$(-\delta/3 - \zeta/2 - Q)$, $\Gamma_5(D_{3h})$ or $\Gamma_6(D_{4h})$ at $\delta/3 + \zeta/2$, and $\Gamma_4(D_{3h})$ or $\Gamma_7(D_{4h})$ at $^1/_2(-\delta/3 - \zeta/2 + Q)$, where $Q^2 = \delta^2 + \delta\zeta + (^3/_2\zeta)^2$ and δ is the axial ligand field strength. Applying these expressions to the data of Table III we find $\delta = -4.0$ kK and $\zeta = 2.7$ kK which are quite reasonable values when we consider $\delta = -3.15$ kK and $\zeta = 3.15$ kK for $Os^{III}(acac)_3$[5] and ζ_{5d} is usually 2.5–3.5 kK.[21,26,27]

The origin of the four visible bands is less clear. By comparison with Ir(III) in LiCl–KCl[19] we might anticipate $\Delta = 25$ kK and $B = 0.3$ kK and taking $C = 4.5B$ for pure octahedral symmetry would expect transitions to the states $^4T_1$, $^4T_2$, and $^6A_1$ at 18.5, 21.0, and 32.5, respectively. If spin–orbital coupling is considered instead of interelectronic repulsion, then bands are predicted at 5, 22.5, 27.5, and 32.5 kK.[27] The addition of the axial distortion to a mixture of these sets could conceivably yield a series of bands

starting at 16 kK but not obviously one at 12 kK nor, in particular, bands of high intensity relative to those found in the near-ir spectrum. It is tempting to speculate that Os(III), like Re(III), is polymeric in compounds with chloride. Further work on this system is in progress.

Voltammetry.—No reduction waves were obtained for $RuCl_3$, $OsCl_3$, or K_2OsCl_6 in LiCl–KCl eutectic melt. A similar situation was noted for K_2RuCl_6, $K_2RuCl_5 \cdot H_2O$, and $K_4Os(CN)_6$ in several aqueous media[28] and it appears[29–31] that reduction waves of Ru and Os compounds are only observed when oxygen is involved in one of the complexing ligands.

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Microwave Spectrum, Molecular Structure, and Quadrupole Coupling in 2-Chloro-1,6-dicarbahexaborane(6)[1a]

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The microwave spectrum of 2-chloro-1,6-dicarbahexaborane(6) has been observed and rotational constants have been assigned for nine isotopic species. The boron–boron and boron–chlorine bond lengths were determined and the molecule was shown to exist as a distorted octahedron. The ^{35}Cl quadrupole coupling constant is 49.7 ± 2 MHz and the asymmetry parameter is zero within experimental error.

Introduction

The class of carbon–boron–hydrogen compounds commonly known as carboranes has received considerable attention in recent years. The unusual bonding arrangements in these molecules have made the determination of their molecular structures and properties particularly significant and intriguing. Though the nmr and ir spectra of some of the carboranes that have been studied in the past were insufficient to determine their gross structures, there was little doubt of the atomic arrangement and shape of the symmetric $C_2B_4H_6$ carborane. In spite of this, the determination of the accurate molecular structure of this octahedral framework is important in order to compare its bond lengths to those in other systems and to understand better the chemical bonding in carboranes. Since sym-$C_2B_4H_6$ has no dipole moment, we had to await the synthesis of a substituted derivative before the structure could be determined by microwave spectroscopy. In this study we report the microwave spectrum and partial molecular structure of 2-chloro-1,6-dicarbahexaborane(6). Unfortunately at this time the synthesis of the compound

is not efficient enough to allow an economical preparation of enriched ^{13}C isotopic species, and the structure determination is incomplete.

Experimental Section

A sample of the title compound (*ca.* 50 mmol) was obtained from J. Spielman and was used without further purification. The compound is stable at room temperature, and despite repeated reusage of the same sample for a period of nearly 2 years, no serious decomposition was noted. The microwave spectrum was observed in the range 8–38 GHz using a conventional 100-kHz Stark-modulated spectrometer and 10–12-ft wave guide sample cells which were cooled below room temperature. Phase-locking techniques were employed for study of the quadrupole splittings of some low J transitions.

