused by C-Hg-C bending due to thermal agitation, but it was later shown that the calculated period of oscillation for mercuri-bis-chlorobenzene¹¹ (1.5×10^{-12} sec.) is too small to account for orientation polarization of the observed magnitude. Coop and Sutton then attempted to ascribe the observed polarization to an atomic contribution such as that in *p*-benzoquinone. However calculation of the atomic polarization of mercuri-bis-chlorobenzene by the relationship $P_A = 4\pi N\mu^2/9V_i$ gave a value of about 2 cc. using a bond moment, μ , of 1.6 for the Cl-C₆H₄-Hg group (assuming mercury negative with respect to carbon) and a force constant, V_i , of 0.025 erg/radian²/molecule, whereas the difference between total and electronic polarization ($P - P_E$) is 19.7 cc. It was concluded that the diphenylmercury moments could not be ascribed to atomic polarization unless the force constants of bending were anomalously low.

We have now tried to measure directly the atomic polarization of diphenylmercury. In an apparatus precise to $\pm 0.001 \mu\mu\text{f.}$ which is described elsewhere¹² a series of diphenylmercury pellets of density 2.37 have been measured. Extrapolation of the observed dielectric constants at 0.5 mc to an infinitesimal pellet thickness (Fig. 1) eliminates the "edge-effect" capacitance error and thus provides a true dielectric constant of 2.87. The distortion polarization (P_{E+A}) calculated from this value is 59.2 cc. This value is lower than that which Hampson calculated ($P_E = 65.3$ cc.) for the electronic polarization of diphenylmercury, and also is lower than the 61.9 cc. calculated by us using refraction data more recent^{13,14} than those used by Hampson. It is possible that our value will be raised to a number comparable with these calculated ones by small improvements in the pressed density of the pellets. It may be significant that these pellets are still opaque, and attempts are still being made to eliminate air interfaces so completely that

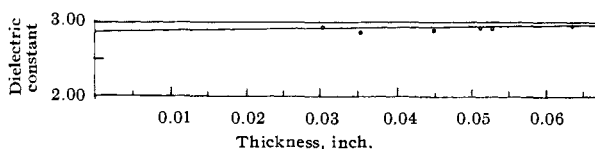


Fig. 1. Extrapolated dielectric constant.

(11) I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).

(12) C. C. Meredith and G. F. Wright, *Can. J. Technology*, submitted.

(13) A. I. Vogel, *J. Chem. Soc.*, 134 (1946); 607 (1948).

(14) W. K. Wilde, *ibid.*, 72 (1949).

they will be translucent. However our studies with pellets of various densities indicate at this time that the dielectric constant will not be raised beyond the value calculated according to Vogel and Wilde's refractometric data. Tentatively we must therefore interpret the total polarization by an electric moment of about 0.6 D based on molecular refraction or 0.79 D as calculated from our observed electronic plus atomic polarization. Meanwhile we are seeking another explanation for the apparent anomaly that diphenylmercury has a measurable moment.

This evidence that the C-Hg-C linkage is angular has prompted a further investigation concerning the C-Hg-X linkage in aromatic compounds. Three substituents, chloro, carbomethoxy and, principally, methoxy have been studied in phenylmercuric chlorides and bromides. Since the resultant moments are rather insensitive to difference in group moment angle we have sought a precision of $\pm 0.005 D$ by use of a stainless steel cell of 14-ml. liquid capacity and about 220 $\mu\mu\text{f.}$ of air capacitance measurable to at least $\pm 0.002 \mu\mu\text{f.}$ ¹² The density determination ($\pm 1 \times 10^4$) thus limits the precision of the electric moments, which are calculated using the refractometric data of Vogel¹³ and Wilde.¹⁴ These moments are listed in Table I.

TABLE I

DIPOLE MOMENTS FROM DIELECTRIC MEASUREMENTS IN DIOXANE AT 20° AT 0.5 MC.

