

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## The Dipole Moments and Structures of Five Organometallic Halides

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The dipole moments of a number of organometallic halides have been measured with the object of obtaining bond moments and considering molecular structures.

## Purification of Materials

**Triphenylgermanium Bromide.**—A sample kindly given us by Professor L. S. Foster of Brown University was used without purification.

**Triphenyltin Chloride.**—Material from the Eastman Kodak Company was recrystallized from benzene; m. p. 103°.

**Benzylmercury Chloride.**—An old sample from the laboratory stock room was found to have the correct melting point 104–105° and was, therefore, used without purification.

**Triphenylantimony Dichloride.**—Material from the Eastman Kodak Company, found to have the correct melting point, 142°, was used without purification.

**Triphenylbismuth Dichloride.**—Material from the Eastman Kodak Company was recrystallized from alcohol; m. p. 146–149°.

Thorough purification of these substances was prevented by the smallness of the amounts of material available.

**Benzene.**—The purification was carried out in the usual manner.<sup>1</sup> The dielectric constant and density of the solvent benzene were measured every day on which the solutions in it were run, the values being given in Table I.

## Experimental Results

The dielectric constants were measured at a frequency of 520 kilocycles with a crystal-controlled heterodyne beat apparatus previously described,<sup>2</sup> and the densities were determined with an Ostwald-Sprengel pycnometer in a manner described previously.<sup>3</sup> The dielectric constants,  $\epsilon$ , and the densities,  $d$ , of benzene solutions containing mole fraction,  $c_2$ , of the compound indicated are given in Table I, the polarizations,  $P_2$ , being listed in the last column. Table II lists in the second column the values of  $MR_D$ , the molar refraction for the D sodium line, calculated from the atomic and molar refractions

given in Landolt-Börnstein, and, for triphenylbismuth dichloride, the experimental value obtained from the densities and refractive indices measured for the two most concentrated solutions. The third column gives the polarizations,  $P_\infty$ , obtained by extrapolation to  $c_2 = 0$  of the values of  $P_2$  in Table I, and the fourth column gives the dipole moments calculated in the usual manner. The probable errors in the moment val-

TABLE I  
DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AND POLARIZATIONS AT 25°

$c_2$	$\epsilon$	$d$	$P_2$
Triphenylgermanium Bromide			
0.00000	2.2777	0.87230	...
.00163	2.2902	.87483	197
.00414	2.3122	.87855	207
Triphenyltin Chloride			
.00000	2.2811	.87238	...
.00512	2.3621	.88098	311
.00922	2.4270	.88788	309
.01382	2.5000	.89606	305
.02268	2.6397	.91070	301
Benzylmercury Chloride			
.00000	2.2794	.87244	...
.00342	2.3229	.88065	223
.00428	2.3392	.88301	238
.00704	2.3720	.88935	228
Triphenylantimony Dichloride			
.00000	2.2760	.87259	...
.00354	2.2901	.88007	139
.00621	2.2978	.88573	131
.01273	2.3202	.89916	131
.02293	2.3519	.91977	129
Triphenylbismuth Dichloride			
.00000	2.2766	.87303	...
.00286	2.2883	.88185	140
.00477	2.2959	.88802	137
.00952	2.3146	.90238	138
.01434	2.3325	.91700	136
.02580	2.3765	.95033	137

TABLE II  
MOLAR REFRACTIONS, POLARIZATIONS (AT 25°) AND DIPOLE MOMENTS

Substance	$MR_D$	$P_\infty$	$\mu \times 10^{18}$
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeBr	93	205	2.35
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnCl	95	315	3.28
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> HgCl	49	240	3.05
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SbCl <sub>2</sub>	104	133	1.19
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> BiCl <sub>2</sub>	112	140	1.17

(1) Smyth and Walls, *THIS JOURNAL*, **54**, 1854 (1932).

(2) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

(3) Lewis and Smyth, *THIS JOURNAL*, **61**, 3063 (1939).

ues are about 1% for triphenyltin chloride, 2% for benzylmercury chloride, and 5% for the three other substances. Measurements made by Mr. Marshall Pease on five additional solutions of triphenylantimony dichloride were in satisfactory agreement with those in Table I.