Observed Spectrum and Assignment

The microwave spectrum shows a multitude of weak- to medium-intensity lines owing both to the presence of several observable isotopic species and to the effects of the quadrupolar nuclei. Some difficulty was experienced at first in assigning the spectrum since Stark effects were not readily apparent and R-branch series for some isotopic species overlapped. The spectra of the nine major isotopic species were eventually assigned with the help of a good initial rigid-rotor approximation and by making approximate relative intensity measurements.

Table I

Observed Transitions and Deviations from Rigid-Rotor Frequencies of 2-Chloro-1,6-dicarbahexaborane(6)

a. isotopic species all ^{11}B ^{35}Cl

Transitions	F-F'	Observed	Deviation
3_{13}-2_{12}	7/2-5/2	10394.67	+.06
	9/2-7/2	10397.75	-.01
3_{03}-2_{02}	9/2-7/2	10451.71	+.01
	5/2-3/2	10448.52	-.06
3_{12}-2_{11}	9/2-7/2	10508.62	-.07
	7/2-5/2	10505.52	-.02
4_{14}-3_{13}	7/2-5/2	13860.53	+.09
	9/2-7/2	13861.12	+.03
	11/2-9/2	13862.34	-.02
4_{04}-3_{03}	7/2-5/2	13932.71	+.07
	11/2-9/2	13934.14	+.04
4_{13}-3_{12}	7/2-5/2	14008.38	+.03
	9/2-7/2	14009.01	0.00
	11/2-9/2	14010.27	0.00
6_{16}-5_{15}	15/2-13/2	20791.53	-.08
	13/2-11/2	20791.17	-.08
	11/2-9/2	20790.81	0.00
6_{06}-5_{05}	15/2-13/2	20896.15	+.03
	11/2-9/2	20895.58	+.02
6_{24}-5_{23}	15/2-13/2	20896.15	+.03
	11/2-9/2	20895.58	+.02
6_{24}-5_{23}	15/2-13/2	20910.21	+.10
6_{15}-5_{14}	15/2-13/2	21013.37	+.06
	13/2-11/2	21013.02	+.05
	11/2-9/2	21012.72	-.09
8_{18}-7_{17}	- - - -	27719.55	-.09
8_{08}-7_{07}	19/2-17/2	27852.50	-.15
	15/2-13/2	27852.80	-.19
8_{26}-7_{25}	19/2-17/2	27888.71	+.15
	15/2-13/2	27888.20	+.07
8_{27}-7_{26}	- - - -	27869.10	-.14
8_{17}-7_{16}	19/2-17/2	28015.33	-.08
	17/2-15/2	28015.20	-.06
	15/2-13/2	28015.01	0.00
9_{19}-8_{18}	- - - -	31183.21	0.00
9_{09}-8_{08}	- - - -	31328.59	+.01
9_{18}-8_{17}	- - - -	31515.61	+.01

b. 2-^{10}B ^{35}Cl

Transitions	F-F'	Observed	Deviation
3_{03}-2_{02}	9/2-7/2	10453.16	-.01
6_{06}-5_{05}	15/2-13/2	20899.04	-.17
	11/2-9/2	20898.53	-.01
7_{17}-6_{16}	- - - -	24258.8	-0.3
8_{18}-7_{17}	- - - -	27723.36	-.20
9_{19}-8_{18}		31187.59	-.02
9_{09}-8_{08}		31332.89	-.09
9_{18}-8_{17}		31519.98	-.02
$10_{1,9}$-$9_{1,8}$		35020.06	-.21
$10_{1,10}$-$9_{1,9}$		34650.79	-.41

c. 3-^{10}B ^{35}Cl

Transitions	F-F'	Observed	Deviation
4_{04}-3_{03}	11/2-9/2	14013.53	-.02
	7/2-5/2	14012.16	+0.07
5_{15}-4_{13}	11/2-9/2	17588.3	-0.1
6_{16}-5_{15}	- - - -	20935.7	0.0
6_{06}-5_{05}	15/2-13/2	21017.26	-.04
	11/2-9/2	21016.70	+.03
6_{15}-5_{14}	- - - -	21105.5	-.2
8_{18}-7_{17}	- - - -	27912.99	-.03
8_{08}-7_{07}	- - - -	28017.83	-.07
8_{17}-7_{16}	- - - -	28139.59	-.06
9_{19}-8_{18}	- - - -	31401.35	+.01
9_{09}-8_{08}	- - - -	31516.81	+.02
9_{18}-8_{17}	- - - -	31656.24	+.01
$10_{4,7}$-$9_{4,6}$	- - - -	35036.82	+.31
	- - - -	35037.18	-.13