Substance	P_2	MR_D	μ
Phenylmercuric chloride	227.26	41.37	2.99
<i>o</i> -Chloromercurianisole	354.80	48.81	3.84
<i>m</i> -Chloromercurianisole	281.56	48.81	3.35
<i>p</i> -Chloromercurianisole	326.58	48.81	3.65
<i>o</i> -Bromomercurianisole	368.47	51.71	3.90
<i>m</i> -Bromomercurianisole	304.72	51.71	3.49
<i>p</i> -Bromomercurianisole	359.03	51.71	3.85
<i>o</i> -Iodomercurianisole	422.48	56.92	4.19
<i>p</i> -Iodomercurianisole	318.63	56.92	3.55
<i>m</i> -Chlorophenylmercuric chloride	223.56	47.27	2.91
Methyl <i>p</i> -chloromercuribenzoate	218.29	53.24	2.82
Phenylmercuric cyanide	359.86	40.35	3.92
Diphenylmercury	72.12	59.2 ^a	0.79
Nitrobenzene	390.98	32.40	4.15

^a From solid dielectric measurements.

The observed moments are compared with those calculated assuming free rotation of the substituent groups of moment angle α and β according to Fuchs' equation¹⁵

$$\mu^2 = a^2 + b^2 + 2ab \cos \alpha \cos \beta \cos \theta$$

wherein θ is the angle between the substituent groups in the benzene ring. Because of degeneracy inherent in the benzene nucleus the moment angles will differ according to the position of the substituent group.

The moment angle of the *para* methoxy group has been evaluated from anisole, bromobenzene and *p*-bromoanisole as 71.5°¹⁶ and from *p*-chloroanisole¹⁷ as 73°. We have used a 72° angle for cal-

(15) O. Fuchs, *Z. physik. Chem.*, **14B**, 339 (1931).

(16) W. F. Anzilotti and B. C. Curran, *THIS JOURNAL*, **65**, 607 (1943).

(17) M. Calvin and G. E. K. Branch, "Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1949, p. 142.

ulation of both *o*- and *p*-anisylmercurials. In like manner the moment angle of the *meta*-methoxyl has been calculated as 66° from the comparable moments of anisole (1.23 *D*), nitrobenzene (3.93 *D*) and *m*-nitroanisole (3.86 *D*). This value may be too low because of the degenerative effect of the nitro group which in *p*-nitroanisole ($\mu = 4.74$ *D*) causes a calculated moment angle of 55° for the methoxyl group. Therefore both moment angles, 66° and 72°, will be used in evaluation of the aryl-attached halogenomercuri group.

The *para*-carbomethoxyphenyl moment angle may be calculated from the moments of 1.82 *D* for methyl *p*-bromobenzoate, 2.01 *D* for methyl benzoate and 1.53 *D* for bromobenzene. This moment angle value of 120° is in good agreement with that reported by Halverstadt and Kumler.¹⁸

The direction of the C-Hg-X moment has been defined by Smyth^{1,2} and Curran⁹ with halogen negative and carbon positive. The correctness of this assumption is substantiated by the high moment of phenylmercuric cyanide. If one assumes further with Curran and Hampson that the carbon-mercury moment is small, or else zero, then the moment is negative at halogen and positive at mercury; in consequence the bond angle of C-Hg-X is essentially identical with the moment angle.

The *ortho*-anisylmercurials are of little value in evaluation of the C-Hg-X bond angle. Thus *o*-chloromercurianisole with an observed moment of 3.84 *D* should have a moment of 2.15 *D* if the group moments were directed (*cis*) away from one another. If the groups were freely-rotating the resultant would be 3.08 *D* whereas resultants of 4.21 or 3.92 *D* (depending, respectively, on a C-Hg-Cl bond angle of 130 or 180°) are calculated if the group moments (*trans*) support one another. Similarly the resultant moment of *o*-bromomercurianisole (obsd. 3.90 *D*) would be 2.27 *D* if groups were *cis*, 3.20 *D* if freely-rotating and 4.34 or 4.05 *D* (depending on 130 or 180° for C-Hg-Br). Of course the observed moments show that the methyl group is directed away from the chloromercuri group, but this would be anticipated by the results of Anzilotti and Curran¹⁶ for *o*-halogenoanisoles.

