

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

The Molecular and Crystal Structure of Tetramethylammonium 1,6,8-Trichloroheptaahydro-*closo*-decaborate(2-)

BY F. E. SCARBROUGH AND W. N. LIPSCOMB*

Received March 30, 1971

The anion of the formula $[N(CH_3)_4]_2[B_{10}H_7Cl_3]$, tetramethylammonium 1,6,8-trichloroheptaahydro-*closo*-decaborate(2-), has C_{2v} symmetry, with the three chlorines attached to one apical boron and two opposite equatorial borons which are nearest the other apical boron. The B_{10} cage shows no large distortion from the D_{4d} symmetry. The molecular packing is monoclinic with eight molecules in a unit cell of dimensions $a = 13.75$, $b = 18.01$, $c = 18.35$ Å, and $\beta = 90.89^\circ$. The space group symmetry is $P2_1/n$. Direct methods-symbolic addition was used to phase initially 305 of 2270 independent, nonzero reflections which were subsequently refined to an R factor of 0.12.

Introduction

The $B_{10}H_{10}^{2-}$ anion forms an interesting series of substitution derivatives^{1,2} of the type $B_{10}H_{10-n}X_n^{2-}$, where $0 \leq n \leq 10$ and $X = F, Cl, Br, \text{ or } I$. Reaction of $K_2B_{10}H_{10}$ with excess $FeCl_3$ yields, as one product, the $B_{10}H_7Cl_3^{2-}$ ion.³ For a species of type $B_{10}H_7X_3^{2-}$ there are theoretically 16 possible isomers, if d and l pairs are counted separately (12 if they are not). Under conditions where the transition state is dominated by the initial ground-state charge distribution, LCAO-MO⁴⁻⁷ calculations indicate that sequential electrophilic substitution would yield the 1,2,10 isomer (see Figure 1 for the numbering scheme), in which the two apical hydrogens would be replaced first and second with the third chlorine going into any one of the remaining eight, chemically equivalent equatorial positions. The ¹¹B nmr,³ however, indicates that only one apex is substituted and thus questions this simplest picture of the reaction. In order to establish with certainty the positions of halogenation, we have carried out a determination of the structure of the tetramethylammonium salt of $B_{10}H_7Cl_3^{2-}$.

Experimental Section

Needlelike crystals of $[N(CH_3)_4]_2[B_{10}H_7Cl_3]$ were obtained by slow recrystallization of the compound from acetonitrile-water solutions. The quality of these crystals was poor, as indicated by an abnormal decline of diffraction intensities with increasing angle of scattering of Cu K α radiation. Hence, high accuracy of the final structure is not to be expected. Reciprocal lattice symmetry of C_{2h} and systematic absences of $h0l$ for $h + l$ odd and $0k0$ for k odd indicated that the space group is $P2_1/n$. Unit cell parameters of $a = 13.751 \pm 0.004$, $b = 18.014 \pm 0.006$, $c = 18.353 \pm 0.007$ Å, and $\beta = 90.89 \pm 0.05^\circ$ were determined from Weissenberg Cu K α photographs which had been calibrated by superposition of a powder diffraction pattern of Al. To obtain these parameters a least-squares procedure minimizing

$$\sum_{n=1}^N w_n (\sin^2 \theta_{\text{obsd}} - \sin^2 \theta_{\text{calcd}})^2 / (\lambda_n^2)^2$$

was used, where the weights $w_n = 1/\sin^2 \theta_{\text{obsd}}$ and $N = 60$ reflections. Assuming $Z = 8$, eight molecules in the unit cell, a den-

sity of 1.080 g/cm³ was calculated, which agrees reasonably well with an experimental density of 1.093 g/cm³ determined by flotation in a mixture of bromobenzene and *m*-xylene. Thus there are two molecules in the asymmetric unit, and no molecular symmetry is imposed by the space group.

Intensity data were collected on two Supper-Pace automated diffractometers with the use of Cu K α radiation (Ni filter) and a Xe proportional counter. The scan interval was $2.0 + 0.6/L$ degrees where L is the Lorentz factor for each reflection, the scan rate was $2^\circ/\text{min}$, and the background was counted before and after the scan for 0.25 times the scan time. A check reflection was monitored after every 15 observations, and 12 zero-level reflections were checked before each level of data. These check tapes revealed that certain, high $\sin \theta$ reflections decayed slowly in the X-ray beam, thereby necessitating the use of several crystals during data collection. After about 72 hr of exposure to X-rays, the decaying check reflections dropped to the arbitrarily set minimum intensity of 0.85 times the original. Data were collected from a total of eight crystals.