d. 4-^{10}B ^{35}Cl

Transitions	F-F'	Observed	Deviation
5_{15}-4_{14}	- - - -	17604.2	-.1
5_{14}-4_{13}	- - - -	17745.2	0.0
6_{14}-5_{13}	- - - -	21124.7	
6_{16}-5_{15}	15/2-13/2	21232.63	+.05
6_{06}-5_{05}	11/2-9/2	21232.08	+.07
6_{15}-5_{14}	- - - -	24644.31	-.04
8_{18}-7_{17}	- - - -	28163.9	+.1
8_{08}-7_{07}	19/2-17/2	28300.80	-.02
	15/2-13/2	28300.49	-.02
8_{17}-7_{16}	- - - -	28649.0	-.1
9_{19}-8_{18}	- - - -	31682.81	+.02
9_{09}-8_{08}	21/2-19/2	31832.20	+.04
9_{18}-8_{17}	- - - -	32026.10	+.04

e. ^{11}B ^{37}Cl

Transition	F-F'	Observed	Deviation
4_{14}-3_{13}	11/2-9/2	13491.27	-.11
	9/2-7/2	13490.36	-.04
4_{13}-3_{12}	11/2-9/2	13631.34	-.05
	9/2-7/2	13630.47	+.01
6_{16}-5_{15}	13/2-11/2	20235.15	-.01
6_{06}-5_{05}	15/2-13/2	20334.90	+.03
	11/2-9/2	20334.45	+.03
6_{24}-5_{23}	15/2-13/2	20348.53	-.08
6_{15}-5_{14}	13/2-11/2	20445.20	-.02
8_{18}-7_{17}	19/2-17/2	26978.52	-.04
	15/2-13/2	26978.30	+.07
8_{08}-7_{07}	19/2-17/2	27105.46	-.02
8_{17}-7_{16}	17/2-15/2	27258.46	-.04
	15/2-13/2	27258.20	+.03
9_{19}-8_{18}	- - - -	30349.55	0
9_{09}-8_{08}	- - - -	30488.44	-.01
9_{18}-8_{17}	- - - -	30644.38	+.03

f. 2-^{10}B ^{37}Cl

Transition	F-F'	Observed	Deviation
6_{16}-5_{15}	- - - -	20236.51	+.05
6_{15}-5_{14}	- - - -	20446.45	-.12
6_{06}-5_{05}	11/2-9/2	20336.51	+.07
8_{18}-7_{17}	- - - -	26980.3	+.1
8_{17}-7_{16}	- - - -	27260.4	-.2
8_{08}-7_{07}	- - - -	27107.23	-.12
9_{19}-8_{18}	- - - -	30351.50	0
9_{09}-8_{08}	- - - -	30490.34	0
9_{18}-8_{17}	- - - -	30686.35	0

g. 3-^{10}B ^{37}Cl

Transition	F-F'	Observed	Deviation
6_{15}-5_{14}	- - - -	20537.75	0.00
7_{17}-6_{16}	- - - -	23772.49	+.19
7_{07}-6_{06}	- - - -	23861.39	+.14
6_{16}-5_{15}	- - - -	23960.19	-.06
8_{18}-7_{17}	- - - -	27167.9	+.1
8_{08}-7_{07}	- - - -	27267.76	+.10
8_{17}-7_{16}	- - - -	27382.54	0
9_{19}-8_{18}	- - - -	30563.02	0
9_{18}-8_{17}	- - - -	30673.15	0

h. 4-^{10}B ^{37}Cl

Transition	F-F'	Observed	Deviation
7_{17}-6_{16}	- - - -	23987.93	0
7_{07}-6_{06}	- - - -	24105.22	0
8_{16}-7_{15}	- - - -	24241.07	0
8_{18}-7_{17}	- - - -	27413.8	+.1
8_{17}-7_{16}	- - - -	27702.87	-.08
9_{18}-8_{17}	- - - -	30839.12	-.02
9_{19}-8_{18}	- - - -	31164.25	-.14

i. 2,3-^{10}B ^{35}Cl

Transition	F-F'	Observed	Deviation
9_{18}-8_{17}	- - - -	31660.07	0
9_{18}-8_{17}	- - - -	31404.59	-.31
$10_{1,9}$-$9_{1,8}$	- - - -	35176.60	0
$10_{1,10}$-$9_{1,9}$	- - - -	34893.36	0
$10_{0,10}$-$9_{0,9}$	- - - -		

Some of the observed R-branch transitions are shown in Table I, together with the best calculated spectrum. The Q-branch transitions are expected to be extremely weak and none were observed despite repeated searches in several regions. The transitions were observed to fit very closely to a rigid-rotor model through $J = 10$. No attempt was made to introduce centrifugal distortion corrections in order to remove small discrepancies appearing in some of the high K–high J transitions.

