

SHORT COMMUNICATIONS

DIPOLE MOMENTS OF SOME ARYLMERCURIC CHLORIDES—VALENCE ANGLE OF MERCURY

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THE present study of the dipole moments of arylmercuric chlorides was undertaken (i) to determine, at least approximately, the valence angle that mercury assumes in these compounds, and (ii) to find out whether mercury can act as an electron acceptor conjugating with electron-releasing groups present in the *para* position of the aryl nucleus.

The arylmercuric chlorides were prepared according to methods described earlier¹⁻⁵. 2,6-Dimethylphenylmercuric chloride was a new compound, m.p. 156–157°C. Found: C, 28.2; H, 2.5. C₈H₁₀HgCl required: C, 28.2; H, 2.7%.

The apparatus used for the determination of dipole moments and the method of calculation have been described earlier⁶. All the measurements were made in dioxane solution (because of insolubility of the compounds in benzene) at 30 ± 0.05°C. The dipole moments are given in table 1.

The angle that the dipole axis makes with the 1-4

Table 1 Dipole moments of arylmercuric chlorides in dioxane at 30°C

No.	Compound	Dipole moment (D)
1.	C ₆ H ₅ HgCl	3.11*
2.	<i>o</i> -CH ₃ .C ₆ H ₄ .HgCl	2.98
3.	<i>m</i> -CH ₃ .C ₆ H ₄ .HgCl	3.22
4.	<i>p</i> -CH ₃ .C ₆ H ₄ .HgCl	3.45
5.	2,6-(CH ₃) ₂ .C ₆ H ₃ .HgCl	3.07
6.	<i>m</i> -Cl.C ₆ H ₄ .HgCl	2.70**
7.	<i>p</i> -Cl.C ₆ H ₄ .HgCl	1.65
8.	<i>o</i> -HO.C ₆ H ₄ .HgCl	4.02
9.	<i>p</i> -(C ₂ H ₅) ₂ N.C ₆ H ₄ .HgCl	5.07
10.	<i>p</i> -(CH ₃) ₂ N.C ₆ H ₄ .HgCl	4.94
11.	2-CH ₃ -4-(CH ₃) ₂ N:C ₆ H ₃ .HgCl	4.87

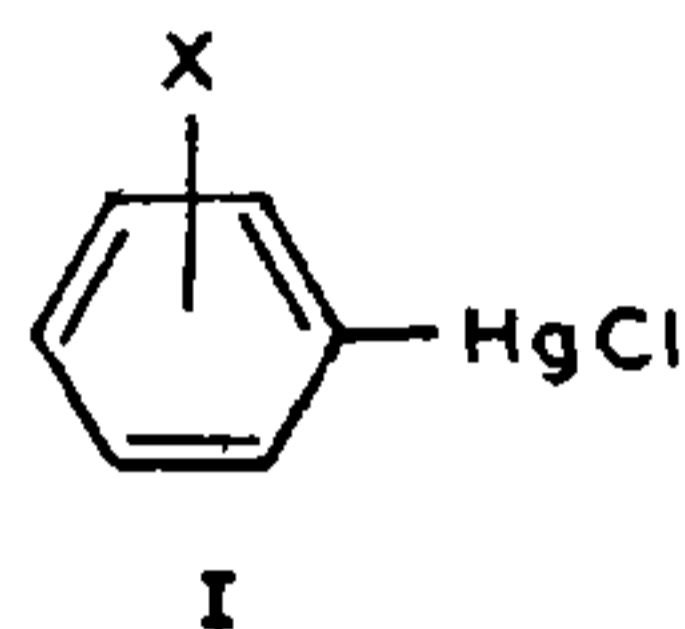
*Lit⁴. value, 2.99 D; **Lit⁴. value, 2.91 D.