Preliminary film investigations indicated that data could only be observed to a value of about 40° . Therefore only reflections with $\theta \leq 45^\circ$ were collected. X-Ray data were collected on a Supper-Pace version of the Buerger automated diffractometer, with the use of equinclination Weissenberg geometry. Levels Hkl for $0 \leq H \leq 12$ were collected from crystals, $0.5 \times 0.2 \times 0.2$ mm, with the needle axis (a axis) mounted along the spindle axis. On the second diffractometer, cut crystals, $0.3 \times 0.2 \times 0.2$ mm, mounted perpendicular to the needle axis were used to collect levels hKl including $0 \leq K \leq 14$. For crystals mounted on nonneedle axes, an empirical absorption curve was determined by monitoring an axial reflection through 360° rotation. This absorption correction was applied to each reflection taken from the particular crystal. Absorption corrections were not made in the data taken when the crystal was rotated about the needle axis, in view of the relatively small angular range for all data.

A total of 4749 intensities were measured. An estimated error in each measurement was calculated from the expression⁸

$$\sigma(I) = [C_T + 0.25(t_o/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where C_T is the total peak count obtained in scan time t_o , B_1 and B_2 are the two background counts each obtained in time t_b , and $I = C_T - 0.5(t_o/t_b)(B_1 + B_2)$. The value of p was taken as 0.05. A standard deviation in each F was then calculated from the expression $\sigma(F) = [F^2 + \sigma(F^2)]^{1/2} - |F|$, where F^2 is the intensity corrected for Lorentz-polarization factors. Those small reflections for which $|F| \leq 3\sigma(F)$ were considered unobserved and were therefore removed from the data. Also reflections for which the background was asymmetric by more than a factor of 2 were eliminated. After these two procedures were applied, a total of 3695 intensity measurements remained before correlations were used to reduce the list to the independent reflections.

After corrections mentioned above, for Lorentz and polarization factors, the data were correlated by a least-squares procedure in which the function⁹

(8) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(9) P. Simpson, Ph.D. Thesis, Harvard University, 1963.

(1) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S. A.*, **48**, 729 (1962).

(2) W. H. Knoth, D. C. England, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **84**, 1056 (1962).

(3) A. Kaczmarczyk, private communication.

(4) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, pp 100-105.

(5) E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(6) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962).

(7) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 520 (1962).

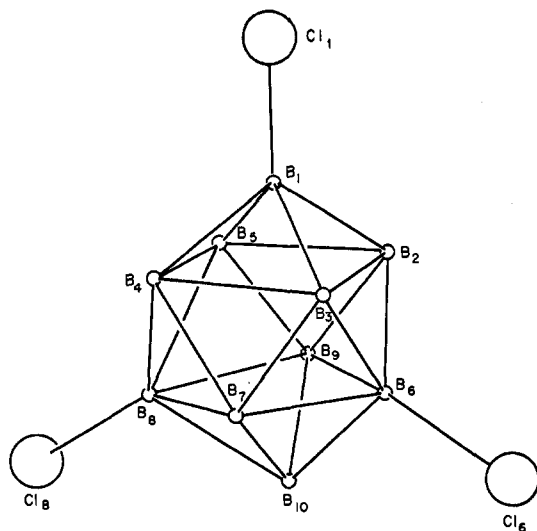


Figure 1.

$$R = \sum_{hij, i \neq j} w_{hij} [\ln (s_i F_{hi}^2) - \ln (s_j F_{hj}^2)]^2$$

was minimized, where s_i is the scale factor for the i th data set, F_{hi}^2 is the corrected measurement of reflection h on set i , $w_{hij} = (\sigma_{hi}^2 + \sigma_{hj}^2)^{-1}$, and σ_{hi} is the statistical error in F_{hi}^2 . The correlation factor, after correction for the scale factor

$$R_c = \sum_h |F_{hi}^2 - F_{hj}^2| / \sum_h |F_{hi}^2 + F_{hj}^2|$$

is 0.104 for these data. There were, finally, 2159 independent, nonzero reflections of which 219 had been assigned zero weight because of their small values as noted above.

Structure Determination

After a lengthy attempt to unravel the structure using Patterson maps, the phase problem was solved with direct methods using symbolic addition.¹⁰ First, the normalized structure factors

$$E_{hkl}^2 = F_{hkl}^2 \left[\epsilon \sum_{i=1}^N f_i^2(hkl) \right]^{-1}$$

were calculated for all reflections, where F_{hkl}^2 has been corrected for thermal motion, $\epsilon = 2$ for $0k0$ and $h0l$, and $\epsilon = 1$ for all other reflections in the $P2_1/n$ space group (Table I). The sum of f_i^2 's

TABLE I
EXPERIMENTAL AND THEORETICAL^a VALUES OF
NORMALIZED STRUCTURE FACTORS

	Obsd	Theoret
$\langle E \rangle$	0.829	0.798
$\langle E^2 - 1 \rangle$	0.032	0.000
$\langle E^2 - 1 \rangle$	0.980	0.968