Moments of Inertia and Structure

Since all isotopic species yield a-type spectra and are only slightly asymmetric, A moments of inertia are quite insensitive to R-branch transition frequencies and could be determined at best only to within about 0.5%. The rigid-rotor approximation holds quite well through $J = 10$, as determined by variations of the B and C moments. Also the higher J transitions are not broadened appreciably by unresolved quadrupole splittings. For these reasons the $8 \rightarrow 9$ transitions were used in order to obtain the best possible value for the A moments. The rotational constants of the various isotopic species as determined from the calculated spectra of Table I are shown in Table II.

TABLE II
ROTATIONAL CONSTANTS AND QUADRUPOLE COUPLING
CONSTANTS OF 2-CHLORO-1,6-DICARBAHEXABORANE(6)[a]

Isotopic species	A	A'[b]	B	C
$^{11}B^{35}Cl$	6194	6198	1760.493	1723.514
$2\text{-}^{10}B^{35}Cl$	6201	6198	1760.737	1723.759
$3\text{-}^{10}B^{35}Cl$	6307	6313	1765.982	1737.641
$4\text{-}^{10}B^{35}Cl$	6170	6198	1789.184	1750.990
$^{11}B^{37}Cl$	6202	6198	1712.662	1677.646
$2\text{-}^{10}B^{37}Cl$	6172	6198	1712.781	1677.754
$3\text{-}^{10}B^{37}Cl$	6314	6313	1718.272	1691.416
$4\text{-}^{10}B^{37}Cl$	6237	6198	1740.757	1704.579
$2,3\text{-}^{10}B^{35}Cl$	5800	6313	1766.23	1737.87

^{a} $\chi_{\alpha\alpha}(^{35}Cl) = 49.7 \pm 2$ MHz; $\chi_{\alpha\alpha}(^{37}Cl) = 39.0 \pm 2$ MHz; $\eta = 0$. ^{b} Derived value—see text.

The A moments for all singly substituted species except the $3\text{-}^{10}B$ entity are equal within experimental error, as is expected if the substituted atom lies on the a

Because the ^{13}C and ^2H species were not studied, a complete structure determination is not possible. However, with data on nine isotopically substituted molecules and the reasonable assumption of C_{2v} symmetry, a significant skeletal structure may be deduced.

Calculations were performed using Kraitchman's equations[2] to determine the positions of B(2), B(3), and B(4) relative to the center of mass of both $C_2{}^{11}\text{-}B_4H_5{}^{35}Cl$ and $C_2{}^{11}B_4H_5{}^{37}Cl$. (See Table III.) The B(2)–Cl bond distance could similarly be determined relative to $C_2{}^{11}B_4H_5{}^{35}Cl$ and to $3\text{-}^{10}B\text{-}C_2{}^{11}B_3H_5{}^{35}Cl$. The latter molecule also was used to calculate the B(2)–B(3) bond distance since B(2) lies near the center of mass where the accuracy of the coordinate calculation is low. The B(2) atom is central to the calculation of most bond lengths and angles, and the uncertainties in the structure shown in Figure 1 and Table IV are predominantly traceable to the inexact location of B(2).
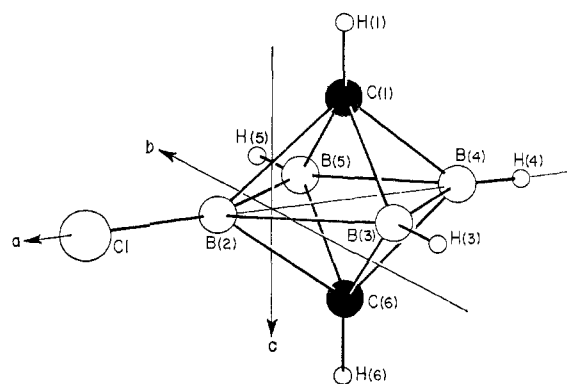
Figure 1.—Structure of 2-chloro-1,6-dicarbahexaborane(6).

