simple and reasonable "charge distribution rule" not only these observed structures, but also other information concerning the cyanate ion and the chemistry of cyanic acid derivatives may be easily correlated with valence bond structures.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 16, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moments of Alkyl and Phenyl Lead Halides

BY G. L. LEWIS, P. F. OESPER AND C. P. SMYTH

As part of a program of measurements of the dipole moments of molecules containing metallic atoms with the object of obtaining bond moments and studying their relation to the electronegativities of the bonded elements, the dipole moments of triphenyllead and of a number of methyl, ethyl and phenyl lead halides have been measured. The triphenyllead was given us by Professor Henry Gilman of Iowa State College, the several alkyl lead halides listed were given us by Dr. George Calingaert of the Ethyl Gasoline Corporation, and the three triphenyllead halides were given by Professor L. S. Foster of Brown University. The writers wish to express their gratitude for this assistance and wish further to thank Dr. Calingaert for advice on the purification of materials.

Purification of Materials

Benzene, for use as solvent, was purified as in previous work.[1] Because of the tendency of the lead compounds to decompose, it was necessary to purify most of them immediately before they were measured. The triphenyllead was twice precipitated from chloroform solution by addition of ethyl alcohol, being washed each time with petroleum ether. The crystals were placed in an evacuated desiccator and nine hours later dissolved to form clear benzene solutions, which were measured immediately. The alkyl lead halides were crystallized out of a warm petroleum ether–benzene solution, washed with a little petroleum ether, and dried in a stream of dry nitrogen. Everything was kept as close to 25° as possible so that the solutions could be made up and measured immediately at 25°. Several sets of measurements made before the development of this technique were discarded because of impurities in the materials as evidenced by high conductance and the development of opalescence in the solutions. The occasional appearance of a slight opalescence in some of the solutions finally used was insufficient to throw the results out of line with those in which no evidence of decomposition could be detected. The effects of the tendency to form an equilibrium mixture of the mono-, di-, trihalides, etc., although eliminated in part by the recrystallization of the materials, increased the probable errors in the results. The more stable triphenyllead halides were purified by recrystallization and measured in the usual manner.

Experimental Results

The dielectric constants were measured at a frequency of 520 kilocycles with a crystal-controlled heterodyne beat apparatus previously described,[2] and the densities were determined with an Ostwald–Sprengel pycnometer in a manner described previously.[3] The dielectric constants, ϵ, 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. The polarization of the pure benzene is given as P_1. The constants of the benzene used for the solutions of triphenyllead and the alkyl lead halides are given for $c_2 = 0$ under triphenyllead, while the slightly different constants of another lot of benzene used for the triphenyllead halide solutions are given under triphenyllead chloride. Table II lists in the second column the values of MR_D, the molar refraction for the D sodium line, calculated from the atomic refractions and the refraction of benzene given in Landolt–Börnstein, and the atomic refraction of lead 17.9 listed by Eisenlohr.[4] The third column gives the polarizations P_∞ 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 values are unusually large because of the instability and low solubility of the substances, being approximately 0.1×10^{-18}, except in the cases of trimethyllead chloride and diethyllead dichloride, where they are 0.15×10^{-18}, because of the exceptionally low solubility of the former and of the greater than usual instability of the latter. Any errors introduced by calculation of the MR_D values are

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[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).

[4] Eisenlohr, "Spektrochemie organischer Verbindungen," F. Enke, Stuttgart, 1912, p. 72.

negligible in comparison with those in P_∞. The simplest formula is written for triphenyllead and the molar refraction and polarization are calculated on this basis, although magnetic susceptibility measurements show it to exist as a dimer in benzene solution.[5] Treatment of the molecule as the dimer $(C_6H_5)_3PbPb(C_6H_5)_3$ would double the values of the molar refraction and polarization, leaving the difference between them still so small as to render the moment value obtained from it indistinguishable from zero.