^a For structures with randomly distributed atoms.

extends over the $N = 432$ atoms in the unit cell. Second, three of the larger E_{hkl} 's which are linearly independent were assigned positive phases in order to fix the origin. Two additional reflections, selected on the basis that they had many relationships applicable to eq 1, where s indicates the sign of $E_h = E_{hkl}$ and

$$sE_h \approx s \sum_k E_k E_{h-k} \quad (1)$$

$E_k = E_{h'k'l'}$, among themselves and the origin-specifying reflections, were assigned symbols a and b . In the present study reflections 126, 638, and $\bar{1}, 10, 1$ fixed the origin while 497 and 064 were assigned a and b , respectively. Equation 1 was applied, by hand, to the 101 reflections with $E \geq 1.95$. The symbols were carried throughout the procedure, but there were many indications that a should be negative and b positive. When these assignments were made, there were only three contradictions in the 1159 terms of eq 1 generated by these 101 reflections.

(10) J. Karle and I. L. Karle, *Acta Crystallogr.*, **16**, 969 (1963).

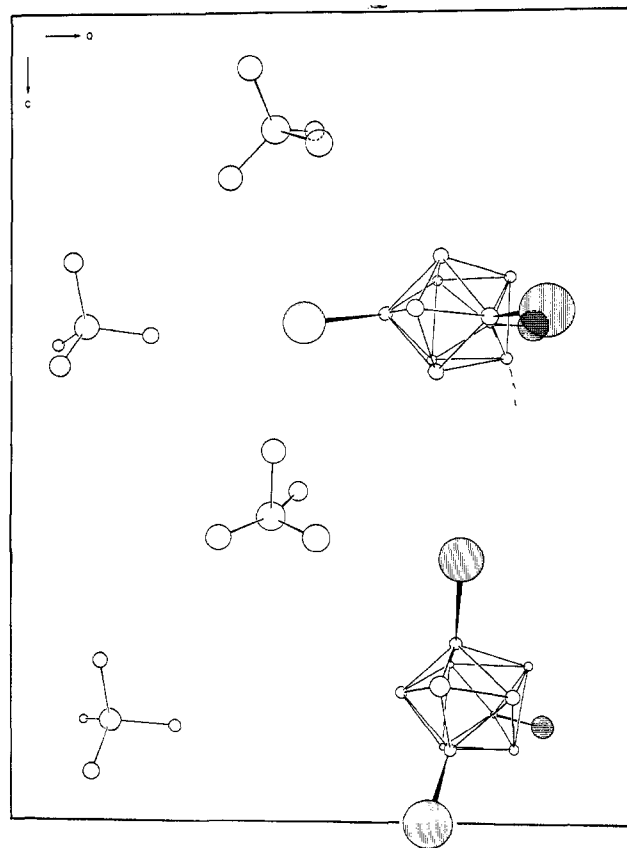


Figure 2.

Therefore, 98 signed reflections were used as a starting set in our IBM 7094 program *FAZE* which extended the phasing to the 307 reflections with $E \geq 1.30$ by use of the tangent formula. This procedure phased 305 reflections with an R_E factor¹¹

$$R_E = \sum ||E_o| - |E_c|| / \sum |E_o|$$

of 0.27 and a consistency index

$$C = \sum E_o (1 - \langle \phi \rangle^2) / \sum E_o$$

where $\langle \phi \rangle$ is the average of all determinations of the given reflection, taken as a unit vector, of 0.241. A comparison of the phases of the 305 reflections after the structure was completed showed that three signs had changed.

As an aside, we note that the most probable set of phases for the 171 reflections with the largest E_{hkl} values produced by application of Sayre's method¹² with the use of a modified form of Long's program¹³ (*REL*) agreed with the signs determined by the symbolic addition procedure in all but three cases, when the same origin-determining reflections were used. Although the signs for this program yielded an E map with six chlorine peaks, they did not give a refinable structure, possibly due to the limited number of reflections which were phased (<8% of the total).

An E map computed with the 305 phased E 's yielded six large peaks that were readily interpretable as the chlorine atoms in the asymmetric unit. Incomplete cage and cation structures were also visible. The six chlorines, using a Wilson temperature factor of 5.9 \AA^2 , gave a value of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.50$ for all 2159 reflections before refinement. Comparison of a Fourier map, computed with the chlorines as the phasing model, with the E map gave the locations of all boron and nitrogen atoms and 12 of the 16 carbons. Using this nearly complete model, another Fourier map was computed and all peaks were tentatively located. When a single isotropic temperature factor was applied to all atoms, this structure gave an R factor of 0.32. A difference Fourier map indicated large anisotropy associated with the chlorine atoms. Block-matrix least-squares refinement of the scale factor, all atomic coordinates, anisotropic thermal parameters

(11) J. Karle and I. L. Karle, *ibid.*, **21**, 849 (1966).

