THE ELECTRICAL POLARIZATIONS OF *BIS*-MERCURIALS[1]

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ABSTRACT

Very dilute solutions of diphenylmercury in carbon tetrachloride have been found not to have orientation polarization, but in not-so-dilute carbon tetrachloride or in dioxane and benzene at any concentration there is evidence of moment. Moreover, these moments vary negatively in carbon tetrachloride and dioxane and positively in benzene with respect to temperature. The angular C–Hg–C linkage responsible for orientation polarization is also demonstrated by appreciable moments for para methylmercuri-*bis*-benzene and the homologous durene. Magnitudes comparable with the aryl analogues are found for several alkyl *bis*-mercurials, but the similarity in the moments of trifluoromethyl and methyl-*bis*-mercury as well as a temperature coefficient for moment of the latter compound indicates that the C–Hg–C linkage may vary widely and easily. However, a lower limit may be set by the moments of mercuracyclohexane and mercuracycloheptane in which the mercury angle is fixed by the cyclic structure.

INTRODUCTION

For several decades the electrical polarization of diphenylmercury has seemed to be anomalous. Originally Bergmann and Schütz found the solute polarization in benzene to be 64 cc at 14.15° and concluded that it was due entirely to electronic polarization (1). Later Hampson (2) found the polarization to be 68.8 cc at 25° in benzene. Since this value exceeded the electronic polarization, and since greater deviations from electronic polarization were found for a number of *p*-disubstituted analogues of diphenylmercury, Hampson concluded that the C–Hg–C bond was angular in these substances. Others, and most recently Armstrong, LeFevre, and LeFevre (3), consider that the data may be better interpreted in terms of abnormal atom polarization. However, a direct measurement (4) has shown that diphenylmercury has a distortion polarization which actually

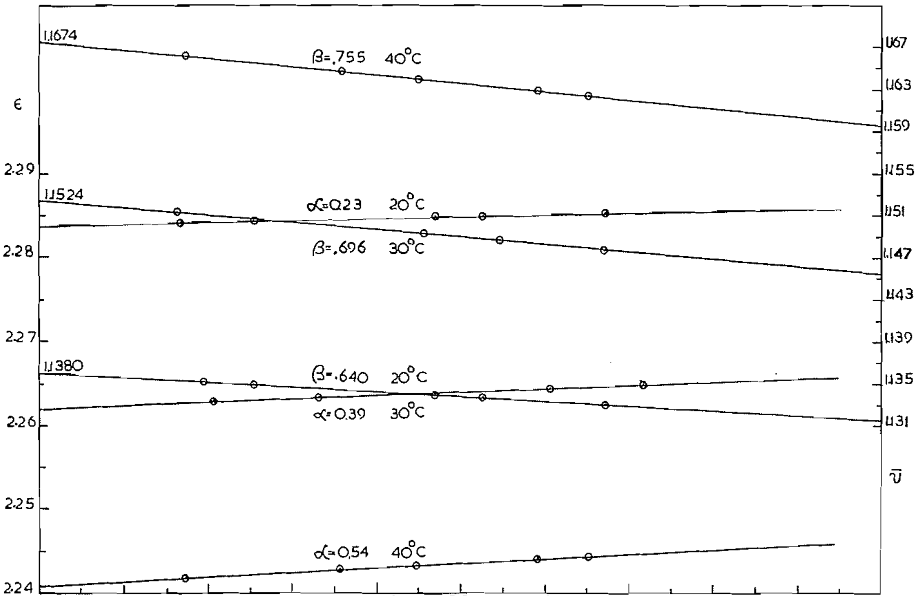

Fig. 1.

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is lower than that calculated from refractometric data. In view of this anomalous situation we have now examined a wider variety of *bis*-mercurials and of conditions under which the polarization is determined.

Diphenylmercury

The variation of electric polarization with respect to solvent, concentration, and temperature is shown in Table I. It may be seen in Fig. 1 that in benzene the relationship of both specific volume and dielectric constant is linear with respect to weight fraction even at concentrations less than 0.002, and extrapolation conforms closely with the values for the pure solvent. This seemingly normal behavior is belied by the augmentation of apparent moment as the temperature is increased from 20° to 40° (Table I). By contrast the apparent moment in dioxane (in which equally good linearity and extrapolation of $\delta\epsilon/\delta\omega$ and $\delta\bar{V}/\delta\omega$ have been observed) has shown a diminution as the temperature has been increased. Likewise with weight fractions (ω) of 0.005 to 0.01 it may be seen (Fig. 2) that the apparent moment in carbon tetrachloride decreases as the temperature rises from 20° to 40°. These variations have been plotted in Fig. 3. It is of interest that these curves (which might be straight lines within the ±0.01 D precision) intersect at about 25°.

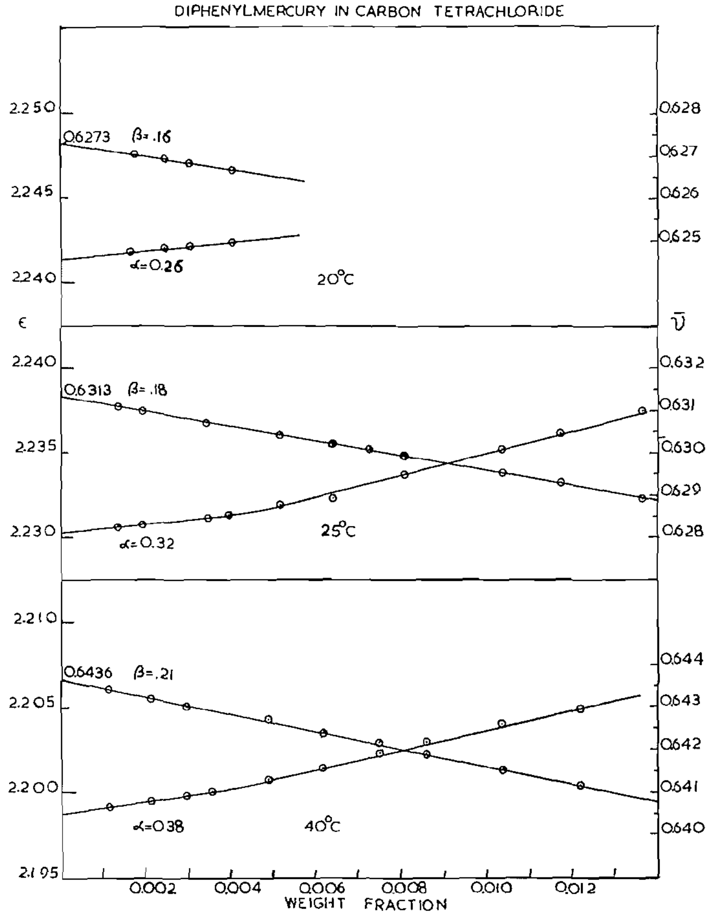


Fig. 2.