Because of strong degeneracy usually associated with 1,4-disubstituted benzenes one might anticipate little to be learned from *para*-substituted phenylmercurials. However Table II shows that the mesomeric contributions are consistent if a

TABLE II

CALCULATED MOMENTS OF FREELY-ROTATING *para*-SUBSTITUTED PHENYLMERCURIALS USING MOMENT ANGLES OF 72° FOR METHOXYL AND 120° FOR CARBOMETHOXYL

Compound	C-Hg-X bond angle						Obsd. μ
	180°		150°		130°		
	Calcd.	obsd.	Calcd.	obsd.	Calcd.	obsd.	
<i>p</i> -Chloromercurianisole	3.57	0.98	3.52	0.96	3.45	0.95	3.65
<i>p</i> -Bromomercurianisole	3.69	.96	3.64	.95	3.57	0.93	3.85
Methyl <i>p</i> -chloromercuribenzoate	2.64	.94	2.79	.99	3.02	1.07	2.82

(18) I. F. Halverstadt and W. D. Kumler, *THIS JOURNAL*, **64**, 2988 (1942).

C-Hg-X bond angle of 130° is assumed. The mesomerism related to methoxyl and carbomethoxyl ought to be opposite in polarization, which should reverse the ratio of calculated to observed moment. It may be seen that this condition is not met by assumption of a 180° C-Hg-X bond angle. There is a trend toward reversal by assumption of a 150° angle, but closest agreement with that expected when +M becomes -M is found (0.93, 0.95 *versus* 1.07) when a 130° angle is assumed.

Evaluation of the angularity of the C-Hg-X bond should be most satisfactory in *meta*-substituted phenylmercuric halides, because degeneracy is minimal in 1,3-disubstituted benzenes. Although the methoxyl moment angle is not exactly known (66° *vs.* 72°) it may be seen in Table III that this doubt has little effect on the calculated moments. Furthermore the agreement between calculated and observed moments for the *m*-methoxyphenylmercuric halide is comparable with those of *m*-chlorophenylmercuric chloride in which only one group capable of free rotation is present. Therefore the 130° bond angle of C-Hg-X is favored for the *meta*- as well as the *para*-substituted phenylmercuric halides.

TABLE III

CALCULATED MOMENTS OF FREELY-ROTATING *meta*-SUBSTITUTED PHENYLMERCURIC HALIDES

Compound	C-Hg-X bond angle at 66 and 72° methoxy moment angles						Obsd. moment
	180°		150°		130°		
	66	72	66	72	66	72	
<i>m</i> -Chloromercurianisole	3.45	3.40	3.42		3.38	3.35	3.35
<i>m</i> -Bromomercurianisole	3.57	3.53	3.54		3.50	3.47	3.49
<i>m</i> -Chlorophenylmercuric chloride		2.61		2.72		2.90	2.91

Experimental¹⁹

Purification of Materials.—Benzene was washed repeatedly with concentrated sulfuric acid until the acid layer was colorless, then twice with water and with aqueous sodium bicarbonate. After calcium chloride drying the benzene was refluxed under nitrogen over sodium until the addition of a *small amount* of benzophenone produced a deep blue color. After distillation of the colored solution under nitrogen from the sodium the heart cut was stored over sodium.

Dioxane was boiled 6 hr. with concentrated hydrochloric acid (5 ml./l.), then neutralized and dried with solid sodium hydroxide. After separation of the salt phase the dioxane was distilled, then refluxed over sodium under nitrogen until addition of benzophenone gave a blue color. After distillation of the blue solution through a column without ebullition in order to avoid spray the distillate was stored over sodium. It was freshly redistilled for use in each determination in order to avoid peroxides.

