On the Quadrupole-coupling Constants of Halogen Atoms in Methylmercury Halides

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Summary A comparison of the crystal structure of MeHgCl with the quadrupole-coupling constants of halogens in MeHgHal (Hal = Cl,Br,I) in the vapour and the solid phase shows that mercury and halogen atoms are bonded by intermolecular co-ordination bonds.

FOR molecular crystals with van der Waals intermolecular interactions, quadrupole-coupling constants of halogens are higher for the vapour phase than for the solid phase. The ratio α [$=eQq_{zz}$ (solid)/eQq_{zz} (vapour)] is 0·911, 0·916, and 0·913 for MeCl, MeBr, and MeI respectively.[1]† This ratio changes sharply, if, besides van der Waals interactions, other forces like co-ordination and hydrogen bonding provides the cohesion in a crystal.[2]

In halogen n.q.r. spectra of organomercury compounds abnormalities caused by intra- and inter-molecular co-

† This is also valid for molecules where the halogen atom is attached to a less electronegative atom.

ordination interactions Hal · · · Hg have been observed.[3,4] A comparison of the halogen quadrupole-coupling constants in MeHgHal in the vapour and solid phases shows rather low α-values.

N.q.r. spectra of ^{35}Cl, ^{79}Br, ^{81}Br, and ^{127}I at 77 K, quadrupole-coupling constants in the vapour phase taken from microwave spectra,[5,6] and α ratios are given in the Table.

TABLE

N.q.r. spectra of halogens and Hg–Hal bond lengths of methylmercury halides in vapour and solid[a]

Compound	Solid state: N.Q.R. frequency 1/2—3/2 (MHz)[c]	eQq_{zz} solid (MHz)	eQq_{zz} vapour (MHz)	$\frac{eQq_{zz}\text{ solid}}{eQq_{zz}\text{ vapour}}$ (α)	Bond length Hg–Hal (Å) vapour[e]
$MeHg^{35}Cl$[b]	14·75	29·5	−42	0·70	2·282
$MeHg^{79}Br$[b]	121·20	242·4	+350	0·69	2·406
$MeHg^{81}Br$	101·27	202·5	+290		
$MeHg^{127}I$[d]	127·42	849·5 ± 0·3	−1674	0·51	2·528

[a] The accuracy in measuring n.q.r. frequencies is ±0·05 MHz. [b] In the calculations for α the asymmetry parameter for MeHgCl and MeHgBr was assumed to be zero. [c] 3/2—5/2 for $MeHg^{127}I$ is 254·85. [d] η 0 ± 1·8%. [e] Hg–Hal for solid MeHgCl is 2·50 Å.

The value for MeHgI is the lowest known up to now. These large changes in quadrupole constants may be due to intermolecular co-ordination interactions Hg · · · Hal. *X*-ray data, available for MeHgCl only, supports this hypothesis.[7] A structural pattern where four neighbouring molecules have non-parallel Hg-Cl bonds exists, MeHgCl having a linear configuration in the vapour as well as in the solid phase.[5–7] There are intermolecular Cl · · · Hg contacts in the crystal. The Hg–Cl bond in the crystal is lengthened by 0·2 Å while the length of the C–Hg bond does not change (compared to the vapour phase) and is 2·06 Å.

The fact that α for MeHgCl is higher than for both MeHgBr and MeHgI may be due to an increase in the amount of π-bonding, between the mercury and halogen atoms on neighbouring molecules, as the atomic number of the halogen atom increases.

From the n.q.r. data it is expected that the increase in bond length on going from the vapour to the solid phase should be greater for the Hg–Br and Hg–I bonds than for the Hg–Cl bonds.

The authors wish to thank Dr. V. I. Pakhomov and Dr. T. L. Khotsyanova for useful discussions throughout the work.

(*Received, 12th June* 1972; *Com.* 996.)

[1] T. P. Das and E. L. Hahn, Solid State Physics, 1. suppl. 'Nuclear Quadrupole Resonance Spectroscopy,' Academic Press, 1958, p. 167.
[2] T. A. Babushkina, Dissertation, Moscow, 1968.
[3] G. K. Semin and V. I. Robas, 'Radiospektroscopyja tverd. tela,' Atomizdat, Moscow, 1967, p. 229; V. I. Bregadze, T. A. Babushkina, O. Yu. Okhlobystin, and G. K. Semin, *Theoretich. Eksp. khim.*, 1967, **4**, 547; D. N. Kravtsov, A. P. Zukov, B. A. Faingor, E. M. Rokhlina, G. K. Semin, and A. N. Nesmeyanov, *Izvest. Akad. Nauk SSSR, Ser. khim.*, 1968, 1703; T. A. Babushkina, E. V. Bryuchova, F. K. Velichko, V. I. Pakhomov, and G. K. Semin, *Zhur. Strukt. Khim.*, 1968, **9**, 207.
[4] E. V. Bryuchova, T. A. Babushkina, M. V. Kashutina, O. Yu. Okhlobystin, and G. K. Semin, *Doklady Akad. Nauk SSSR*, 1968, **183**, 827; A. N. Nesmeyanov, O. Yu. Okhlobystin, E. V. Bryuchova, V. I. Bregadze, D. N. Kravtsov, B. A. Fainger, L. S. Golovchenko, and G. K. Semin, *Izvest. Akad. Nauk SSSR*, Ser. khim, 1969, 1928.
[5] W. Gordy and J. Sheridan, *J. Chem. Phys.*, 1954, **22**, 92.
[6] C. Feige and H. Hartmann, *Z. Naturforsch.*, 1967, **22a**, 1286.
[7] D. R. Grdenich and A. I. Kitaigorodskii, *Zhur. Fisich. khim.*, 1949, **23**, 1161.