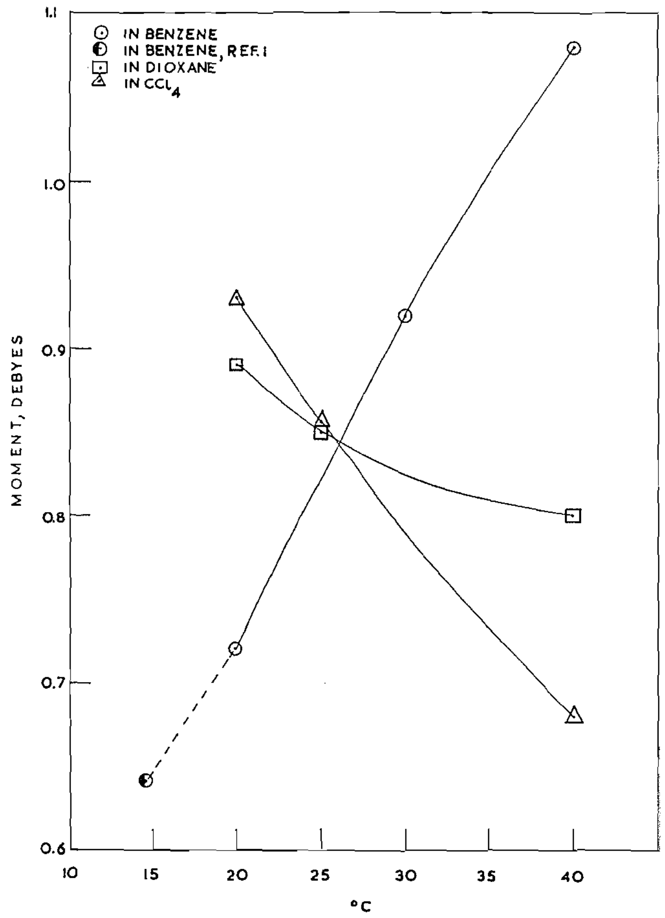


Fig. 3.

TABLE I

Dipole moment data for diphenylmercury

Temp., ° C	Wt. fraction range	Solvent	α	β	$P_{2\infty}$, cc	μ, D*
40	0–0.01	Benzene	0.54	0.755	80.1	1.08
30	0–0.015	Benzene	0.39	0.696	74.3	0.92
20	0–0.01	Benzene	0.23	0.640	68.2	0.72
40	0–0.015	Dioxane	0.40	0.536	69.8	0.80
25	0–0.010	Dioxane	0.43	0.572	72.2†	0.85
20	0–0.015	Dioxane	0.46	0.507	73.9	0.89
40	0–0.005	CCl_4	0.38	0.21	58.7	—
25	0–0.005	CCl_4	0.32	0.18	58.4	—
20	0–0.005	CCl_4	0.26	0.16	58.2	—
40	0.005–0.01	CCl_4	0.58	0.212	66.3	0.68
25	0.005–0.01	CCl_4	0.67	0.174	72.2	0.85
20	0.005–0.01	CCl_4	0.73	0.163	75.2	0.93

*The P_{e-a} of 57.1 as obtained from solid dielectric data is used for the calculations of the dipole moments.
†Contrasted to Curran's 69.02 (6).

The observed polarization at 25° in carbon tetrachloride (71.6 cc) is not far from that reported (70.2 cc) by Armstrong, LeFevre, and LeFevre (3). However, it may also be seen in Fig. 2 that the latter agreement was attained only by using the concentration range specified by the three authors (3). In the concentration range of 0–0.005 weight fraction it is apparent that a sharply different $\delta\epsilon/\delta\omega$ (α) prevails at all temperatures, although no such inflection is observed in the $\delta\bar{V}/\delta\omega$ slope. The latter evidence for the constancy of β is confirmed by isopiestic measurements which show that diphenylmercury does not associate in carbon tetrachloride.

There have been doubts (3) about the significance of the value for distortion polarization (57.1 cc) determined from the dielectric constants of solid diphenylmercury pellets. The critics considered this value to be low, but the criticism is not entirely justified in view of the total polarizations (in cc, 58.2, 58.6, and 58.7) found at 20, 30, and 40° for diphenylmercury in very dilute tetrachloride solution. An assignment of orientation polarization which exceeds these values must be erroneous. Although our measured distortion polarization (57.1 cc) is 1.1 to 1.6 cc below the total polarizations mentioned above, we cannot safely assign the differences to orientation polarization. These differences are only slightly outside our experimental error. We cannot say whether the moment of diphenylmercury in dilute carbon tetrachloride solution is zero or whether it has a very low value which cannot be defined by the present experimental techniques. But we can say that the minimal polarizations which we have observed in very dilute carbon tetrachloride solutions are contradictory rather than confirmatory to recent claims (3) of zero dipole moment for diphenylmercury, because we have set a minimum which the distortion polarization cannot exceed.

In order to arrive at these conclusions it has been necessary to give careful attention to the purity of the carbon tetrachloride. For example the use of an old sample (ϵ_0 = 2.2303 and $\bar{V}$ = 0.6312) for the polarization study of diphenylmercury shows a decrease in $\delta\epsilon/\delta\omega$ at 25° (in the concentration range ω = 0.005 to 0.01) from 0.67 (in the pure solvent where ϵ_0 = 2.2268) to 0.50 in the old solvent, although the change in $\delta\bar{V}/\delta\omega$ does not exceed 0.01. Of course, this behavior is not unprecedented (p. 130, ref. 5) when the polarity of the solvent is increased. While we have been unable to characterize the impurity which raised the dielectric constant of the old carbon tetrachloride, we have found that deliberate addition of water to our purest solvent (resultant ϵ_0 = 2.2289 at 25°) lowers $\delta\epsilon/\delta\omega$ from 0.67 to 0.48, while $\delta\bar{V}/\delta\omega$ decreases from 0.174 to 0.163. Since these differences lower the apparent moment from 0.85 D to 0.63 D it is evident that rigorously purified solvent must be used for meaningful results.

