Mercury-199 Chemical Shift Anisotropy in Methyl Mercuric Bromide

By JOHN D. KENNEDY and WILLIAM MCFARLANE*

(*Department of Chemistry, Sir John Cass School of Science and Technology, City of London Polytechnic, Jewry Street, London* EC3)

Summary The magnetic shielding anisotropy $\sigma_{\parallel} - \sigma_{\perp}$ of ^{199}Hg in methyl mercuric bromide dissolved in the nematic phase of 4,4′-dihexyloxyazoxybenzene has been determined by nuclear magnetic double resonance, and has a value of 5345 ± 25 p.p.m., an order of magnitude larger than values so far observed for other nuclei in nematic phase n.m.r. investigations.

MEASUREMENTS of the magnetic shielding of many nuclei have provided valuable insight into molecular and electronic structure, and the results can be used in the critical assessment of theories of chemical bonding. However, the shielding parameters are in general anisotropic, and high resolution measurements on freely tumbling molecules in isotropic media yield only their traces: much more information is available if individual tensor components can be determined.[1a] Recently, the nematic phases of liquid crystal solvents have been used to achieve partial orientation of solute molecules, and chemical shift anisotropies for several of the lighter nuclei (^{1}H, ^{13}C, ^{14}N, ^{15}N, ^{19}F, ^{31}P) have been determined[1] in some simple compounds. We now report heteronuclear double resonance experiments which give the chemical shift anisotropy of a heavy nucleus, ^{199}Hg, in a molecule with C_{3v} symmetry.

Methyl mercuric bromide, CH_3HgBr, containing the isotope ^{199}Hg ($I = \frac{1}{2}$) in natural abundance (*ca.* 17%) was examined as a 21·3 mol % solution in the nematic phase of 4,4′-dihexyloxyazoxybenzene at several temperatures in the range 83—110°. The proton spectrum was recorded at 60 MHz and was a 1:2:1 triplet (splitting $3D_{HH}$ flanked by ^{199}Hg satellites (splitting $J_{HgH} + 2D_{HgH}$) which were observed at a signal to noise ratio of 5:1. The line width was *ca.* 9 Hz at the centre of the spectrum. The ^{199}Hg spectrum is a 1:3:3:1 quartet (splitting $J_{HgH} + 2D_{HgH}$) and the frequencies of the two central components were determined by ^{1}H — {^{199}Hg} double resonance experiments involving observation of the satellite lines of the central peak in the proton spectrum. A plot of ν_{HgH} against (J_{HgH} + 2 D_{HgH}) is linear (Figure) with a negative slope which also passes through the point obtained by measurements in the isotropic phase ($D_{HgH} = 0$). It is clear from this graph that J_{HgH} and D_{HgH} are of like sign and since the former is known[2] to be −200 Hz it follows that D_{HgH} is negative also. Plots of this type provide a convenient way of settling this point rather than use of the calculated geometry.

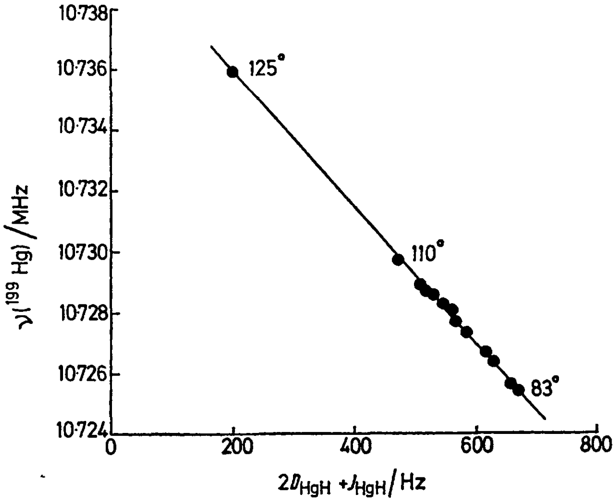

FIGURE. Plot of mercury-199 resonance frequency, ν(^{199}Hg) against the splitting ($2D_{HgH} + J_{HgH}$) in the mercury-199 spectrum of methyl mercuric bromide dissolved in 4,4′-dihexyloxyazoxybenzene at several different temperatures. The solution was isotropic at 125° and nematic in the range 83—110°.