Phenylmercuric chloride was crystallized from ethyl acetate (30 ml./g.), m.p. 258.4–258.9°. Phenylmercuric cyanide²⁰ was crystallized from chloroform (50 ml./g.) and ethanol (3 ml./g.), m.p. 208.5–209.3°. Diphenylmercury was crystallized from 1:1 chloroform-ethanol (7 ml./g.), m.p. 123.4–124.1°. Its absorption spectrum was determined in ethanol (214–400 m μ) and in carbon tetrachloride (1.0–2.85 μ) in a Beckman DK spectrophotometer: wide shoulder from 270–248 m μ , *E* 369 at 270 m μ ; *E* 2564 at 228 m μ ; *E* 2.1 at 1.68 μ ; *E* 2.3 at 2.15 μ ; *E* 5.1 at 2.44 μ ; *E* 4.3 at 270 μ . Nitrobenzene was fractionated, b.p. 81–82°

(19) Melting points have been corrected against known standards. The strongest lines of X-ray diffraction patterns were determined with Cu K α (Ni filtered) radiation and reported as relative intensities [*I*/*I*].

(20) R. Otto, *J. prakt. Chem.*, [2] **1**, 182 (1870).

(8 mm.) and then redistilled, b.p. 79.7° (8 mm.), m.p. 5.75°. *m*-Chloromercurianisole,²¹ prepared in 58% yield, m.p. 157–160°, was crystallized from carbon tetrachloride (6 ml./g.) and dioxane (2 ml./g.), m.p. 163.9–164.4°. Crystallization of *o*-bromomercurianisole²³ from dioxane (2 ml./g.) gave a melting point of 188.6–189.5°. Interaction of silver acetate and *o*-chloromercurianisole followed by potassium iodide gave *o*-iodomercurianisole,²⁴ m.p. 171.3 and 171.7° after crystallization from benzene (6.5 ml./g.) and dioxane (7 ml./g.). Methyl *p*-chloromercuribenzoate, prepared according to Nesmeyanov²¹ in 17% yield, m.p. 248–254°, was crystallized from ethanol (10 ml./g.) and ethyl acetate (50 ml./g.), m.p. 253.4–255.0° as contrasted to Nesmeyanov's 259°.

o-Chloromercurianisole.—Mercuric acetate (318 g., 1 mole) was heated with 864 g. (8 moles) of anisole for 48 hr. The hot mixture was filtered and cooled to precipitate 55 g. (15%) of *p*-acetoxymmercurianisole, m.p. 171–175°, which was crystallized from ethanol (17 ml./g.), m.p. 176–177°. The reaction and crystallization liquors were treated with an excess of aqueous sodium chloride and the mixture was steam distilled. From the distillate 2.5 g. (0.7%) of *o*-chloromercurianisole, m.p. 175–177°, was collected. It was crystallized from chloroform (17 ml./g.) and ethanol (30 ml./g.), m.p. 179–179.4°.

p-Chloromercurianisole.—The residue from the steam distillate yielding the *ortho* isomer was filtered, washed with water and dried. This mixture of mono- and dichloromercurials, m.p. 218–236°, was continuously extracted with dioxane leaving 75 g. of insoluble infusible dichloromercurianisole. The extract, evaporated, left 175 g. (51%) of *p*-chloromercurianisole, m.p. 240–246°. This crude product was crystallized from ethyl acetate (70 ml./g.), m.p. 252.5–252.7°.

m-Bromomercurianisole.—According to the method of Nesmeyanov²¹ a solution of 3.69 g. (0.03 mole) of *m*-anisidine in 11 ml. of 40% hydrobromic acid plus 6 ml. of water (0.075 mole) was diazotized with 2.4 g. (0.03 mole) of sodium nitrite. The cold solution was quickly added to 10.8 g. (0.03 mole) of mercuric bromide in 11 ml. of 40% hydrobromic acid plus 6 g. of ice and shaken. The double salt (13.3 g., 78%, m.p. 72–73°) was filtered and washed with cold water and ether, then added portionwise with stirring to a cooled suspension of 4.4 g. (0.69 atom) of copper pow-

der in 200 ml. of acetone. After 12 hr. the precipitate was filtered and the residue was extracted with acetone. The extract was evaporated until crystals separated which were washed with ether, 3.5 g. (40%), m.p. 137–139.2°, crystallized from carbon tetrachloride (10 ml./g.), m.p. 152.3–152.3°.

