Nuclear Quadrupole Resonance Studies of some Boron-Chlorine Compounds

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RELATIVELY few studies have appeared[1,2] of ^{35}Cl nuclear quadrupole resonance (n.q.r.) spectra in compounds containing boron–chlorine bonds, despite their relevance to the study of bond properties. This note presents measurements of five ^{35}Cl n.q.r. spectra (see Table) recently obtained on a frequency–modulated super-regenerative spectrometer after the design of Dean.[3]

Chlorine-35 n.q.r. frequencies (in Mc./sec.) in some B–Cl *compounds*

Compound	^{35}Cl frequency (relative intensity)	Temp. (°K)	Source
$(HN{\cdot}BCl)_3$	19·638 ± 0·001(2) 19·958 ± 0·001(1)	295°	Dr. H. B. Silver, Borax Consolidated
$(PhN{\cdot}BCl)_3$	20·87 ± 0·01(1) 20·97 ± 0·01(2)	273	Dr. H. B. Silver, Borax Consolidated
$(Me_2N{\cdot}BCl_2)_2$	21·0084 ± 0·0002(1) 21·1561 ± 0·0002(2)	273	Dr. H. B. Silver, Borax Consolidated
(t-Pentyl·N·BCl)$_4$	20·337 ± 0·002(2) 20·359 ± 0·002(1)	293	Dr. H. S. Turner, National Chemical Laboratory.
neo-$B_{10}Cl_{10}C_2H_2$	24·365(2), 24·700(2), 24·799(2), 24·829(2), 24·989(2), 25·185(2), 25·267(1), 25·309(2), 25·601(2), 25·728(2) (all ± 0·003)	273	Dr. H. Schroeder, Olin Mathieson.

Despite previous claims to the contrary,[1] the n.q.r. spectrum of $(BClNH)_3$ *should* contain two signals with an intensity ratio of **2 : 1**, as we observe. Both chlorine atoms appear to be hydrogen-bonded to N–H groups of neighbouring molecules; the low-frequency line corresponds to an N–H···Cl length[4] of 3·56 Å and the high-frequency one to 3·49 Å, which is the same dependence (of frequency on length) that is observed in chloral hydrate.[5] The spectrum of $(BClNPh)_3$ (looked for previously but not detected[1]) also shows two lines with an intensity ratio of about 2 : 1, but the low frequency line is now the weaker. No space-group is available with which to assign frequencies.

The *X*-ray structure analysis[6] of the dimer $\{Me_22N.BCl_2\}_2$ also predicts two frequencies, as observed; despite the different stereochemistry of boron and the change in the B–Cl bond length between the latter (1·83 Å) and $(BClNH)_3$ (1·76 Å), the ^{35}Cl frequencies differ by little more than

[1] Nakamura, Watanabe, and Kubo, *Bull. Chem. Soc. Japan*, 1961, **34**, 142.
[2] Chiba, *J. Phys. Soc. Japan*, 1958, **13**, 860.
[3] In Das and Hahn, "Nuclear Quadrupole Resonance," Academic Press, London, 1958, p. 90.
[4] Coursen and Hoard, *J. Amer. Chem. Soc.*, 1952, **74**, 1742.
[5] Reference 3, p. 170.
[6] Hess, *Zeit. Krist.*, 1963, **118**, 361.

1 Mc./sec. The space-group of the tetramer[7] $(t\text{-pentyl}\cdot N\cdot BCl)_4$, $P4_1$ or $P4_3$ ($Z = 8$), predicts eight lines, but we have so far detected only two.

The most interesting spectrum is that of decachloroneocarborane,[8] which shows ten lines; furthermore, the frequencies are unusually high for B–Cl bonds, which parallels the outstanding chemical inertness of this molecule. By single crystal studies, we hope to investigate the electrical symmetry of the bond.

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[7] Luxmoore and Truter, unpublished work.
[8] Schroeder, Heying, and Reiner, *Inorg. Chem.*, 1963, **2**, 1092.