(12) D. Sayre, *ibid.*, **6**, 60 (1962).

(13) R. E. Long, Ph.D. Thesis, Part III, University of California in Los Angeles, 1965.

for the chlorines, and isotropic thermal parameters for all other atoms gave an R factor of 0.21. Three cycles of full-matrix least-squares refinement of all atomic coordinates and anisotropic thermal parameters for all atoms then yielded an R value of 0.14.

A plot of F_o/F_c vs. I_c for the more intense reflections indicated that secondary extinction might be a factor. We then applied to all data a correction of¹⁴

$$|F_c| = |F_o| [1 + gI_c]$$

where g was determined to be 4.06×10^{-6} by least-squares methods. A difference electron density map yielded indications of all hydrogens of the boron cages, but the locations of these peaks were unreliable. Hence, we assumed that all B-H distances were 1.1 Å and assigned all hydrogen atoms a single isotropic thermal parameter of 9 \AA^2 . At this stage the value of R was 0.13.

In an attempt to improve atomic bond distances, a final full-matrix least-squares refinement of atomic coordinates only yielded $R = 0.127$. A difference map then indicated diffuse electron density suggesting that hydrogen atoms of the methyl groups were either randomly oriented or were rotating. Corrections were made starting from the expression for the contribution to the structure factor, F_{hkl} , from a circularly disordered atom¹⁵

$$F_{hkl} = f e^{-2\pi i \bar{h} \cdot \bar{r}} J_0(k)$$

where f is the scattering factor of the atoms in the disorder, \bar{h} is the reciprocal lattice vector, \bar{r} is the vector from the origin to the center of the disorder, and $J_0(k)$ is the zero-order Bessel function. The quantity k is defined¹⁶ in terms of unit cell dimensions and indices

$$k = (2\pi x/d) \left[1 - \frac{(n_1 h_1 + n_2 h_2 + n_3 h_3)^2}{|\bar{h}|^2 |\bar{n}|^2} \right]^{1/2}$$

where x is the radius of the disorder, d the interplanar spacing $d = \lambda/2 \sin \theta$, and \bar{n} the vector normal to the plane of rotation. For each reflection, contributions from the 64 rotating methyl groups in the unit cell were calculated and added to F_{calcd} . No thermal parameters or coordinates of rotation centroids were varied in the least-squares procedure. Here, the R factor fell only to 0.125, which is not a significant improvement. As a function of intensity, the value of R is 0.35 for the smallest reflections (10% of the total) and falls smoothly to 0.09 for the largest 10% of the reflections. Further results are given in Table II, coordinates are in Table III, and anisotropic thermal

TABLE II
DISAGREEMENT FACTOR^a BASED ON F

$\rho = (\sin^2 \theta)/\lambda^2$	No. of reflections	R factor
0.000-0.013	50	0.13
0.013-0.026	91	0.09
0.027-0.040	118	0.10
0.040-0.053	139	0.10
0.053-0.066	142	0.11
0.066-0.079	165	0.09
0.079-0.092	151	0.11
0.092-0.105	171	0.13
0.106-0.119	176	0.13
0.119-0.132	177	0.13
0.132-0.145	189	0.14
0.145-0.158	161	0.17
0.158-0.171	137	0.17
0.172-0.185	73	0.23

Class	$R(hkl)$	Class	$R(hkl)$
All	0.12	$K + L = 2N$	0.12
$H = 2N$	0.12	$K + L = 2N + 1$	0.12
$H = 2N + 1$	0.12	$L + H = 2N$	0.11
$K = 2N$	0.13	$L + H = 2N + 1$	0.13
$K = 2N + 1$	0.12	$H + K = 2N$	0.12
$L = 2N$	0.13	$H + K = 2N + 1$	0.12
$L = 2N + 1$	0.12	$H + K + L = 2N$	0.13
		$H + K + L = 2N + 1$	0.12

^a $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.118$; $wR = \text{weighted } R \text{ factor} = [\sum w|F_o|^2 - F_c^2]^{1/2} / [\sum w|F_o|^2]^{1/2} = 0.072$ for structures including disordered tetramethylammonium. With disorder removed, $R = 0.125$ and $wR = 0.074$.

(14) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 412.

(15) W. H. Zachariasen, "Theory of X-Ray Diffraction in Crystals," Wiley, New York, N. Y., 1945, p 223.

(16) H. W. Smith, Ph.D. Thesis, Harvard University, 1965.