An attempt was made to estimate the position of the carbon atoms by use of the moment differences and center of mass relations[3]

$$I_a + I_b - I_c = 2\sum_i m_i c_i{}^2$$

$$\sum_i m_i a_i = 0 \tag{1}$$

TABLE III
ATOM COORDINATES IN CENTER OF MASS FRAME

Parent species	Isotopic species	Atom position	Coordinates, Å		
			a	b	c
"Normal" (all $^{11}B^{35}Cl$)	$2\text{-}^{10}B$	2	0.202 ± 0.020	<0.03	Imag
	$3\text{-}^{10}B$	3	0.945 ± 0.010	1.215 ± 0.005	0
	$4\text{-}^{10}B$	4	2.139 ± 0.010	Imag	<0.03
	$^{11}B^{37}Cl$	Cl	2.022 ± 0.010	0.00	0.00
All $^{11}B^{37}Cl$	$2\text{-}^{10}B$	2	0.15 ± 0.020	0.00	0.00
	$3\text{-}^{10}B$	3	0.983 ± 0.010	1.214 ± 0.010	0
	$4\text{-}^{10}B$	4	2.176 ± 0.016	Imag	<0.03
	$^{11}B^{35}Cl$	Cl	1.985 ± 0.010	0.00	0.00
$3\text{-}^{10}B^{35}Cl$	$2,3\text{-}^{10}B$	2	0.198 ± 0.020	Imag	0
	$^{11}B^{35}Cl$	3	0.948 ± 0.010	1.231 ± 0.010	0
	$3\text{-}^{10}B^{37}Cl$	Cl	2.013 ± 0.010	0.037 ± 0.020	0

axis. This prompted use of the average value of A for these species in the calculations that follow. The A moment for the $3\text{-}^{10}B$ isotopes was derived from the more accurately known B and C moments by using the relationship $\Delta I_a + \Delta I_b - \Delta I_c = 0$, which assumes a molecular plane of symmetry containing the a and b axes. This calculated A value agrees with the value obtained by fitting the transitions to within experimental error.

The equations are not unambiguously solvable since N-3 substitutions are unavailable, and simplifying assumptions must be made regarding some hydrogen atom positions. Because inertial defects are omitted from these calculations, the entire uncertainties due to

(2) (a) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953); (b) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1953).

(3) J. E. Wollrab, "Rotational Spectra and Molecular Structure," Academic Press, New York, N. Y., 1967, Chapter 4.

TABLE IV
AVERAGE STRUCTURE FROM ISOTOPIC SUBSTITUTION

⎯⎯⎯Bond length, Å⎯⎯⎯		⎯⎯⎯⎯Angles, deg⎯⎯⎯⎯	
B(2)–Cl	1.823 ± 0.010	B(2)–B(3)–B(4)	87.7 ± 0.5
B(2)–B(3)	1.671 ± 0.010	B(3)–B(4)–B(5)	91.0 ± 0.2
B(3)–B(4)	1.702 ± 0.005	B(3)–B(2)–B(5)	93.6 ± 0.5
C(5)–B(2)	1.59 ± 0.04		
C(5)–B(4)	1.61 ± 0.04		
B(5)–B	1.63 ± 0.04		

differences in zero-point vibrations among the isotopic species are contained in the derived atom positions. However, Beaudet and Poynter[4] have indicated that for hydrogen atoms located far from the center of mass in rigid carborane structures, B–H bond lengths derived from the second moment relations are both internally consistent and comparable to known r_{B-H} values.

Two separate calculations of carbon atom positions were made based on different assumptions regarding the disposition of the hydrogen atoms in the molecule. In the first calculation C–H and B–H bond lengths were taken to be 1.091 and 1.183 Å, respectively, and each such bond was assumed to bisect the exterior angles of the cage structure so that a semblance of octahedral symmetry was retained. In the second instance the C–H and B–H bonds were assumed to be bent from their octahedral positions by an amount (12°) necessary to satisfy both eq 1 and the bond lengths. For either case the derived C–B(2) and C–B(4) bond lengths were calculated to be 1.59 ± 0.04 and 1.61 ± 0.04 Å, respectively. Although these values are quite reasonable and comparable to C–B bond lengths in $2,3\text{-}C_2B_4H_6$ (1.605 Å)[4] and in $2,4\text{-}C_2B_5H_7$ (1.545, 1.563 Å),[5] the consistency of the derived values indicate that our microwave data cannot be used to determine whether the gross structure is considerably distorted from octahedral symmetry. This merely points out the problems involved with estimating heavy-atom positions from second-moment relations *via* assumptions regarding the disposition of the hydrogen atoms.