The variation in polarization with respect to concentration may indeed provide an insight into the molecular behavior of diphenylmercury, especially since the medium, carbon tetrachloride, in which this variation occurs is tetrahedrally symmetrical, with little tendency toward co-ordination. We suggest that in this medium diphenylmercury is self-polarized at the higher concentrations. We presume that the effect of this self-polarization is a reduction in the tendency for diphenylmercury molecules to execute the 360° rotation which is ineffective toward the external field. We believe that this rotation, a consequence of the mass of the central atom, is indicated by the evident perturbation in the spectral absorption at 463 cm^{-1}.

It follows that in very dilute solution more molecules, freed from self-polarization, will completely rotate. The same circumstance ought to reduce the polarization at increased temperatures. This effect is observed (Fig. 3) in carbon tetrachloride.

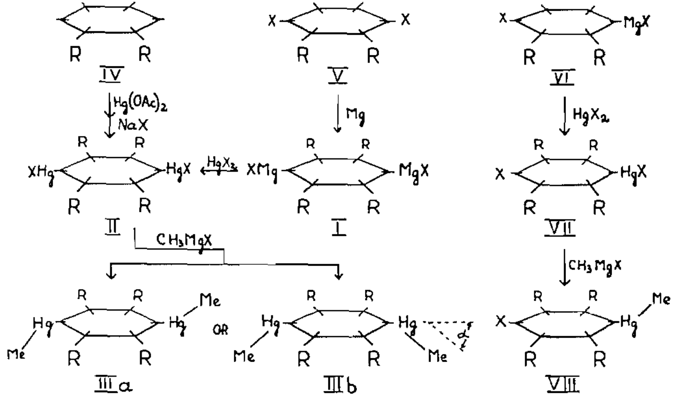
In this connection it is of interest to compare the dielectric constants of pure carbon tetrachloride at the several temperatures with the extrapolation to zero solute concentration. It is evident that the extrapolations for very dilute solutions must differ from those for not-so-dilute solutions. The extrapolation of $\delta\epsilon/\delta\omega$ for very dilute solutions is essentially indistinguishable from that of the pure solvent; ϵ_0 (solvent) minus ϵ_0 (solution) is less than 0.0002. On the other hand the extrapolation of $\delta\epsilon/\delta\omega$ for not-so-dilute solution shows at 20° C that ϵ_0 (solvent) minus ϵ_0 (solution) is 0.001, but at 40° it has decreased to 0.0005. This behavior would indicate that the solvent cavities differ in the two concentration ranges, and suggests that the effectively larger cavity due to self-polarization is decreased either by separation of diphenylmercury molecules, or by thermal agitation.

Benzene is not tetrahedrally symmetrical, so interaction of diphenylmercury with this medium is not unexpected. This interaction ought to minimize self-polarization and it should prevail over the entire concentration range. This expectation is realized in the linearity of the $\delta\epsilon/\delta\omega$ graph over a weight fraction range of 0.001 to 0.008 (Fig. 1) and more.

Table I shows that the apparent moment of diphenylmercury in benzene at 20° is lower than it appears to be in not-so-dilute carbon tetrachloride solution. Assuming that the behavior in the latter medium approaches that in the gas phase the solvent effect in benzene may be called negative. According to the opinions of several workers (5, p. 47), this effect is expected when the molecule contained in a cavity of polarizable solvent has its moment axis in the long dimension of the molecule. This description may apply to a bent molecule with mercury at one end of the dipole.

However, the situation at 20° is reversed at 40° where the moment in benzene is much higher than in carbon tetrachloride. In the absence of any prior opinions (5) about dependence of solvent effect on temperature we suggest that the change of molecular shape within the polarizable solvent cage may be due to C–Hg–C bond angle variation with respect to temperature. While this effect should not be profound, it must be remembered that throughout this argument we are considering moment variations which do not exceed 0.5 debye unit.

It would seem that dioxane is intermediate in behavior between the other two solvents. Indeed the concentration effect and the solvent polarizability effect may largely be compensated in dioxane. In this connection we point again to the intersections of Fig. 3. It is unfortunate that a vapor-phase moment value at this temperature (about 25°) is not available.



In any circumstance the data for diphenylmercury in the several solvents must be interpreted in terms of some type of induced polarization. This interpretation implies a definite dipole moment, even when it is very small (experimentally there are no negative moment values in very dilute carbon tetrachloride). The moments may be ascribed to C–Hg–C angularity and some of the differences may be due to variations in this angle. Evidence for differences in this angle will be presented in the remainder of this report.

Paradisubstituted Methylmercuribenzenes

If one assumes that benzene substituents are bonded coplanar with the ring then evidence of orientation polarization in a 1,4-dimercuribenzene ought to establish an angularity of bonding to mercury. To this end we have prepared 1,4-methylmercuri-*bis*-benzene (III*a* or *b*, R = H) by reaction of methyl chloride Grignard reagent with the 1,4-dibromomercuribenzene (II, R = H) derived from mercuric bromide and 1,4-bromomagnesium-*bis*-benzene (I, R = H).

Although the product III has a tendency toward disproportionation to dimethylmercury and a polymer it is sufficiently stable for determination of its electrical polarization at 20° in carbon disulphide. This polarization should have no orientation component if the methylmercuri group were included in the plane of the ring or if the conformation were entirely III*a* (R = H). On the other hand the substance ought to show evidence of moment if the conformation III*b* were contributory. When the additive electronic polarization (used because III will decompose partially during the time required for determination of the dielectric constant of the solid) is subtracted from the total polarization, the difference may be calculated as a moment of 0.91 debye unit.*

A further test of non-linearity has been accomplished with 1,4-methylmercuridurene (III*a* or *b*, R = Me). This substance has been synthesized by mercuration of durene (IV, R = Me), and treatment of the product II (R = Me) with methyl chloride Grignard reagent. The product III, R = Me, is only a little less prone toward disproportionation than the simpler homologue. From the total polarization in carbon disulphide at 20° is subtracted the electronic polarization, again calculated additively. The remainder represents an electric moment of 1.38 debye unit.