TABLE III
FRACTIONAL COORDINATES^a WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
B-1 ₁	0.8155 (18)	-0.0070 (11)	0.8645 (13)
B-2 ₁	0.8291 (21)	0.0749 (13)	0.9079 (11)
B-3 ₁	0.7119 (19)	0.0284 (13)	0.9036 (12)
B-4 ₁	0.7272 (19)	0.0173 (14)	0.8037 (12)
B-5 ₁	0.8521 (18)	0.0626 (12)	0.8057 (11)
B-6 ₁	0.7279 (23)	0.1260 (12)	0.9085 (13)
B-7 ₁	0.6497 (22)	0.0851 (15)	0.8385 (12)
B-8 ₁	0.7347 (21)	0.1106 (10)	0.7775 (12)
B-9 ₁	0.8281 (19)	0.1509 (13)	0.8442 (12)
B-10 ₁	0.7090 (21)	0.1732 (12)	0.8316 (14)
Cl-1 ₁	0.8740 (4)	-0.0984 (3)	0.8794 (3)
Cl-6 ₁	0.6939 (6)	0.1700 (3)	1.0005 (3)
Cl-8 ₁	0.7435 (5)	0.1257 (3)	0.6728 (3)
H-2 ₁	0.901	0.007	0.945
H-3 ₁	0.675	-0.006	0.954
H-4 ₁	0.693	-0.027	0.759
H-5 ₁	0.923	0.069	0.768
H-7 ₁	0.554	0.078	0.829
H-9 ₁	0.882	0.202	0.856
H-10 ₁	0.625	0.198	0.816
B-1 ₂	0.7847 (14)	0.0250 (13)	0.3858 (10)
B-2 ₂	0.6924 (15)	0.0592 (11)	0.4292 (11)
B-3 ₂	0.6988 (17)	0.0486 (13)	0.3306 (12)
B-4 ₂	0.8143 (15)	0.1006 (12)	0.3270 (11)
B-5 ₂	0.8105 (15)	0.1114 (11)	0.4280 (10)
B-6 ₂	0.6170 (19)	0.1194 (14)	0.3721 (13)
B-7 ₂	0.7040 (16)	0.1471 (13)	0.3000 (14)
B-8 ₂	0.7830 (20)	0.1877 (11)	0.3760 (13)
B-9 ₂	0.6981 (17)	0.1582 (13)	0.4440 (11)
B-10 ₂	0.6642 (23)	0.2056 (14)	0.3657 (16)
Cl-1 ₂	0.8525 (4)	-0.0612 (3)	0.3879 (3)
Cl-6 ₂	0.4866 (4)	0.0991 (3)	0.3704 (3)
Cl-8 ₂	0.8732 (4)	0.2630 (3)	0.3682 (3)
H-2 ₂	0.862	0.094	0.479
H-3 ₂	0.651	0.010	0.460
H-4 ₂	0.658	0.012	0.283
H-5 ₂	0.879	0.104	0.283
H-7 ₂	0.672	0.196	0.495
H-9 ₂	0.692	0.177	0.243
H-10 ₂	0.579	0.229	0.366
N-1	0.4340 (12)	0.1965 (9)	0.1441 (9)
C-1 ₁	0.3917 (21)	0.2093 (16)	0.0691 (12)
C-2 ₁	0.4963 (18)	0.1215 (11)	0.1474 (13)
C-3 ₁	0.3635 (19)	0.1940 (14)	0.2047 (14)
C-4 ₁	0.5046 (19)	0.2613 (14)	0.1577 (19)
N-2	0.1335 (11)	0.0944 (8)	0.3888 (7)
C-1 ₂	0.1087 (14)	0.1106 (10)	0.3097 (8)
C-2 ₂	0.2382 (14)	0.0930 (12)	0.3978 (10)
C-3 ₂	0.0889 (19)	0.0209 (10)	0.4120 (12)
C-4 ₂	0.0915 (17)	0.1539 (11)	0.4377 (10)
N-3	0.4386 (14)	0.1858 (10)	0.6227 (11)
C-1 ₃	0.4419 (57)	0.2037 (54)	0.5412 (36)
C-2 ₃	0.4836 (29)	0.1169 (20)	0.5897 (20)
C-3 ₃	0.3543 (24)	0.1971 (25)	0.6495 (23)
C-4 ₃	0.5098 (26)	0.2381 (18)	0.6492 (23)
C-5 ₃ ^b	0.4587 (36)	0.1217 (32)	0.6903 (24)
N-4	0.1814 (12)	0.0428 (8)	0.8745 (8)
C-1 ₄	0.1632 (20)	0.0822 (12)	0.8025 (11)
C-2 ₄	0.1513 (17)	0.0896 (13)	0.9384 (11)
C-3 ₄	0.2855 (18)	0.0289 (16)	0.8815 (12)
C-4 ₄	0.1388 (22)	-0.0335 (13)	0.8741 (14)

^a Coordinates are given so that all atoms refer to the same molecule. ^b Carbon C-5₃ is the disorder peak from the difference Fourier.

parameters are in Table IV. The list of observed and calculated structure factors has been deposited elsewhere.¹⁷

The properly numbered¹⁸ anion is shown in Figure 1, without the hydrogens attached to the unsubstituted borons. Figure 2

(17) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(18) *Inorg. Chem.*, **7**, 1945 (1968).