*For correspondence.

axis in arylmercuric chlorides can be estimated from group moments by vector addition. According to the Fuchs⁷ equation

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta \cos \alpha \cos \beta, \quad (1)$$

in a compound like I,

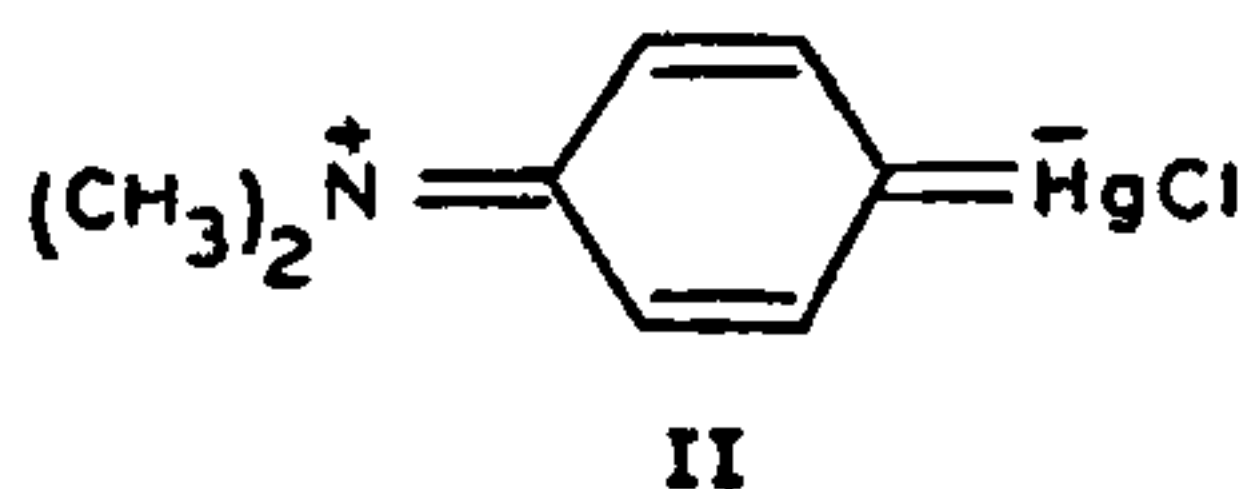


μ is the dipole moment of the molecule, μ_1 is the moment of group X, μ_2 is the moment of $-\text{HgCl}$, θ is the angle between the axes of rotation of the groups, and α and β are the angles that the moments make with their respective axes of rotation. The axes of rotation are assumed to be directed to the group. Using (1) and the moments of *m*-chlorophenylmercuric chloride, and $-\text{Cl}$ and $-\text{HgCl}$ groups, the angle that the moment of $-\text{HgCl}$ makes with its axis of rotation can be calculated. The moments of chlorobenzene⁸ (1.61 D in dioxane at 30°C) and phenylmercuric chloride (3.11 D) may be taken as the moments of $-\text{Cl}$ and $-\text{HgCl}$ groups respectively. Computation of the angle that the dipole axis makes with the C–Hg bond gives a value of 7°. The moment angle can also be calculated using the moment of *p*-chlorophenylmercuric chloride, and this gives 18°. But we can exclude it from consideration in view of the possibility of conjugative interaction between *p*-Cl and $-\text{HgCl}$ groups. Sipos *et al.*⁴ calculated the angle to be 50° from their dipole moment of 2.91 D for *m*-chlorophenylmercuric chloride but we found, by repeated determinations using a highly purified sample, that the dipole moment of the *m*-chloro compound is only 2.70 ± 0.02 D. The value of 2.91 D of Sipos *et al.*, therefore, seems to be in error and consequently the moment angle of 50° is also unacceptable.

There is a critical dependence of the moment angle on the dipole moment of arylmercuric chloride. For example, if the dipole moment of *m*-chlorophenylmercuric chloride is 0.01 D less (i.e. if taken as 2.69 D instead of as 2.70 D), the angle will be almost

180°. In view of the fact that the observed dipole moment can vary by ± 0.02 D owing to experimental errors, the moment angles or bond angles computed from dipole moments are approximate and should only serve as useful guides in understanding the structure of molecules. Hence it may be concluded that the mercury valence angle in arylmercuric chlorides is very nearly 180°. This conclusion is also in accordance with the view that the two σ -bonds of mercury, resulting from 6s, 6p hybridized orbitals, should be linear.