TABLE I

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

c_2	ε	d	P_2
	Triphenyllead		
0.00000	2.276	0.8733	(26.67 = P_1)
.00151	2.278	.8770	94
.00262	2.280	.8797	97
.00506	2.283	.8856	95
.00760	2.287	.8918	96
	Trimethyllead Chloride		
.000285	2.284	.8738	460
.000528	2.289	.8742	407
.000603	2.291	.8744	406
.000837	2.296	.8749	388
	Triethyllead Chloride		
.00271	2.349	.8790	438
.00313	2.359	.8798	431
.00620	2.439	.8863	422
.00815	2.491	.8903	411
	Diethyllead Dichloride		
.00101	2.307	.8756	496
.00184	2.328	.8776	454
.00253	2.347	.8790	451
	Triethyllead Bromide		
.00320	2.364	.8809	451
.00474	2.410	.8845	459
.00625	2.443	.8882	434
.00950	2.531	.8958	430
	Triphenyllead Chloride		
.000000	2.2709	.87260	(P_1 = 26.643)
.000215	2.2766	(.87312)	437
.000579	2.2856	.87424	437
.001156	2.2980	.87604	411
	Triphenyllead Bromide		
.000582	2.2924	.87410	417
.001174	2.3092	.87606	453
.001797	2.3242	.87800	446
	Triphenyllead Iodide		
.001858	2.3182	.87907	387
.003273	2.3446	.88409	373
.007407	2.4362	.89859	388

TABLE II

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

Substance	MR_D	P_∞	$\mu \times 10^{18}$
$(C_6H_5)_3Pb$	93.2	95.5	0
$(CH_3)_3PbCl$	41	455	4.47
$(C_2H_5)_3PbCl$	55	455	4.39
$(C_2H_5)_2PbCl_2$	51	510	4.70
$(C_2H_5)_3PbBr$	58	470	4.46
$(C_6H_5)_3PbCl$	99	465	4.21
$(C_6H_5)_3PbBr$	102	470	4.21
$(C_6H_5)_3PbI$	107	396	3.73

Discussion of Results

It is unfortunate that the existence of triphenyllead as a dimer with zero moment prevents it from giving any information as to the moment associated with the lead–carbon bond. It is natural to picture the dimer as having an ethane-like structure, the symmetry of which would give it zero moment. The difference between trimethyl and triethyllead chloride should be negligible and is actually less than the experimental error. The moment of diethyllead dichloride should, because of the tetrahedral structure of the molecule, be 15% larger than that of the monochloride. It has been shown previously[6] that the ratio of the dichloride to the monochloride in the series of fourth group element halides increases as the size of the central atom increases from carbon through silicon and germanium to tin, where the metal–halogen dipoles are apparently so far apart that their mutual inductive effects are too small to lower the ratio below the value 1.15 required by an undistorted tetrahedral structure. It is not impossible that conversion of the dichloride into monochloride, trichloride, etc., may have occurred to an extent sufficient to have lowered the observed moment by an amount larger than the probable error of 0.15×10^{-18}, which may be the explanation of the 7% difference instead of the expected 15% difference between the monochloride and the dichloride.

The moment of triethyllead bromide happens to be larger than that of the chloride by just the amount by which the moment of *t*-butyl bromide exceeds that of the chloride, but the small difference is well within the experimental errors in the values of the lead compounds. Also triphenyllead chloride is smaller than triethyllead chloride by practically the amount by which the moment of triphenylmethyl chloride is smaller

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(5) Preckel and Selwood, Abstracts of Papers Presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society, Detroit, Mich., September, 1940.

(6) Smyth, Grossman and Ginsburg, THIS JOURNAL, **62**, 192 (1940)

than that of *t*-butyl chloride. This would indicate the same amount of resonance in the triphenyllead as in the triphenylmethyl radical, but the difference between the two lead compounds is too uncertain because of experimental error to lend itself to precise interpretation. The identity of the moment values for triphenyllead chloride and bromide parallels the agreement commonly observed between the moments of chlorides and bromides. Although *t*-butyl iodide has practically the same moment as the chloride, the moment of iodobenzene is 0.2 lower than those of chlorobenzene and bromobenzene, but the moment of triphenyllead iodide is lower than those of the chloride and bromide by more than twice this amount. The lower negativity of the iodine atom may account for this decrease in moment, which should lie largely in the Pb–I bond.

