Nuclear Quadrupole Resonance of B-Trichloroborazole

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In an attempt to obtain some informations on the electronic structure of borazole and its derivatives, the pure quadrupole resonance of ^{35}Cl in solid *B*-trichloroborazole was observed using a spectrometer previously reported[1]. The compound was synthesized by Brown and Laubengayer's method[2] and purified by sublimation immediately before measurements. The observed frequency was 19.937 and 19.639± 0.001 Mc. at liquid nitrogen temperature and room temperature (22.0°C), respectively. The signal-to-noise ratio was about 3 as observed on an oscilloscope display. The compound underwent gradual decomposition, a sample left to stand in a sealed glass tube for a month showing no observable resonance line on the oscilloscope screen. A search for the resonance lines of *B*-trichloro-*N*-trimethylborazole and *B*-trichloro-*N*-triphenylborazole was unsuccessful, presumably because the lines were broadened to escape detection.

The X-ray crystal analysis carried out on *B*-trichloroborazole by Coursen and Hoard[3] has shown that all the chlorine atoms are equivalent in the crystal lattice. This is in agreement with the observation of a single resonance line in the present study.

The B-Cl distance 1.75 Å in this molecule determined by both X-ray crystal analysis and electron diffraction investigation[4] is practically identical with that in a boron trichloride molecule[5]. In addition, chlorine and nitrogen have the same value of electronegativity equal to 3.0 as proposed by Pauling[6]. This suggests a striking similarity existing between the atomic environments about chlorine atoms in these two compounds. Accordingly, one may expect the same p-electron defect[7] on these chlorine atoms leading to nearly the same frequency of the quadrupole resonance. As a matter of fact, the observed frequency of ^{35}Cl in solid boron trichloride at liquid nitrogen temperature, 21.6 Mc.[8,9] is fairly close to that in *B*-trichloroborazole, 19.9 Mc., of the present study. The reason for the difference must be looked for in the partial aromatic character of a borazole ring[10], in which π-electrons are presumed to migrate to some extent from nitrogen to boron[11]. As a result of Kekulé type resonance, the ionic character of B-Cl bonds will increase. Accordingly, the p-electron defect on chlorine atoms decreases, leading to the decrease in the frequency of quadrupole resonance as observed in the present investigation. A quantitative treatment must be postponed until the asymmetry parameter of field gradient is determined and complications involved in the partial ionic character and double bond character* of the B-Cl bond are clarified in future.

Mention shuld be made here of studies on the ^{35}Cl pure quadrupole resonances of some heterocyclic compounds made by Negita and coworkers[12], who showed that the observed resonance frequencies of $(-\mathrm{SCl{=}N}-)_3$, $(-\mathrm{PCl_2{=}N}-)_3$ and $(-\mathrm{CCl{=}N}-)_3$ were fairly close to those of $\mathrm{SOCl_2}$, $\mathrm{POCl_3}$ and $\mathrm{COCl_2}$, respectively. The partial molecular structure of these heterocyclic compounds is more or less analogous to that of the corresponding oxychlorides as in the pair of compounds, *B*-trichloroborazole $(-\mathrm{BCl{=}NH}-)_3$ and boron trichloride $\mathrm{BCl_3}$.

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1) D. Nakamura, Y. Kurita, K. Ito and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5783 (1960).

2) C. A. Brown and A. W. Laubengayer, ibid., **77**, 3699 (1955).

3) D. L. Coursen and J. L. Hoard, ibid., **74**, 1742 (1952).

4) K. P. Coffin and S. H. Bauer, *J. Phys. Chem.*, **59**, 193 (1955).

5) M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 195 (1957).

6) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, New York (1960).

7) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy. Solid State Physics, Supplement 1", Academic Press, New York (1958).

8) R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).

9) T. Chiba, *J. Phys. Soc. Japan*, **13**, 860 (1958).

10) K. Ito, H. Watanabe and M. Kubo, *J. Chem. Phys.*, **32**, 947 (1960); This Bulletin, **33**, 1588 (1960); H. Watanabe and M. Kubo, *J. Am. Chem. Soc.*, **82**, 2428 (1960); H. Watanabe, K. Ito and M. Kubo, ibid., **82**, 3294 (1960).

11) B. L. Crawford, Jr. and J. T. Edsall, *J. Chem. Phys.*, **7**, 223 (1939); C. C. J. Roothaan and R. S. Mulliken, ibid., **16**, 118 (1948); C. W. Rector, G. W. Schaeffer and J. R. Platt, ibid., **17**, 460 (1949).

* The double bond character of B-Cl bonds was estimated at only 6% in boron trichloride[9].

12) H. Negita and S. Satou, This Bulletin, **29**, 426 (1956); H. Negita, S. Satou, T. Yonezawa and K. Fukui, ibid., **30**, 721 (1957); H. Negita and Z. Hirano, ibid., **31**, 662 (1959).