In order to compare the moments of the two 1,4-disubstituted phenylene mercurials it is necessary to assign a group moment to methylmercuri. Although we realize the limitation of group moment evaluations, we have used 1-bromo-4-methylmercuribenzene (VIII, R = H, X = Br) obtained by treatment of 1-bromo-4-bromomercuribenzene (VII, R = H) with methyl chloride Grignard reagent. Actually VII is a by-product in the preparation of II as a consequence of the partial Grignardization (VI) of 1,4-dibromobenzene (V, R = H).

The moment of VIII, calculated from additive electronic polarization, in carbon disulphide at 20° is 1.94 debye unit. If a value (m_1) of 1.5 debye is assumed (excluding mesomeric effects) for the 4-bromophenyl group then an equation in two unknowns, the methylmercuri moment (m_2) and its angular deviation from linearity (α), may be formulated

$$(1.94)^2 = (1.5)^2 + (m_2)^2 - 2(1.5)(m_2)\cos\alpha.$$

The disproportionation of the bis-mercurials described in this report is sufficiently slow that reliable polarization measurements can be made. This reliability has been demonstrated by recovery of the substance after the polarization measurement. However, the time required for analyses to be made elsewhere is detrimental. Additionally the high percentage of mercury in such compounds makes the results non-definitive. Consequently we have chosen to characterize the bis-mercurials analytically by quantitative conversion to the chloromercuri derivatives rather than by analysis of the elements.

If one now combines this equation algebraically with the equation which defines the moment of 1,4-methylmercuri-*bis*-benzene (III, R = H)

$$(0.91)^2 = \sqrt{2} \cdot m_2 \cdot \sin \alpha,$$

then assuming that the methylmercuri group moment and the moment angle α are the same in both compounds, two sets of values may be calculated. One value ($m_2 = 0.72$ debye unit; $\alpha = 62°$) seems to be more probable than the other ($m_2 = 3.37$ debye unit, $\alpha = 10.9°$) because the methylmercuri moment ought to be much lower than the group moment (3.5 debye unit) assigned previously to the chloromercuri group (6). Actually the more probable moment value is in approximate agreement with that expected in consideration of the polarizations of diphenylmercury and dimethylmercury. Likewise the C–Hg–C angle (180° minus 62°) is comparable with that estimated for the aliphatic *bis*-mercurials described below.

It is of interest to compare the moments of methylmercuri-*bis*-benzene and the homologous durene. If the C–Hg–C linkage were linear then the moments of both compounds (III, R = H or Me) ought to be identically zero. Actually the moment of the durene (1.38 D) is found to be $\sqrt{2}$ times that (0.91 D) of the benzene. If the substituents in 1,4-methylmercuri-*bis*-benzene are simple-harmonically rotating then this ratio specifies that the substituents in the homologous durene (III, R = Me) are hindered from free rotation. Moreover, the ratio indicates that the hindrance retains the methylmercuri group on one side of the ring (III*b*, R = Me), since any contribution from III*a* (R = Me) would decrease the ratio.

This "on-side" conformation is not unexpected in view of recent observations in respect of the moment of 1,4-dinitrobenzene (7). On the other hand it must be realized that quantitative estimations of this sort are unjustified, despite their common use, and the $\sqrt{2}$ relationship may be fortuitous. For example the group moment and moment angle may differ among the compounds, the bond angle may differ from the moment angle, and the assumption of planarity of the aromatic rings with coplanarity of the substituent methyl groups is nowadays equivocal. However, the quantitative estimation does accentuate the qualitative fact that the observed moments establish the non-linearity of the C–Hg–C linkage.

Aliphatic bis-Mercurials

The electrical polarization data for a series of aliphatic *bis*-mercurials is shown in Table II. It may be seen by reference to the three solid substances with which the combined electronic-plus-atomic polarizations can be determined that the additive values for electronic polarization are not greatly in error. In no instance can a zero moment be designated. Even the polarization of hexafluorodimethylmercury in carbon tetrachloride is appreciable (*ca.* 0.3 D), although the range of concentrations ($\omega = 0.0008$ to 0.0025) is comparable with that of diphenylmercury in carbon tetrachloride where no orientation polarization can be detected.

The trend in moment among the homologous series (methyl > ethyl > propyl) is not very informative except for the unexpectedly low moment of hexafluorodimethylmercury.* In view of the high polarity of the C–F linkage a much higher polarization than has been observed, irrespective of the polarity (necessarily low) of the mercury–carbon

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**We are indebted for this compound to Mr. D. Fishel, Ohio State University, who prepared it from trifluoromethyl iodide and cadmium amalgam by the procedure of Emelcus and Haszeldine (8).*

linkage, would have been expected. In the absence of this difference one may assume that the C–Hg–C angular relationship is variable in respect of the polarity of the substituent groups.

TABLE II

POLARIZATION DATA, ALIPHATIC *bis*-MERCURIALS, R_2Hg

R_2Hg	Solvent	Temp., ° C	P_{total}, cc	P_{e+a}, cc	P_e additive cc	μ, D
$(CH_3)_2Hg$	Dioxane	20	33.3	—	22.6†	0.71
	Benzene	20	32.7	—	22.6	0.69
	Benzene	40	33.8	—	22.6	0.74
$(CF_3)_2Hg$	Benzene	20	47.3	27.5*	24.7	0.97
	CCl_4	20	29.2	27.5	24.7	0.29
$(C_2H_5)_2Hg$	Benzene	20	38.1	—	31.9	0.55
$(n\text{-}C_3H_7)_2Hg$	Benzene	20	47.3	—	41.1	0.54
1,7-Dioxa-4,10-mercura-cyclododecane	Benzene	20	91.0	65.7‡	62.6	1.17
Mercuracyclohexane	Benzene	20	49.8	—	34.3	0.86
Mercuracycloheptane	Carbon disulphide	20	56.0	—	38.9	0.90

*Density at 22°, 4.693.
†Additive atomic constant for mercury, 11.2 cc, as determined by Wilde.
‡Density at 22°, 3.30.