The observed dipole moments 5.07 D and 4.94 D for the compounds 9 and 10 of table 1 are higher than the sums (4.92 D and 4.74 D respectively) of the group moments (dipole moments: $C_6H_5N(C_2H_5)_2$, 1.81 D⁹; $C_6H_5N(CH_3)_2$, 1.63 D¹⁰; C_6H_5HgCl , 3.11 D). The observed moment cannot be higher than the sum of the group moments without the existence of conjugative interaction of the *para* substituents. For example, the high moment of *p*-dimethylaminophenylmercuric chloride should be due to structure II making some contribution to its ground state.



This structure involves the utilization of one of its vacant 6p orbitals by mercury. Mercury can thus act as an electron acceptor and show a valence of 3.

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1. Nesmeyanov, A. N., *Ber.*, 1929, B62, 1010.
2. Michaelis, A., *Ber.*, 1895, 28, 588.
3. Blatt, A. H. (ed.), *Organic Syntheses*, Coll. Vol. I, 2nd edn, John Wiley, New York, 1947, p. 519.
4. Sipos, J. C., Sawatzky, S. and Wright, G. F., *J. Am. Chem. Soc.*, 1955, 77, 2759.
5. Piccinini, R., *Gazz. Chim. Ital.*, 1893, 23, 534.
6. Baliah, V. and Ganapathy, K., *Trans. Faraday Soc.*, 1963, 59, 1784.
7. Fuchs, O., *Z. Phys. Chem.*, 1931, B14, 339.
8. Brooks, C. S. and Hobbs, M. E., *J. Am. Chem. Soc.*, 1940, 62, 2851.
9. Cowley, E. G., *J. Chem. Soc.*, 1952, 3557.
10. Few, A. V. and Smith, J. W., *J. Chem. Soc.*, 1949, 753.

INTENSITY VARIATION OF X-RAY REFLECTIONS IN SINTERED MATERIALS

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SINTERED materials, with desirable mechanical, electrical and magnetic properties, are gradually replacing unsintered materials. Sintering is an agglomeration or consolidation of loosely packed or pressed fine powder particles by heat treatment below the melting temperature. Many attempts have been made to understand the phenomena involved in sintering. Metallic sintering was considered to be a diffusion process¹. The initial stage of sintering² of solids by viscous flow, evaporation and condensation and self-diffusion was also suggested. Sintering was considered to occur by the rearrangement of particles at low temperatures in copper and silver powder^{3,4}. Recently it has also been described as transport of mass⁵. But so far no satisfactory explanation of the mechanism of sintering has been available. It was felt that X-ray diffraction would be useful in studying the problem.

Samples were prepared from copper powder of size 100 μ m obtained from Bharat Metallic Powders Limited, India. The copper powder was pressed in a stainless steel die of the push-pull type. The cylindrical powder pellets were 13.1 mm in diameter. Polyvinyl alcohol was used as binder as it is volatile at about 573 K. The pellets thus prepared were sintered by keeping them in granular petroleum coke powder at temperatures in the range 773 to 1273 K for five different durations of sintering.

X-ray diffraction studies of the sintered samples were done on a Philips P. W. 1730 X-ray diffractometer. In order to study the variation in intensity of diffracted X-rays as a function of temperature parameters like pressure, duration of sintering and the size of the samples were kept constant. Diffractometer parameters like radiation, filter, tube voltage, current, chart speed, scanning rate, time constant, etc were also kept constant. It can be observed from the curve of $I_{(111)}/I_{(200)}$ versus sintering temperature (figure 1) that there is a change in the intensity of reflections with temperature. The (hkl) reflections were found to vary in intensity systematically (table 1). A plot of intensity of X-ray reflections versus sintering temperature is shown in figure 2.