### Discussion of Results

The moment values for the first two substances in Table II have already been used to obtain lower limits for the values of the metal-to-halogen bond moment, from which the corresponding amounts of ionic character in the bonds have been calculated.<sup>4</sup> Revision of the data has altered these values and those of the next two substances by amounts too small to affect any of the considerations involved. Because of the 180° angle between the two mercury bonds,<sup>5</sup> the moment of the benzylmercuric chloride molecule may, as a rough approximation, be regarded as the difference between the moments of the two opposed metal-to-carbon and metal-to-chlorine bonds, as was shown to be the case for tetrahedral molecules like the first two in Table II.<sup>6</sup> The approximate lower limit for the Hg-Cl bond moment obtained by setting the Hg-C moment equal to zero and subtracting 0.3 as the amount associated with the H-C bond is thus given as 2.8. This rough calculation neglects the effect of the benzene ring, which, giving rise to a moment of 0.4 in toluene, would approximately cancel the H-C bond moment and leave the value to be assigned to the Hg-Cl bond limit as 3.0. It is probably this compensation of moments which prevents the value for benzylmercuric chloride from being slightly higher than the values, 3.14, found for phenylmercuric chloride.<sup>7</sup> On the assumption that the Hg-Cl distance is the same as in mercuric chloride, 2.34 Å,<sup>5</sup> the lower limit for the amount of ionic character in this Hg-Cl bond may be calculated as  $3.0 \times 10^{-18} / 4.80 \times 10^{-10} \times 2.34 \times 10^{-8} = 0.27$ , which is considerably lower than the lower limit 0.34 found for the Pb-Cl bond.<sup>4</sup> Insofar as this lower limit for the amount of ionic character of a bond may be used as a basis for the comparison of electronegativities, mercury is placed on a level with tin, the lower limit in the Sn-Cl bond being 0.27.<sup>4</sup>

(4) Smyth, *THIS JOURNAL*, **63**, 57 (1941); *J. Org. Chem.*, **6**, 421 (1941).

(5) Brockway and Beach, *THIS JOURNAL*, **60**, 1836 (1938).

(6) Smyth, Grossman and Ginsberg, *ibid.*, **62**, 192 (1940).

(7) Jenkins, private communication to Coop and Sutton, *J. Chem. Soc.*, 1282 (1938).

The previously mentioned slight revision of the data lowers the Ge-Br bond moment to 2.0, identical with the value for Ge-Cl, than which it might be expected to have slightly less ionic character. The lower limit calculated for the amount of ionic character is then 0.17 as compared to 0.19 previously calculated for the Ge-Cl bond.<sup>4</sup> It is interesting to note that the small differences found between triphenyltin chloride, 3.28, and triethyltin chloride, 3.44,<sup>8</sup> and between triphenyllead chloride, 4.21, and triethyllead chloride, 4.39,<sup>9</sup> indicate that the possible contributions of structures containing quinoid rings, which have acquired a pair of electrons from the atom of the metal or, ultimately, from the halogen with consequent increase of moment in the metal-to-ring direction and decrease of the total moment, must be small. Resonance thus causes only a small difference between the moments of these alkyl and aryl compounds.

The small moments, 1.19 and 1.17, found for triphenylantimony dichloride and triphenylbismuth dichloride, respectively, are surprising. X-Ray analysis is reported<sup>10</sup> as indicating a trigonal bipyramidal structure for the trimethylantimony dihalides with the three methyl groups occupying the equatorial plane, the two halogens above and below this plane, and the antimony atom at the center. Analogous structures would seem probable for the triphenylantimony and triphenylbismuth dichlorides with the phenyl groups and the antimony or bismuth atoms in the equatorial plane and the chlorines equally spaced above and below the antimony or bismuth atom. Such structures would, however, be symmetrical and, consequently, possess no moments. The interchange of a phenyl group and a chlorine atom at apices of this bipyramid would destroy its symmetry and give rise to a moment. However, the Sb-Cl bond moment in antimony trichloride has been found to be about 2.6<sup>11</sup> and the Bi-Cl bond moment should be even larger. It is probable, therefore, that these unsymmetrical bipyramidal structures would have moments greater than  $3 \times 10^{-18}$ , about three times the observed values. The small moments would be accounted for if the specimens measured consisted of mixtures of the symmetrical and the unsymmetrical stereoisomers. The gradual melting

(8) Spaght, Hein and Pauling, *Physik. Z.*, **34**, 212 (1933).