The effect of temperature on the polarization of dimethylmercury in benzene has been examined briefly. The apparent augmentation of moment with increasing temperature is similar to that found for diphenylmercury in the same solvent, but is so slight (0.05 debye unit from 20 to 40°) that it might be ascribed to experimental error. However the difference is substantiated by comparison of the moment of diethylmercury (0.55 D at 20° in benzene) with that (0.39 D) reported in the same solvent at 14.5° (1).

In view of the evidence for a C–Hg–C angularity in these aliphatic *bis*-mercurials we have sought to examine analogues in which the angularity would be intrinsic in the structure. Of the last three items in Table II the first was once thought to be 1-oxa-4-mercuracyclohexane (9) but Grdenic proved by X-ray diffraction studies (10) that it is the dimer, 1,7-dioxa-4,10-mercuracyclododecane. Because of the flexibility of a 12-membered ring and also because of a possible tendency toward co-ordination of mercury with oxygen, the substance is not the ideal example we sought for examination of rigid angularity. Nevertheless a significant orientation polarization is observed which cannot be attributed alternatively to an abnormal atom polarization. At most the latter cannot exceed 3 cc, according to the value which we have obtained for the dielectric constant of the solid substance.

When 1,5-dichloromercuripentane is treated with sodium stannite the dimer of mercuracyclohexane is formed exclusively, and this dimer seems to be the stable form. However, by treatment of 1,5-dibromopentane with sodium amalgam in ethyl acetate (11) the monomer may be obtained in varying yield. Although this monomer, $C_5H_{10}Hg$, tends to transform easily to the dimer or polymer, it may be purified for immediate use by avoidance of elevated temperatures. The moment calculated from the electric polarization in benzene (0.86 D at 20°) is closely comparable with the moments of the non-cyclic *bis*-mercurials shown in Table II.

Application of Hilpert and Gruttner's method for the preparation of mercuracyclopentane (13, 12) yields only one product which seems to be the dimer, according to an isopiestic determination of molecular weight. Since the same product is obtained by various reductions of 1,4-dichloromercuributane it would seem that monomeric mercuracyclopentane is too unstable for isolation in sufficient purity for electric polarization studies. The polarization of the dimer (probably 1,6-dimercuracyclodecane, since it can be reconverted to 1,4-dichloromercuributane by treatment with mercuric chloride) has not been measured.

The preparation of monomeric mercuracycloheptane has been more successful, and leads from either 1,6-dibromohexane or 1,6-dichloromercurihexane to a single product which is monomeric according to isopiestic molecular weight determinations (15, 14). The product can be reconverted to 1,6-dichloromercurihexane by means of mercuric chloride. Its moment is not strictly comparable with that of mercuracyclohexane because it has been necessary to use carbon disulphide as the solvent. However, the observed moment at 20° (0.9° D) is almost identical with that of mercuracyclohexane.

From these results it would seem that the C–Hg–C angle must be greater than 108–110°, but it may be as low as 120–130° in a stable configuration. Moreover, since the observed moments are less than twice as great as that of the comparable diethyl- and dipropyl-mercury the C–Hg–C angles in the latter substances need not exceed 150°.

But this estimate should not be construed to imply a fixed C–Hg–C angle for *bis*-mercurials. Indeed the apparent anomalies which have been observed by variation of temperature and solvent with diphenyl- and dimethyl-mercury, and also the lack of correlation of moment with polarity of substituents, is a strong indication that the C–Hg–C angle is widely variable. Perhaps this variability ought to be expected with a large atom-like mercury. Conversely one might say that mercurials are poor candidates for stereochemical studies. On the other hand the behavior of *bis*-mercurials may predict the day of better precision in measurement when no polyatomic substance is known that will not be oriented by an electrical field.

The authors are grateful for studentship aid and direct grants from the National Research Council of Canada which supported this research. They wish to thank Mrs. L. Westland and Mr. F. Lautenschlaeger for aid in the experimental work. Any experimental data not presented in the paper is available in the doctoral thesis of H. Sawatzky.

EXPERIMENTAL*

1,4-Chloromercuri-bis-durene

A mixture of 5.40 g (0.04 mole) of durene, 51.2 g (0.16 mole) of mercuric acetate, 40 ml of acetic acid, and 120 ml of methanol were refluxed for 4 days. The precipitated solid was removed by hot filtration and was washed with boiling ethanol, 11.7 g. This acetoxymercurial was then dissolved in 300 ml of hot acetic acid and the partially cooled system was treated with a solution of 10 g (0.17 mole) of sodium chloride in 50 ml of water. The solid product was filtered off and washed with boiling ethanol, 11.38 g (47%). It may be crystallized from pyridine but has no melting point. X-Ray diffraction pattern is [10] 7.59; [5] 4.45; [4] 3.97; [3] 2.85; [2] 3.52, 3.33, 2.96; [1] 4.63, 3.84, 3.21, 3.01, 2.63. Anal. Calc. for $C_{10}H_{12}Hg_2Cl_2$: C, 20.0; H, 2.01. Found: C, 20.3; H, 2.00.

1,4-Methylmercuri-bis-durene

Into 15 ml (0.0189 equiv.) of stirred methyl chloride or iodide Grignard reagent under nitrogen was added 2.00 g (0.0033 mole) of 1,4-chloromercuri-*bis*-durene. To the warm

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Melting points have been corrected against standards according to Can. J. Technol.* ***34**, 89 (1956). X-Ray diffraction is reported at relative intensities I/I_1 at d spacings in angstroms using* CuKα (Ni *filtered) radiation.*

suspension was added 20 ml of dry diethyl ether. After 18 hours of stirring the system was poured on 50 g of crushed ice. Then 1% aqueous sulphuric acid was added until the system was slightly acidic. After evaporation of the ether the solid (1.47 g) was filtered off and almost dissolved in hot benzene. Evaporation of the filtered solution left 1.35 g (73%) of product which did not melt. Purification may be effected by crystallization from hot benzene (25 ml per g) but prolonged heating will cause disproportionation. X-Ray diffraction pattern is [10] 7.65; [9] 3.50; [6] 6.83; [5] 4.38; [4] 5.05; [3] 4.68, 4.03, 3.64, 2.26; [2] 2.92, 2.71; [1] 6.30, 3.35. In carbon disulphide α is 0.66 and β is 0.409, so $P_{2\infty}$ is 116.9 cc. With $R_D = 76.4$ cc, the moment is 1.38 D. Anal. Calc. for $C_{12}H_{18}Hg_2$: C, 25.6; H, 3.22. Found: C, 25.7; H, 3.25.