Quadrupole Couplings

Quadrupole hyperfine structure of the rotational spectrum can be predicted in a satisfactory manner by a first-order correction to the rigid-rotor Hamiltonian. Quadrupole effects of the boron nuclei result only in broadening of the low J transitions. Because the lowest observable frequencies correspond to $2 \rightarrow 3$ transitions, even the observable quadrupole splittings due to the chlorine nuclei are not great and consequently the coupling constants can be determined only to within a few per cent. The coupling constants shown in Table II were determined by analysis of the splittings of several low J transitions. It is observed that the ratio of ^{35}Cl to ^{37}Cl coupling constants is the same as the literature value of 1.278 to within the quoted limits of error. As nearly as can be determined, the asymmetry parameter

$$\eta = \frac{\chi_{\beta\beta} - \chi_{\gamma\gamma}}{\chi_{\alpha\alpha}}$$

is zero, where (α, β, γ) is the principal quadrupolar axis system. The principal inertial a axis is coincident with the B–Cl bond direction as is also the principal α axis.

Hence only $\chi_{\alpha\alpha}$ can be determined independently. The β and γ directions are ambiguous but this fact is of no quantitative consequence since $\eta = 0$ implies $\chi_{\beta\beta} = \chi_{\gamma\gamma} = -\frac{1}{2}\chi_{\alpha\alpha}$ and the β and γ axes are equivalent in the magnitude of any interaction.

Discussion

The derived structure shown in Figure 1 indicates some minor deviations from other carborane parameters that have been determined to date. The B–B bond lengths exhibit a slight asymmetry which is outside the experimental error, and the shorter B_2–B_3 distance is among the shortest B–B bond lengths that have been determined. Of particular interest is the marked shortening of the B–B distances in $C_2B_4H_5Cl$ compared to that in B-methyldicarba-*closo*-pentaborane(5), C_2B_3-$H_4(CH_3)$.[6] The long B–B bonds in the latter compound are not retained in the C_2B_4 structure, indicating that any bond strain in the trigonal bipyramid has disappeared in the octahedral structure. Bond lengths are comparable to those in $2,3\text{-}C_2B_4H_6$.[4]

The B–Cl distance observed here is essentially equal to the sum of single-bond radii and is considerably longer than is observed in the boron halides and related compounds, as shown in Table V. The bond length is

TABLE V
BOND LENGTHS IN BORON–CHLORINE COMPOUNDS

Compd	r_{B-B}, Å	r_{B-Cl}, Å	Ref
BCl_3		1.75	a
$[HN \cdot BCl]_3$		1.754	b
$[BCl_2 \cdot N(CH_3)_2]_2$		1.825, 1.835	c
$m\text{-}B_{10}Cl_{10}C_2H_2$	1.69–1.81	1.794–1.84	d
$1,6\text{-}C_2B_4H_5Cl$	1.67, 1.70	1.82	

a M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 195 (1957). *b* D. L. Coursen and J. L. Hoard, *J. Amer. Chem. Soc.*, **74**, 1742 (1952). *c* See ref 7. *d* J. A. Potenza and W. N. Lipscomb, *Proc. Nat. Acad. Sci., U. S.*, **56**, 1917 (1966).

comparable, however, to that in dimethylaminoboron dichloride, where the boron atoms are four-coordinate and involved in a strained four-membered ring.[7]

The features of the quadrupole coupling are interesting and somewhat puzzling. The ^{35}Cl coupling constant of 49.7 MHz with a zero-asymmetry parameter is comparable to that in $m\text{-}B_{10}Cl_{10}C_2H_2$[8] and higher than in simpler boron–chlorine compounds,[8,9] where a value of 40 MHz is typical.