TABLE IV
 ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$)^a
 WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B-1 ₁	14.6 (3)	4.9 (1)	8.6 (1)	-4.1 (3)	-12.3 (4)	0.9 (3)
B-2 ₁	21.5 (4)	6.7 (1)	4.8 (1)	-7.8 (4)	-0.1 (3)	-0.1 (2)
B-3 ₁	14.9 (3)	5.7 (1)	7.9 (1)	5.7 (3)	-4.5 (3)	-1.4 (2)
B-4 ₁	14.7 (2)	7.1 (1)	6.9 (1)	-0.3 (3)	-5.1 (3)	2.6 (2)
B-5 ₁	14.5 (2)	6.6 (1)	6.4 (1)	-6.3 (3)	-6.7 (3)	-1.4 (2)
B-6 ₁	23.3 (3)	4.9 (2)	7.2 (1)	6.2 (4)	-11.6 (4)	-2.2 (2)
B-7 ₁	21.5 (4)	7.8 (2)	5.8 (1)	4.6 (4)	-7.4 (3)	-1.7 (2)
B-8 ₁	22.1 (3)	3.9 (1)	7.2 (2)	2.0 (3)	-18.2 (4)	3.7 (2)
B-9 ₁	15.4 (4)	7.0 (2)	6.6 (1)	-8.3 (4)	4.6 (4)	1.1 (2)
B-10 ₁	19.5 (3)	4.1 (1)	8.8 (1)	3.6 (3)	-1.8 (3)	-1.5 (2)
Cl-1 ₁	19.8 (1)	6.3 (1)	7.5 (1)	10.9 (1)	-9.5 (1)	-0.3 (1)
Cl-6 ₁	28.9 (1)	6.9 (1)	7.4 (1)	7.6 (1)	-7.0 (1)	-2.6 (1)
Cl-8 ₁	21.1 (1)	5.8 (1)	6.9 (1)	1.2 (1)	-9.5 (1)	0.8 (1)
B-1 ₂	7.0 (2)	8.7 (1)	5.4 (1)	-2.5 (3)	-7.0 (3)	-0.4 (2)
B-2 ₂	7.9 (3)	5.9 (1)	7.0 (1)	-0.1 (3)	-7.3 (3)	-0.5 (2)
B-3 ₂	10.3 (2)	7.0 (1)	7.4 (1)	1.4 (3)	-2.9 (3)	0.8 (2)
B-4 ₂	9.4 (2)	7.4 (1)	6.2 (1)	-2.9 (3)	-9.6 (2)	1.1 (2)
B-5 ₂	10.0 (3)	6.6 (1)	5.4 (1)	-5.2 (3)	-4.6 (2)	0.3 (2)
B-6 ₂	13.7 (4)	9.0 (2)	6.9 (1)	-5.5 (4)	-10.2 (4)	4.3 (2)
B-7 ₂	9.4 (2)	6.4 (1)	10.7 (2)	5.1 (3)	-13.4 (3)	0.6 (3)
B-8 ₂	19.6 (3)	4.4 (1)	8.6 (1)	-7.9 (3)	-12.7 (3)	3.4 (2)
B-9 ₂	11.7 (3)	8.4 (1)	5.8 (1)	-4.2 (3)	-4.3 (3)	-0.7 (2)
B-10 ₂	19.0 (4)	7.6 (2)	10.1 (2)	-6.9 (4)	-16.8 (4)	3.1 (3)
Cl-1 ₂	17.4 (1)	5.4 (1)	8.2 (1)	-0.1 (1)	-12.0 (1)	-0.2 (1)
Cl-6 ₂	11.7 (1)	8.6 (1)	9.8 (1)	-0.1 (1)	-8.3 (1)	-0.2 (1)
Cl-8 ₂	14.1 (1)	5.6 (1)	10.3 (1)	2.7 (1)	-11.6 (1)	-3.3 (1)
N-1	12.7 (1)	7.8 (1)	7.9 (1)	-1.7 (2)	-3.5 (1)	-0.9 (1)
C-1 ₁	22.5 (2)	13.8 (2)	7.5 (1)	-0.0 (3)	-10.6 (2)	0.7 (2)
C-2 ₁	17.3 (2)	6.9 (1)	11.2 (1)	2.6 (2)	-8.2 (3)	-1.4 (2)
C-3 ₁	16.1 (2)	10.1 (1)	11.0 (1)	4.9 (3)	-2.7 (3)	4.4 (2)
C-4 ₁	12.4 (2)	8.1 (1)	22.5 (2)	5.9 (3)	-6.0 (3)	2.1 (3)
N-2	11.3 (1)	6.2 (1)	6.4 (1)	-3.9 (1)	-3.8 (1)	-0.4 (1)
C-1 ₂	13.0 (2)	9.7 (1)	4.3 (1)	3.7 (2)	-7.4 (2)	1.1 (1)
C-2 ₂	9.6 (2)	9.6 (1)	8.1 (1)	-0.1 (2)	-3.2 (2)	-3.8 (2)
C-3 ₂	21.6 (3)	5.6 (1)	11.3 (1)	-12.2 (2)	-7.6 (3)	2.3 (1)
C-4 ₂	18.4 (2)	6.9 (1)	6.7 (1)	2.0 (2)	-3.5 (2)	-1.6 (1)
N-3	13.9 (1)	7.2 (1)	14.0 (1)	1.3 (2)	3.5 (2)	-5.3 (1)
C-1 ₃	45.7 (10)	39.9 (9)	15.8 (4)	8.7 (13)	9.0 (9)	22.3 (8)
C-2 ₃	29.1 (5)	13.2 (2)	16.2 (2)	-9.3 (4)	5.4 (5)	-6.3 (3)
C-3 ₃	13.8 (3)	20.8 (3)	22.9 (3)	-0.7 (4)	20.7 (5)	-3.6 (5)
C-4 ₃	24.9 (4)	12.7 (2)	26.4 (3)	-25.7 (4)	-8.4 (5)	-7.0 (4)
C-5 ₃	18.8 (5)	18.8 (4)	9.5 (4)	10.3 (6)	6.7 (6)	15.0 (5)
N-4	13.2 (1)	6.3 (1)	8.5 (1)	1.0 (2)	-3.7 (2)	0.5 (1)
C-1 ₄	24.2 (2)	8.6 (1)	6.6 (1)	6.7 (3)	-5.8 (2)	5.6 (1)
C-2 ₄	16.5 (2)	8.8 (1)	8.2 (1)	4.1 (3)	2.5 (2)	-0.7 (2)
C-3 ₄	15.2 (2)	14.8 (2)	8.3 (1)	4.3 (3)	2.9 (2)	0.1 (2)
C-4 ₄	28.3 (3)	8.0 (1)	11.9 (1)	-16.1 (3)	-7.2 (3)	2.7 (2)