When a benzene solution of this material was treated with 2 mole equivalents of mercuric chloride in ether a white precipitate could be filtered off after 20 minutes. When this precipitate (88.7% after ether washing) was treated with bromine in aqueous potassium bromide it was converted to 1,4-dibromodurene, m.p. 200–203°. The benzene filtrate left methylmercuric chloride (83%, m.p. 164–168°) when it was evaporated.

1,4-Methylmercuri-bis-benzene

To a stirred suspension of 2.40 g (0.1 atom) of magnesium in 50 ml of dry ether was added 2 ml of ethyl bromide in 50 ml of ether during 30 minutes. Then a solution of 4.72 g (0.02 mole) of *p*-dibromobenzene and 3.85 ml (total 0.06 mole) of ethyl bromide in 100 ml of ether was added during 75 minutes. Strong reflux was maintained and continued during 12 hours, then 1.2 ml more of ethyl bromide was added. After 1 hour all the magnesium was consumed, so 27.2 g (0.1 mole) of mercuric chloride was introduced during 24 hours from a soxhlet extractor.

The solid product was filtered off and washed thoroughly with water, boiling ethanol, and boiling benzene. There remained 4.88 g (38%) of 1,4-bromomercuribenzene, identified by conversion in 93% yield to 1,4-diiodobenzene, m.p. 127–129°, by means of iodine in an alcoholic suspension of the mercurial.

The filtrate from which this product was obtained was evaporated and then steam-distilled to remove 11.9 g of ethylmercuric bromide. The residue yielded 1.96 g (23% as *p*-bromophenylmercuric bromide) which may be crystallized from benzene, m.p. 234–236°. It has been converted to *p*-bromophenylmercuric acetate, m.p. 198–201°, by means of silver acetate, and subsequently to *p*-bromophenylmercuric chloride, m.p. 251–253°, by means of sodium chloride (16). Also it was converted quantitatively to *p*-dibromobenzene by treatment with bromine in aqueous potassium bromide.

To a stirred suspension of 1,4-bromomercuri-*bis*-benzene (4.30 g, 0.0074 mole) in 25 ml of dry ethyl ether at 0° under nitrogen was gradually added 20 ml (0.02 equiv.) of Grignard reagent from methyl chloride or iodide. After subsequent stirring for 90 minutes the system was poured onto 200 g of crushed ice. The ether was evaporated and the remainder was extracted by 100 ml of pure carbon disulphide. Evaporation of the extract left 2.26 g (61% of the bromomercuri-*bis*-benzene) which was crystallized from 50 ml of 1:1 benzene – diethyl ether. The melting point of this methylmercuri-*bis*-benzene is 190–193° with decomposition at 185° indicating disproportionation. It does not contain halogen; X-ray diffraction pattern is [10] 4.56; [3] 3.75, 3.63, 3.34, 3.21; [2] 5.92, 5.23; [1] 5.62. In carbon disulphide α is 0.29 and β is 0.460 so $P_{2\infty}$ is 75.7 cc. If R_D is 57.9 cc the moment is 0.91 D.

Although a satisfactory elemental analysis was not obtained the methylmercuri-*bis*-benzene was analytically characterized when a suspension of 0.044 g (0.00087 mole) in

1 ml of ethyl ether was shaken for 3 hours with a solution of 0.047 g (0.018 mole) of mercuric chloride in 5 ml of ether. The solid was filtered off and ether-washed, 0.047 g (98%) of 1,4-chloromercuri-*bis*-benzene which was converted quantitatively to 1,4-dibromobenzene. Anal. Calc. for $C_6H_4Hg_2Cl_2$: Cl, 12.93. Found: Cl, 12.97. The ether filtrate was evaporated to yield 0.0441 g (100%) of methylmercuric chloride, m.p. 168–170°, after crystallization from ethanol.

1-Bromo-4-methylmercuribenzene

A suspension of 0.87 g of *p*-bromophenylmercuric bromide (0.002 mole, obtained from the experiment reported above) in 25 ml of diethyl ether was stirred and ice-cooled under nitrogen, while 3.50 ml (0.0033 equiv.) of Grignard reagent from methyl chloride was added during 5 minutes. After 3 hours of subsequent stirring at ice-bath temperature the system was poured onto 75 g of crushed ice. The non-aqueous phase, dried by magnesium sulphate, was evaporated to leave an oil (0.63 g, 82%) which solidified when chilled to 4°. It was twice crystallized by solution (at 25°) in 1:1 ethanol–chloroform (32 ml per g) and subsequent chilling to −78°. The purified product, m.p. 52.1–52.7°, was characterized by cleavage with mercuric chloride, yielding methylmercuric chloride and *p*-bromophenylmercuric chloride, each in 100% yield. The Grignard reagent from methyl iodide cannot be used in this preparation because disproportionation occurs. In carbon disulphide this mercurial has $\alpha = 2.01$ and $\beta = 0.436$ so $P_{2_\infty} = 122.9$ cc, and $\mu = 1.94$ D if $R_D = 49.9$ cc.

Mercuracycloheptane

A mixture of 450 g (0.195 atom Na) of 1% sodium amalgam, 16.5 g (0.07 mole) of 1,6-dibromohexane, 3 ml of ethyl acetate, and 25 ml of benzene was shaken at 70° (infrared lamp) for 1 day, after which time 25 ml each of benzene and water was added with agitation. After separation of the non-aqueous phase a subsequent extraction with 25 ml of benzene was accomplished. Evaporation of the benzene left 7.6 g of oily solid which was purified first by three crystallizations from chloroform (3 ml per g) from 25° to −78° and then by repeated crystallization from 4:1 ether–benzene and from 1:5 ethanol–benzene (3 ml per g) to melt at 58.5–60.2°. Anal. Calc. for $C_6H_{12}Hg$: Mol. wt., 285. Found (Willard and Blank (15)): Mol. wt., 273. Found (Barger-Rast (14)): Mol. wt., 286.

