The Structure of Methylmercuric Chloride

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Summary The HCH bond angle and the angle subtended by the hydrogen atoms at the mercury atom have been determined by nuclear magnetic resonance; together with previously published microwave data, this allows the C–H and Hg–C bond lengths to be calculated.

THREE forms of methylmercuric chloride which contain spin-$\frac{1}{2}$ nuclei occur in sufficient natural abundance to be observable by n.m.r. methods: CH_3HgCl, $CH_3{}^{199}HgCl$ and $^{13}CH_3HgCl$. We have studied the spectrum of each of these molecules in a partially oriented state produced by dissolving it in the nematic phase of a liquid-crystal mixture described previously.[1] In this state the spectra are dominated by dipolar couplings which depend on the inverse cubes of internuclear separations. The first of these molecules exhibits a 1:2:1 triplet of total splitting $3D_{HH} = 3\hbar\gamma_H{}^2 \cdot S_{33}/\pi r^3_{HH}$ where S_{33} is an orientation parameter.[2,3] The other molecules both yield AX_3 spectra, the proton region of which consists of two triplets similar to the above, the centres of which are separated by $|D_{AX} + J_{AX}|$ where D_{AX}, as before, is a dipolar coupling and J_{AX} is the spin–spin coupling constant. The central pair of lines of the spectrum of each of these molecules was observed on a Varian A60A spectrometer although in the case of the ^{13}C side-bands spectral accumulation using a Biomac 1000 computer was necessary. The size of the proton–proton dipolar coupling was too great for the outer lines of the triplet to be observed on the A60A and recourse was made to a JEOL C60 HL instrument. At 345 K the overall splitting observed was 8760 ± 80 Hz. whereas $|D_{HgH} + J_{HgH}| = 472{\cdot}5 \pm 0{\cdot}5$ Hz. At 353 K on the A60A, $|D_{HgH} + J_{HgH}| = 394{\cdot}0 \pm 0{\cdot}5$ Hz and $|D_{CH} + J_{CH}| = 1320 \pm 10$ Hz. The spectrometer callibration was checked carefully by standard methods. The J values were determined in independent experiments in which the liquid crystal was heated until it became isotropic. This gave $|J_{HgH}| = 204{\cdot}0 \pm 0{\cdot}2$ Hz and $|J_{CH}| = 140{\cdot}0 \pm 0{\cdot}2$ Hz. This procedure was necessitated by the variation of J_{HgH} observed in solution in normal solvents (see Table). This variation, which has been noticed in the spectra of other mercury compounds[4] is not linear with the dielectric constant of the solvent, as was suggested previously. A rough calculation of the geometry of the molecule sufficed to show that J_{HgH} must be negative if J_{CH} is positive. This conclusion is consistent with the negative geminal mercury–proton coupling observed in dimethylmercury[5] and implies that the orientation parameter S_{33} is positive, *i.e.* that the molecule tends to align with its axis parallel to the magnetic field direction.

It has been shown that in AX_3 spectra the ratios of dipolar couplings are independent of orientation parameters:[3] for the molecule $^{13}CH_3HgCl$,

$$D_{\mathrm{CH}}/D_{\mathrm{HH}} = 16(\gamma_{\mathrm{C}}/\gamma_{\mathrm{H}})\sin^3\phi(2\sin^2\phi - 1)$$

where ϕ is one half the HCH bond angle. Similarly, if α is half the angle subtended by the protons at the mercury atom,

$$D_{\mathrm{HgH}}/D_{\mathrm{HH}} = 6\sqrt{3}(\gamma_{\mathrm{Hg}}/\gamma_{\mathrm{H}})(\tfrac{3}{2}\sin^5\alpha - \sin^3\alpha).$$

Values of the dipolar couplings derived from the above results yield $2\phi = 106{\cdot}2 \pm 0{\cdot}6^0$ and $\alpha = 23{\cdot}6 \pm 0{\cdot}1°$.

TABLE

Solvent	J_{HgH} ($\pm 0{\cdot}2$ Hz.)
CCl_4	196·1
Benzene	203·1
Nitrobenzene	204·2
Methanol	210·2
Acetone	211·1
Nitromethane	212·0
Pyridine	215·4
Dimethyl sulphoxide	220·1

These angles result from the ratios of the averages of the inverse cubes of the distances between the atoms and they may differ therefore from equilibrium values. A full calculation of the effect of molecular vibration on these quantities is impossible since the potential functions of the molecule are unknown. However it has been shown[6] that to a good approximation a measurement of a bond length by n.m.r., $r_{\mathrm{n.m.r.}}$, is related to the equilibrium internuclear distance, r_{e}, by the expression

$$r_{\mathrm{n.m.r.}} = r_{\mathrm{e}}(1 - 2a^2/r_{\mathrm{e}}^2)$$

where 'a' is the root-mean-square vibrational displacement.

From simple geometric considerations we find that

$$\sin\phi_{\mathrm{n.m.r.}} = \sin\phi_{\mathrm{e}}(1 - 2a^2_{\mathrm{HH}}/r^2_{\mathrm{HH}} + 2a^2_{\mathrm{CH}}/r^2_{\mathrm{CH}})$$

where it is assumed that the root-mean-square displacement is much less than the bond length. Errors in $\phi_{\mathrm{n.m.r.}}$ due to molecular vibrations tend to cancel, therefore, although in this case the major contributions to the two values of 'a' correspond to distortion of a bond angle and of a bond length, respectively. However, previous results[3] have shown remarkably good agreement between HCH bond angles determined in methyl groups by n.m.r. and microwave methods and there appears to be no evidence of systematic differences. Any discrepancies of this type are certainly less than the experimental error and we conclude that the HCH bond angle in methylmercuric chloride is the smallest yet measured in a methyl group. Only three other molecules are known in which this angle is significantly less than the tetrahedral: methylacetylene[7] (108·4°) methylgermane[8] (108°25′), and methylsilane[9] (107·7°). In each case the decrease in the angle perhaps implies extra p-character in the C–H bond.

The previously published[10] structure of methylmercuric chloride obtained from microwave data assumed a bond angle of 110°42′. If we assume that there exists no significent difference in the structure of the molecule in the gas and in solution we may calculate its complete geometry from a combination of the n.m.r. and microwave data. Firstly, the microwave experiments showed that the CHgCl bond angle is 180° and that the Hg–Cl bond length is $228{\cdot}2 \pm 0{\cdot}5$ pm, independent of any assumptions. The n.m.r. data combined with a B_0 value of 2077·18 MHz[11] yield the C–H bond length as 115 ± 4 pm and the Hg–C one as 199 ± 4 pm. These contrast with the previous values of 110 (assumed) and $206{\cdot}1 \pm 2$ pm, respectively.

J.W. thanks the S.R.C. for financial support.

(*Received, June 9th, 1969; Com.* 815.)

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