The tetrahedral structure, which electron diffraction has shown[7] to be characteristic of the silicon, germanium, tin and lead tetramethyls and, hence, almost certainly of the molecules under consideration here, requires that the moment of the R_3PbX should, in the absence of distortion and other complicating effects, be the sum of the moments R–Pb and Pb–X, while, as previously indicated, the moment of the molecule R_2PbX_2 should be 1.15 times this sum. Subtraction of the rough value 0.3 for the H–C bond moment from the moment of the R_3PbX molecule should, therefore, give the difference between the bond moments, (Pb–X) − (Pb–C). It has been pointed out[6] that, if the moment of a bond depended simply on the intrinsic electronegativities of the two bonded atoms, the moments of these tetrahedral molecules would be independent of the nature of the central atom, which would make all of them have the same moments as the *t*-butyl halides. It is evident that the factors which tend to increase the individual bond moments as the electropositive character and polarizability of the central atom increases must produce a greater absolute change in one moment than the other and it is only reasonable to suppose that the larger metal–halogen moment undergoes a greater absolute change than the metal–carbon moment, which must be smaller because the carbon is less negative than the halogen. Direct evidence of small metal–carbon bond moment values is given by the rather small moment found for aluminum trimethyl by Mr. R. H. Wiswall in this Laboratory and by the low moments of antimony and bismuth triphenyl.[8]

It seems fairly certain that the large moments of these lead compounds arise mainly from the excess of the moment of the lead–halogen bond over that of the lead–carbon bond. The moments of these molecules minus 0.3, the value used for the H–C moment, plus the Pb–C moment gives the Pb–X moment. If the presumably small lead–carbon bond moment is arbitrarily assumed to be zero, lower limits are obtained for the lead–halogen moment values by subtracting 0.3 from the values for the R_3PbX molecule moments. If the Pb–X bonds had no covalent character but were 100% ionic, their moments would be calculated as the products of an electronic charge, 4.80×10^{-10}, times the distances between the ionic centers. Division of the lower limits found for the Pb–X moments by these calculated ionic moments gives quotients which are the lower limits for the fractions of ionic character in the bonds. The Pb–C distance[7] in lead tetramethyl is 2.30 Å. Subtraction of the carbon bond radius 0.77 Å. gives 1.53 as the lead radius and addition to this of the chlorine radius 0.99 gives 2.52 as the approximate nuclear separation in the Pb–Cl bond. The corresponding ionic moment value is 12.1×10^{-18} and the calculated lower limit for the Pb–Cl moment in triethyllead chloride 4.1 gives 34% as the lower limit for the amount of ionic character in the bond. The amount of ionic character in the Pb–Cl bond in trimethyllead chloride and in diethyllead dichloride would be expected to be practically the same and is, obviously, experimentally indistinguishable from this value. A similar calculation for the Pb–Br bond gives 33% as the lower limit for the amount of ionic character. Resonance in the triphenyllead halides reduces the accuracy of a similar calculation for the lead–halogen bonds in their molecules. However, for comparative purposes, the calculation has been carried out in the same way as for triethyllead chloride. The lower limits thus found for the amounts of ionic character in the lead–halogen bonds are as follows: Pb–Cl, 32%; Pb–Br, 31%; Pb–I, 25%. The chloride and bromide bonds show an amount of ionic character indistinguishable from that found in the alkyl compounds and differing from one another by the same insignificant amount. The markedly smaller

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(7) Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(8) Bergmann and Engel, *Z. physik. Chem.*, **B19**, 401 (1932).

amount of ionic character found for the Pb–I bond is consistent with the more positive character of iodine. These lower limits for the amounts of ionic character in the bonds are not far from the value 35% calculated by the same method for the amount of ionic character of the bond in the sodium iodide molecule and from the value 44% for the bond in the potassium iodide molecule. It is evident that the metal–halogen bonds in these tetrahedral molecules increase in ionic character with increasing size and electropositive character of the central metallic atom until they are comparable in character to the bonds in typical salt molecules.