1,6-Dichloromercurihexane

A solution of 2.84 g (0.01 mole) of mercuracycloheptane in a minimum of benzene was treated with 2.72 g (0.01 mole) of mercuric chloride and then 10 ml of ethyl ether was added. The white suspension formed by stirring was filtered off and washed thoroughly with ether, 5.60 g (100%) of 1,6-dichloromercurihexane. Anal. Calc. for $C_6H_{12}Hg_2Cl_2$: Cl, 12.75. Found: Cl, 12.69. After crystallization from hot dimethylsulphoxide (15 ml per g) it melts questionably at 290° with decomposition. The X-ray powder diagram is [10] 11.72; [9] 3.31; [7] 2.65; [5] 2.38; [2] 2.99; [1] 2.25, 3.99, 4.44. Reduction of this high-melting mercurial by alkaline sodium stannite forms mercuracycloheptane, m.p. 58–60°, in 90% yield. Identity was established by mixture melting point.

Mercuracyclohexane

A mixture of 15 g (0.065 mole) of dibromopentane, 450 g (0.2 atom) of 1% sodium amalgam, 3 ml of ethyl acetate, and 50 ml of dry benzene was shaken in a stout sealed bottle at 75° for 24 hours. After treatment with 100 ml of cold water the spent amalgam was separated and washed with 50 ml each of water and benzene. The benzene solutions, adequately dried, were vacuum evaporated leaving 8.20 g of oil. This oil was twice extracted by 5-minute reflux with 25 ml of absolute ethanol. The quickly cooled extract was filtered and further chilled to 40°. Slowly there appeared 0.53 g of crystals. Contrary to Hilpert and Gruttner the substance was found only in the extract. Three rapid crystallizations from a benzene–hexane mixture gave a product, m.p. 122.4–122.8°. The monomer seems to be very unstable thermally, and sometimes is not obtainable.

When this product was treated with mercuric chloride, a quantitative yield of 1,5-dichloromercuripentane was obtained. The X-ray diffraction pattern of this *bis*-chloromercurial is: [10] 4.33; [9] 3.34; [8] 3.18; [7] 3.56; [6] 1.97; [5] 2.71; [3] 2.11; [2] 2.45, 2.35, 2.30, 2.07; [1] 2.86, 2.17, 1.82, 1.78. Regeneration of the *bis*-mercurial by treatment with sodium stannite yielded only the dimer described by Hilpert and Gruttner (11). The monomeric *bis*-mercurial decomposed in boiling ethanol to yield an oil which seems to contain the dimer.

1,6-Dimercuracyclodecane

(*a*) *From dibromobutane.* —A mixture of 450 g (0.2 mole) of 1% sodium amalgam, 15.3 g (0.07 mole) of 1,4-dibromobutane, 3 ml of ethyl acetate, and 25 ml of benzene was shaken for 36 hours at 70°. The cooled system was then shaken with 25 ml of water and the benzene layer was separated and combined with a subsequent 25 ml benzene washing. Evaporation left an oil, 10.79 g, which was washed with cold ether leaving 3.79 g of sticky solid. Crystallization from an ether–benzene mixture gave a product, m.p. 44–45.2°.

(*b*) *From 1,4-dichloromercuributane.*—A sample of 0.50 g (10^{-4} mole) of 1,4-dichloromercuributane was treated with 40 ml of 10% aqueous sodium hydroxide and then with a solution of 1 g of stannous chloride dihydrate in 20 ml of 20% aqueous sodium hydroxide. The black suspension was filtered off when no more color change occurred. The black product was extracted with boiling xylene which was evaporated at low temperature leaving 0.17 g (66%) m.p. 37–40°. Crystallization from ether–benzene raised this melting point to 43–45°. Molecular weight determinations by the isopiestic method of Willard and Blank gave an average value of 499, while a freezing-point depression in diphenylmercury gave a value of 517. The calculated molecular weight is 513.

1,4-Dichloromercuributane

When 0.1294 g (253×10^{-6} mole) of dimercuracyclodecane in benzene is treated with 0.1390 g of mercuric chloride dissolved in a minimum of ethyl ether the resulting precipitate, washed with benzene and ether, weighs 0.253 g (93%). Its X-ray diffraction pattern is [10] 3.18; [9] 4.61; [7] 2.09; [5] 2.62; [4] 2.41; [3] 3.55, 1.78; [2] 2.53; [1] 4.00, 3.47, 2.49, 2.03 after crystallization from hot dimethylsulphoxide; m.p. 292–293° (with decomposition). Anal. Calc. for $C_4H_{10}Hg_2Cl_2$: Cl, 13.5. Found: Cl, 13.3.

Dialkylmercury Homologues

These mercurials were prepared from alkylmercuric halides according to the following general procedure. The alkylmercuric halide (0.026 mole) was dissolved and suspended in 150 ml of 10% aqueous sodium hydroxide. A solution of 8.33 g (0.035 mole) of stannous chloride dihydrate in 100 ml of aqueous sodium hydroxide was added. After 3 hours of agitation the system was steam-distilled (methyl and ethyl) or ether-extracted (propyl and butyl). All were dried with magnesium sulphate over an ether solution or (methyl) directly by potassium hydroxide pellets and then distilled. All except dimethylmercury (m.p. −42.8 to −41.9°) are unstable in light and dibutylmercury is unstable to heat.

PHYSICAL PROPERTIES OF DIALKYLMERCURY HOMOLOGUES

Alkyl	Boiling point, °C	mm	n_D^{20}
Methyl	90.7–91.1	755	1.54512
Ethyl	50–51	16	1.54541
n-Propyl	80.0–80.6	16.5	1.51755
n-Butyl	67	0.55	1.50812
	48	0.35	

Other bis-Mercurials

Diphenylmercury was dissolved in hot 93% ethanol (40 ml per g) and allowed to cool very slowly with stirring, m.p. 125–126°. The purification of 1,7-dimercura-4,10-dioxacyclododecane (10) was effected by crystallization from chloroform, m.p. 145–146°, and its dielectric constant at 22° was found to be 2.975. Hexafluorodimethylmercury as received from Mr. Fishel was sublimed at 85–95° and 750 mm until the melting point was constant at 166–166.5°.