(9) Lewis, Oesper and Smyth, *THIS JOURNAL*, **62**, 3243 (1940).

(10) Wells, *Z. Krist.*, **99**, 367 (1938).

(11) Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

point 146–149° of the triphenylbismuth dichloride, for which the literature values range from 136 to 150°, would not rule out such a possibility for the bismuth compound, but the fairly sharp melting point of the antimony compound is not indicative of a mixture.

Another possibility to consider is that the differences of 29 and 28 cm.<sup>3</sup> between the molar refraction and the total polarization from which the small moment values have been calculated are not dipole polarizations but atomic polarizations. Antimony pentachloride, which might be expected to have this trigonal bipyramidal structure, which has been found also for phosphorus pentachloride, has been reported to have a polarization<sup>12</sup> of about 54 in the pure liquid and about 49 in carbon tetrachloride solution. The molar refraction  $MR_D$  calculated for it by the method used in obtaining the refraction in Table II is 47 which indicates an atomic polarization not greater than 8 or much less than 3. As the atomic polarization of triphenylantimony dichloride would, probably, arise largely from its two Sb–Cl dipoles, it should not be greater than that of antimony pentachloride. It, therefore, appears extremely improbable that triphenylantimony dichloride should have an atomic polarization of 29, a value altogether abnormal in any case. It seems reasonable, therefore, to regard these two moment values as real, although they may be somewhat high because of

(12) Simons and Jessop, *THIS JOURNAL*, **53**, 1263 (1931).

neglect of atomic polarization. The conclusion to be drawn from these data is, therefore, that the molecular structures of triphenylantimony dichloride and triphenylbismuth dichloride are slightly unsymmetrical or that the specimens here measured were mixtures of a symmetrical with an unsymmetrical structure. It is to be regretted that it has thus far been impossible to obtain a sufficient concentration in solution of the ethylbismuth dichloride and dibromide very kindly sent to us by Dr. George Calingaert of the Ethyl Gasoline Corporation for measurement.

### Summary

The dipole moments of triphenylgermanium bromide, triphenyltin chloride, benzylmercury chloride, triphenylantimony dichloride, and triphenylbismuth dichloride have been measured in benzene solution. Minimum values have been calculated for the metal-to-halogen bond moments in the first three compounds and used to estimate the minimum amounts of ionic character in the three bonds. The small moments found for triphenylantimony dichloride and triphenylbismuth dichloride are smaller than would be expected for unsymmetrical arrangements at the apices of a trigonal bipyramid, but argue against the expected symmetrical, trigonal bipyramidal arrangement as the only structure for these molecules.

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## NOTES

### Note on the Specific Gravity of Sodium Dichromate Solutions

BY DAVID F. ALTIMIER

The "International Critical Tables" and similar reference handbooks have based their tables for the density of sodium dichromate solutions on the erroneous work of Stanley.<sup>1</sup> The specific gravity of sodium dichromate solutions has been more accurately determined in the low concentration ranges by Jones and Bassett.<sup>2</sup>

(1) Arthur Stanley, *Chemical News and Journal of Industrial Science*, **54**, 194–195 (1886).

(2) H. C. Jones and H. P. Bassett, *Am. Chem. J.*, **24**, 290–349 (1906).

The results of recent determinations in this Laboratory are presented in the accompanying table.

**Experimental.**—The customary experimental procedure was followed in determining the specific gravity. The sodium dichromate, granular dihydrate, was prepared by recrystallization of the technical grade and the impurities were less than those specified by the American Chemical Society for c. p. potassium dichromate.<sup>3</sup> The solutions were made by dissolving weighed amounts of sodium dichromate in distilled water and then deaerating the solutions. The temperature of the bath was maintained at  $15.6 \pm 0.1^\circ\text{C}$ . ( $60 \pm 0.2^\circ\text{F}$ ). After weighing, the di-

(3) Committee on Analytical Reagents, American Chemical Society, *Ind. Eng. Chem.*, **17**, 756 (1925); *Ind. Eng. Chem., Anal. Ed.*, **1**, 171 (1929); **3**, 221 (1931); **13**, 639 (1940).