Anal. Calcd. for C₇H₇BrHgO: C, 21.7; H, 1.82. Found: C, 21.7; H, 1.92.

m-Chlorophenylmercuric Chloride.—Nesmeyanov's method, as outlined above, was employed with *m*-chloroaniline to yield the double salt (88%, m.p. 128.4–128.7°, dec.) which was converted in 57% yield to *m*-chlorophenylmercuric chloride, m.p. 210–212°. When crystallized from ethanol (25 ml./g.) this melted at 212.0–212.4°.

Anal. Calcd. for C₆H₄Cl₂Hg: C, 20.7; H, 1.11. Found: C, 20.6; H, 1.37.

p-Bromomercurianisole.—A mixture of 10 g. (0.027 mole) of *p*-acetoxymmercurianisole and 8.5 g. (0.07 mole) of potassium bromide in 250 ml. of ethanol was refluxed for 15 min. It was then cooled and the crystals filtered, ethanol washed and dried, 10 g. (96%), m.p. 232–237°. Repeated crystallization from dioxane (9 ml./g.) and ethyl acetate (50 ml./g.) gave a m.p. of 258.5–259.5° as contrasted to 187° previously reported.²³

p-Iodomercurianisole.—Use of potassium iodide in the previous procedure gave an 82% yield, m.p. 226–229°. This was crystallized from ethyl acetate (55 ml./g.) and dioxane (8 ml./g.), m.p. 237.8–238.1°, contrasted to 227° previously reported.²³

Dielectric Constant of Diphenylmercury.—A series of pellets varying in thickness as shown in Fig. 1 was prepared in a cylindrical die²⁵ having a 0.25 inch bore. The compound was finely ground and was pressed at 8000 lb. dead load under a vacuum of about 20 mm. The pellets, which were not transparent, were weighed and measured. Densities calculated from these measurements were low (av. 2.31) indicating slight pellet distortion. Densities by flotation averaged 2.37 as compared with the reported value of 2.318.²⁶ In order to ensure absence of air space between the pellets and the plates of the modified micrometer caliper which served as a measuring device, the end surfaces were coated completely with a pasty zinc amalgam. From the extrapolated value of dielectric constant at minimal pellet thickness (2.87) the distortion polarization was calculated $P_{E+A} = (\epsilon - 1)M/(\epsilon + 2)d = 59.2$.

(26) "International Critical Tables," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1926, p. 121.

TORONTO, CANADA

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN AND THE NATIONAL BUREAU OF STANDARDS]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XXVIII. The Hydration of Azo Dyes in Organic Solvents

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The addition of water to alcoholic solutions of 4-amino, 4-dimethylamino, 4-hydroxy and 4-methoxy substituted azobenzenes gives rise to a new absorption band at a somewhat longer wave length than that of the main absorption band in the visible region, indicating the formation of some new species. This new band is attributed to the formation of a hydrogen bond between the azo group and water.

Introduction

In connection with some work on conjugated polyazo benzenes, a sample of 4,4'-diaminoazobenzene was prepared and carefully purified. In contrast with the spectra of other aminoazo compounds reported earlier,¹ the spectrum of this compound in 95% ethanol solution showed a strong shoulder on the long wave length side of the principal absorption band in the visible region, strongly suggestive

(1) W. R. Brode, J. H. Gould and G. M. Wyman, *THIS JOURNAL*, **75**, 1856 (1953).

of the presence of another species, perhaps some impurity. However, although the shoulder was not altered in intensity by repeated purification, it was enhanced by dilution of the solvent with increasing amounts of water until it appeared in 10% ethanol solution as a separate band of equal intensity, as shown in Fig. 1. As a result of this observation, it was decided to study the influence of water on the spectra of a large number of similar azo dyes, in the hope of arriving at a better understanding of this unusual solvent effect.