Purification of Solvents

Benzene was purified according to a previous description (17) and was stored over sodium under nitrogen, $\epsilon = 2.284$ and $d = 0.8788$ at 20°. Dioxane, prepared as was described previously (17), was stored under nitrogen without sodium, $\epsilon = 2.224$ and $d = 1.0336$ at 20°. Carbon disulphide was thrice-stirred during 2 hours with 100 ml of 2.5% aqueous potassium permanganate per liter, then for 5 hours with metallic mercury (250 g per liter), and finally with 2.5% aqueous mercuric chloride (100 ml per liter). After drying with phosphorus pentoxide the solvent was distilled and stored under nitrogen in the dark, $\epsilon = 2.646$ and specific volume = 0.79135. Like dioxane it is unstable. The purification of 11 liters of carbon tetrachloride was accomplished by the method of Ingold and Powell (18) by digestion at 50–60° for 3 hours with 750 ml of Fehling's solution. The non-aqueous layer was then refluxed with 5% aqueous sodium hydroxide for 3 hours, then washed with water and stirred about 15 times with 100-ml lots of concentrated sulphuric acid until coloration ceased. After being washed with aqueous sodium carbonate the carbon tetrachloride was azeotropically distilled to remove most of the water. Then it was dried with phosphorus pentoxide, distilled, and stored under nitrogen in dark bottles, $\epsilon = 2.2415$ and $V = 0.62730$ at 20°.

Dielectric Constants of Solutions

All determinations were made at 500 kc in the apparatus described previously (19). Except for the studies with diphenylmercury in carbon tetrachloride no experiment was accepted if the individual determinations did not permit linear plots of $d\epsilon/d\omega$ (α) and $dV/d\omega$ (β). Moreover, no experiment was accepted in which the extrapolations of α and β to zero concentration differed more than ±0.0002 in specific volume and ±0.002 in dielectric constant from the values tabulated as follows.

Dielectric Constants of Solids

The method described previously (17, 20) has been followed. The pellet thickness was measured after the determination at 5 Mc by averaging the gauged value at 4

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF PURE SOLVENTS

	20°		25°		30°		40°	
Solvent	ϵ	V	ϵ	V	ϵ	V	ϵ	V
Benzene	2.2849	1.1381	–	–	2.2612	1.1524	2.2395	1.1670
Dioxane	2.2206	0.9675	–	–	–	–	2.1851	0.9900
Carbon disulphide	2.6470	0.7911	–	–	–	–	–	–
Carbon tetrachloride	2.2426	0.6273	2.2306	0.6313	–	–	2.1986	0.6436
	2.2380	0.6270	2.2272	0.6310*	–	–	2.1962	0.6435

*The final six values are the best obtained for CCl_4 to date.

quadrants of the cylinder; also oftentimes the pellet was broken into halves and the center measured as well. A redetermination of the dielectric constant of diphenylmercury pellets gave a value of 57.1 cc, thus confirming the previously reported value (19).

Infrared Spectrum of Diphenylmercury

Only three absorption bands were found in the 900–300 cm^{-1} spectral region for a 10% solution of diphenylmercury in benzene, although the strong absorption of the solvent at 680 cm^{-1} may have obscured the behavior of diphenylmercury in this frequency range. The bands at 732 cm^{-1} (80% absorption) and 706 cm^{-1} (40% absorption) were symmetrical and well resolved, but the band at 463 cm^{-1} (30% absorption) was unsymmetrical, showing evidence of perturbations on the low frequency side. This band also is of interest because of its possible relationship to the angle of swing postulated by deLazlo (21) for *bis*-bromophenylmercury.

Organomercuric Halides

With the exception of the first and fourth items of Table III these substances were prepared by cleavage of *bis*-mercurials by means of mercuric chloride in ether solution. The methylmercuric chloride was crystallized (13 ml per g) from 95% ethanol, m.p. 168.7–169.6°. The ethyl analogue from 1:1 benzene – carbon tetrachloride melted at 191.8–192.9°. The propyl homologue from 95% ethanol (15 ml per g) melted at 141–143° but after sublimation melted at 142.1° to 142.7°. The butyl homologue crystallized from benzene (5 ml per g) to melt at 125.5–126.2° and then from 95% ethanol (15 ml per g) to melt at 126.9–127.2°.

The preparation of chlormethylmercuric chloride was carried out according to Hellerman and Newman (22). The 97.5% yield was crystallized from ethanol, m.p. 128.5–130°. The X-ray diffraction is [10] 10.59, 3.22; [8] 4.05, 3.26; [6] 2.65, 2.62; [4] 1.90; [2] 2.35, 3.52; [1] 4.87, 2.93, 2.43, 2.00. It is of interest that the compound also may be obtained by the action of diazomethane on 2-hydroxyorganomercuric halides.

These chloromercurials were prepared to demonstrate that the R–Hg group becomes more electropositive with increasing size in the normal homologous series. This behavior is shown in Table III.

TABLE III

POLARIZATION DATA, ORGANOMERCURIC HALIDES, RHgCl

R	Solvent	α	β	$P_{2\infty}$, cc	R_D, cc	μ, D
p-Bromophenyl	Dioxane	1.32	0.690	114.8	50.1	1.75
Methyl	Dioxane	6.02	0.740	261.3	22.9	3.36
Ethyl	Dioxane	6.80	0.778	306.9	27.5	3.64
Chloromethyl	Dioxane	3.80	0.723	197.9	27.8	2.84
n-Propyl	Benzene	5.60	0.822	315.9	32.1	3.67
n-Butyl	Benzene	5.94	0.750	357.7	36.8	3.90

A study of the dielectric constants of these solid organomercurials is in progress with a view to clarify the discrepancy between the P_{e+a} values which we have measured versus the calculated values which appear in the literature (23).

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