^a Anisotropic temperature factors are calculated by the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

 TABLE V
 COMPLETE BOND DISTANCES (Å) WITH
 STANDARD DEVIATIONS IN PARENTHESES^a

	Molecule 1	Molecule 2
B _a -B _e		
B-1-B-2	1.69 (3)	1.60 (3)
B-1-B-3	1.72 (3)	1.79 (3)
B-1-B-4	1.69 (3)	1.77 (3)
B-1-B-5	1.73 (3)	1.63 (3)
B _a -B _{eCl}		
B-10-B-6	1.66 (3)	1.69 (3)
B-10-B-8	1.55 (3)	1.67 (4)
B _a -B _{eH}		
B-10-B-7	1.79 (4)	1.70 (4)
B-10-B-9	1.70 (4)	1.73 (4)
B _e -B _e (type 1)		
B-2-B-5	1.92 (3)	1.88 (3)
B-3-B-4	1.86 (3)	1.85 (3)
B _e -B _e (type 2)		
B-2-B-3	1.82 (4)	1.82 (3)
B-4-B-5	1.90 (4)	1.87 (3)
B _{eCl} -B _e		
B-6-B-7	1.82 (4)	1.87 (3)
B-7-B-8	1.69 (4)	1.90 (3)
B-8-B-9	1.90 (3)	1.80 (3)
B-9-B-6	1.88 (4)	1.85 (3)

TABLE V (Continued)

	Molecule 1	Molecule 2		
B _e -B _{eCl} '				
B-2-B-6	1.67 (4)	1.82 (3)		
B-3-B-6	1.77 (3)	1.87 (3)		
B-4-B-8	1.75 (3)	1.86 (3)		
B-5-B-8	1.90 (4)	1.71 (3)		
B _e -B _{eH} '				
B-3-B-7	1.78 (3)	1.86 (3)		
B-4-B-7	1.75 (4)	1.80 (3)		
B-2-B-9	1.80 (3)	1.81 (3)		
B-5-B-9	1.77 (3)	1.79 (3)		
B _a -Cl				
B-1-Cl-1	1.85 (2)	1.81 (2)		
B _e -Cl				
B-6-Cl-6	1.93 (2)	1.83 (3)		
B-8-Cl-8	1.95 (2)	1.84 (2)		
N-C Distances				
	N-1	N-2	N-3	N-4
C-1	1.50 (3)	1.51 (2)	1.53 (7)	1.52 (3)
C-2	1.60 (3)	1.45 (2)	1.52 (4)	1.51 (3)
C-3	1.49 (3)	1.52 (2)	1.28 (4)	1.46 (3)
C-4	1.54 (3)	1.52 (2)	1.44 (4)	1.49 (3)
			(1.71 (5))	