On the basis[3] of an H–C–H interbond angle of 110·1° and bond lengths r_{CHg} and r_{CH} of 207 and 113·2 pm respectively the degrees of orientation achieved ranged from +0·15 to +0·28 and the relation between ν_{Hg} and S(C_{3v}) is given by equation (1).

$$\nu_{Hg} = \nu g_{Hg(iso)} - 38250\,S(C_{3v}) \qquad (1)$$

where $\nu_{Hg(iso)}$ is the resonant frequency in isotropic solution. The corrections necessary for ^{1}H anisotropy and temperature dependence of $\nu_{Hg(iso)}$ were found to be negligible. This equation yields $\sigma_{\parallel} - \sigma_{\perp} = + 5345 \pm 25$ p.p.m. for the mercury shielding anisotropy, where the positive sign corresponds to diamagnetic shielding. The error quoted is based upon the estimated inaccuracies in our own measurements; any alteration in the geometry would have a much larger effect, *e.g.* a value[4] of 200 pm for r_{CHg} gives $\sigma_{\parallel} - \sigma_{\perp} = 5925$ p.p.m.

The shielding anisotropy is an order of magnitude larger than other reported values[1] and is perhaps not unexpected in view of the larger chemical shift ranges of heavier nuclei such as mercury and the greater values of the radial expansion terms in the expression for the paramagnetic contribution to the shielding.

When the C_{3v} symmetry axis is parallel to the magnetic field, circulation of the electrons in the Hg–C and Hg–Br bonds will be unopposed (*i.e.* no paramagnetic term) and the mercury shielding, σ, will be positive. When the C_{3v} axis is perpendicular to the field, circulation of the electrons in the bond will be hindered (*i.e.* a significant paramagnetic term) and σ will then have a larger negative value. The mercury atom is *sp* hybridised in this and similar species and the remaining two 6*p* orbitals are vacant so that electron circulation in these need not be considered and thus the large anisotropy also reflects the state of hybridisation of the mercury atom. It is not to be expected that changes of the group X in compounds of the type MeHgX will have much effect upon $\sigma_{\parallel} - \sigma_{\perp}$ since there will only be a small change of the electron distribution within the linear system.

We thank the S.R.C. for support.

(*Received*, 22*nd May* 1974; *Com.* 594.)

---

[1] (a) P. Diehl and C. L. Khetrapal, 'N.M.R.', ed. P. Diehl, E. Fluck, and R. Kosfeld, Springer Verlag, Berlin, 1969, **1**, 1. (b) P. K. Bhattacharyya and B. P. Dailey, *Mol. Phys.*, 1973, **26**, 1379; P. K. Bhattacharyya and B. P. Dailey, *J. Mag. Res.*, 1973, **12**, 36; G. Englert, *Z. Naturforsch.*, 1972, **A27**, 715; F. Millet and B. P. Dailey, *J. Chem. Phys.*, 1971, **54**, 5434; (c) C. S. Yannoni, *J. Chem. Phys.*, 1970, **52**, 2005; (d) R. A. Bernheim, D. J. Hoy, T. R. Krugh, and B. J. Lavery, *J. Chem. Phys.*, 1969, **50**, 1350; (e) N. Zumbulyadis and B. P. Dailey, *Mol. Phys.*, 1974, **27**, 633; 1973, **26**, 777.

[2] K. A. McLauchlan, D. H. Whiffen, and L. W. Reeves, *Mol. Phys.*, 1966, **10**, 131.

[3] C. L. Khetrapal and A. Saupe, *Mol. Cryst. Liq. Cryst.*, 1973, **19**, 195.

[4] M. Ayres, K. A. McLauchlan, and J. Wilkinson, *Chem. Comm.*, 1969, 858.