Summary

The dipole moments of triphenyllead or hexaphenyldiplumbane, trimethyl and triethyllead chloride, diethyllead dichloride, triethyllead bromide, and triphenyllead chloride, bromide, and iodide have been measured in benzene solution. The zero moment found for triphenyllead is the result of its existence in benzene solution as the symmetrical dimer, hexaphenyldiplumbane. The large moments found for the other molecules are used to calculate lower limits for the values of the lead–halogen bond moments, which, in turn, are used to calculate lower limits for the amounts of ionic character in the bonds. The bonds are thus found to have more than 25 to 34% ionic character, which is comparable to that found in the bonds of typical salt molecules.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

d-Glucose S-Ethyl O-Methyl Monothioacetal

BY M. L. WOLFROM, D. I. WEISBLAT AND A. R. HANZE

A procedure[1] was developed recently in this Laboratory for transforming *d*-galactose diethyl thioacetal (mercaptal) (IV) into monothioacetals (VII) by exchanging one thioethoxy group in the mercaptal with halogen (V) and replacing the halogen with an alkoxy group. We were interested in the extension of this series of reactions to other sugars and especially to *d*-glucose. A monothioacetal of glucose could not be obtained by this procedure since the intermediate 1-chloro-1-thioethoxy derivative (V) neither crystallized nor was obtained as a sirup of sufficient purity to yield a crystalline alcohol reaction product. The 1-chloro-1-thioethoxy derivative of *d*-gluco-*d*-gulo-heptose[2] (*d*-α-glucoheptose) was obtained in crystalline form in the present work as was also the corresponding 1-bromo derivative of *d*-galactose.

As another method[3] developed in this Laboratory led to the synthesis of stable derivatives of the labile hemiacetals of *aldehydo-d*-glucose pentaacetate (I), it was deemed advisable to attempt the synthesis of a glucose ethyl monothioacetal hexaacetate (III) by an analogous procedure. Since the tendency of *aldehydo-d*-galactose pentaacetate (I) to form stable hemiacetals[4] had been well demonstrated and since the intermediate 1-chloro-1-thioethoxy derivative (V) and several monothioacetals of galactose had been prepared previously,[1] it appeared advisable to attempt this series of reactions in the galactose structure first for exploratory purposes.

We found that *aldehydo-d*-galactose pentaacetate (I) reacted with ethyl mercaptan to form a stable monothiohemiacetal (II) which differed from its previously reported oxygen analog[4a] in that it exhibited no mutarotation in chloroform. The *aldehydo-d*-galactose monothiohemiacetal pentaacetate (II) reacted with acetic anhydride, in the presence of dry pyridine and at low temperature, to produce 1-thioethoxy-*aldehydo-d*-galactose hexaacetate (III). This substance also was obtainable as a by-product from the action of acetyl bromide on galactose diethyl mercaptal pentaacetate and this gave an alternative method of preparation which avoided the use of ethyl mercaptan as a solvent. Halogen replacement of the 1-acetate in III was obtained by

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[1] M. L. Wolfrom and D. I. Weisblat, THIS JOURNAL, **62**, 878 (1940).

[2] Nomenclature of C. S. Hudson, *ibid.*, **60**, 1537 (1938).

[3] M. L. Wolfrom, M. Konigsberg and F. B. Moody, *ibid.*, **62**, 2343 (1940).

[4] (a) M. L. Wolfrom, *ibid.*, **52**, 2464 (1930); (b) M. L. Wolfrom and W. M. Morgan, *ibid.*, **54**, 3390 (1932).