The chlorine coupling constant information and bond length data provide a basis for some discussion concerning the nature of the bonding in the carborane structure. The zero-asymmetry parameter and long bond length are evidence that little or no π bonding occurs between boron and chlorine in these compounds. The coupling constants are larger than in "normal" three- and four-coordinate boron structures and indicates that either the chlorine bonding orbital possesses less s character or the B–Cl bond is somewhat less ionic in the carboranes. However, this is not supported by the bond length values. This dilemma may be explained if it is noted that the hybridization scheme of the boron atom affects the B–Cl bond length but has little effect on chlorine coupling constant. Presumably the greater

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portion of the boron s orbital is required in the cage bonding so that the orbital presented to the chlorine atom is predominantly of p character, and this allows a longer bond length than is afforded by sp^3 or sp^2 hybridization. The larger coupling constant is then due either to slightly less ionic character of the bond or a shift in hybridization of chlorine orbitals toward inclusion of less s character. That the boron s orbitals are usurped by the cage structure may be more pronounced in a chlorocarborane than in the parent car-

borane, as indicated by the shortened B–B bonds adjacent to the chlorine atom in the present case.

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Nature of the Donor–Acceptor Interaction in Boron Trihalide Complexes. Vibrational Spectra and Vibrational Analysis of Acetonitrile–Boron Trichloride and Acetonitrile–Boron Tribromide

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Infrared and Raman spectral data in the 4000–70-cm^{-1} region are reported for polycrystalline samples of Cl$_3$B·NCCH$_3$ and Br$_3$B·NCCH$_3$ at $-196°$. These data include five isotope species of each compound. In addition, Raman polarization data are presented for Cl$_3$B·NCCH$_3$ in nitromethane solution. Normal-coordinate vibrational analyses based on constrained valence force fields show that the B–N stretching force constants follow the order F$_3$B·NCCH$_3$ < Cl$_3$B·NCCH$_3$ ~ Br$_3$B·NCCH$_3$ (k(BN) = 2.5, 3.4, and 3.5 mdyn/Å, respectively). As with previous structural data, the force constants indicate a significantly stronger donor–acceptor bond for BCl$_3$ than for BF$_3$. These results require the abandonment of reorganization energy differences as the sole explanation of relative boron halide acidities. Alternate descriptions of the bonding were explored by CNDO/2 molecular orbital calculations on BF$_3$ and BCl$_3$. These calculations indicate that BCl$_3$ may have a higher electron affinity than BF$_3$.

Introduction

It is well known that the acidity of the boron halides, as judged by either free energy or heat of reaction, follows the order BF$_3$ < BCl$_3$ $\lesssim$ BBr$_3$.[3] This trend is the opposite of that expected from electronegativity arguments, and the explanation generally offered is that the energy necessary to reorganize the planar boron halide to the pyramidal form is more important than inductive effects. Estimates of this reorganization energy along with the thermochemical data on complex formation lead to the conclusion that the boron–donor bond strength follows the order expected from electronegativities: BF$_3$ > BCl$_3$ > BBr$_3$.[4]

In contrast to the estimates of the nitrogen–boron donor–acceptor energies,[4] it was recently shown that BCl$_3$ forms a shorter and presumably stronger B–N bond with acetonitrile than does BF$_3$.[5] The present work was designed to check further the degree of B–N interaction by means of B–N force constant determinations.

Experimental Section

Infrared Spectra.—Calibrations of the Beckman IR-9 and

IR-11 instruments employed in this work were checked with water and CO$_2$ bands and found to be within ± 1.0 cm^{-1}. Spectra were collected at low temperatures[6] on samples which were annealed at *ca.* 0° or lower. The annealing was not performed at room temperature in order to avoid reaction with the KBr window material used for infrared-cell windows in the 4000–400-cm^{-1} region.

Raman Spectra.—The Raman data were collected with Spex 1400-II double monochromator and photon rate detection circuitry.[7] Data for Cl$_3$B·NCCH$_3$ were obtained with 6328-Å He-Ne laser excitation (Spectra Physics Model 125); while for Br$_3$B·NCCH$_3$ a more powerful Ar ion laser (Coherent Radiation Model 52) was employed at 5145 Å. The annealed solids were observed in a simple low-temperature cell.[8] Solutions of Cl$_3$-BNCCH$_3$ were contained in an evacuable cell,[6] and depolarization ratios were calculated from peak areas.

In an attempt to obtain polarization data for Br$_3$B·NCCH$_3$, the Raman spectrum was run for acetonitrile solutions. However, peak positions did not correspond to those of the pure solid, and the background gradually increased as the solution developed a yellow color. Apparently BBr$_3$ undergoes a drastic reaction with liquid acetonitrile; however we could find no evidence for the presence of BBr$_4^-$ in this solution.[9]

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