^a Standard deviations calculated from deviations in atomic coordinates. B_a is B(apical). B_e is B(equatorial).

TABLE VI
BOND SUMMARY^a

Bond	Symmetry-related bonds ^b	Mean value	Av dev ^c	Max dev	Std dev of mean ^d
1-2 B-B	1-3, 1-4, 1-5	1.70	0.05	0.10	0.02
10-6 B-B	10-8	1.64	0.04	0.09	0.03
10-7 B-B	10-9	1.72	0.03	0.06	0.02
2-6 B-B	3-6, 4-8, 5-8	1.79	0.06	0.12	0.03
3-7 B-B	4-7, 2-9, 5-9	1.79	0.02	0.06	0.01
2-5 B-B	3-4	1.87	0.02	0.04	0.01
2-3 B-B	4-5	1.85	0.03	0.04	0.02
6-7 B-B	7-8, 8-9, 6-9	1.84	0.05	0.14	0.02
1-Cl B-Cl		1.83	0.02	0.02	0.02
6-Cl B-Cl	8-Cl	1.88	0.05	0.06	0.03
N-C		1.50	0.02	0.09	0.02

^a The average deviation for boron-boron bonds is ± 0.04 Å. The average deviation for boron-chlorine bonds is ± 0.04 Å. The average deviation for nitrogen-carbon bonds is ± 0.03 Å. The average deviation for all bonds is ± 0.04 Å. ^b Assuming C_{2v} symmetry for the anion, we have averaged distances for equivalent bonds, including both molecules. ^c Average of deviations for equivalent bonds. ^d Calculated by the formula $\sigma = (\sum_{i=1}^N (D_i - \bar{D})^2)^{1/2} / (N - 1)$ where D_i are the individual bond distances, \bar{D} is the mean distance, and N is the number of equivalent bonds.

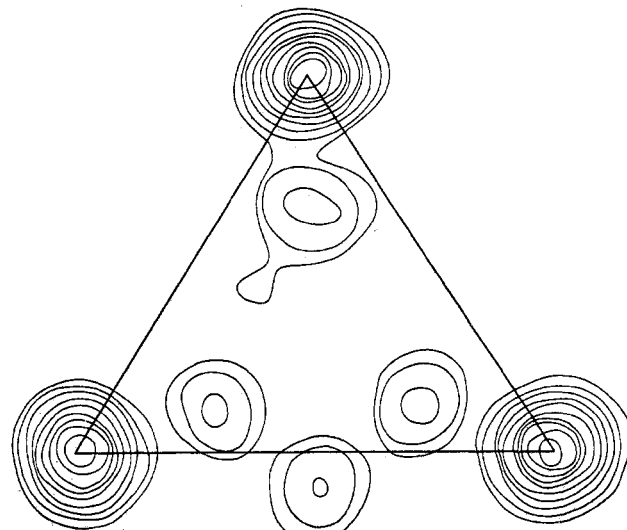


Figure 3.

TABLE VII
 COMPLETE BOND ANGLES (DEG) WITH STANDARD DEVIATIONS IN PARENTHESES^a

	Molecule 1	Molecule 2		Molecule 1	Molecule 2		
	$B_e-B_{eCl}-Cl$			$B_e-B_{eCl}-B_e$			
2-1-Cl	131.6 (1.7)	135.9 (1.5)	7-6-9	94.8 (1.6)	87.0 (1.5)		
3-1-Cl	128.8 (1.5)	128.0 (1.5)	7-8-9	98.3 (1.6)	90.4 (1.4)		
4-1-Cl	129.3 (1.5)	123.0 (1.3)		$B_e-B_e-B_{eH'}$			
5-1-Cl	127.3 (1.6)	130.1 (1.3)	4-3-7	57.4 (1.3)	57.9 (1.2)		
	$B_e-B_e'-Cl$		3-4-7	59.0 (1.3)	61.5 (1.2)		
2-6-Cl	116.5 (1.6)	116.1 (1.5)	2-5-9	58.2 (1.2)	58.9 (1.2)		
3-6-Cl	114.8 (1.5)	116.9 (1.5)	5-2-9	56.9 (1.1)	58.1 (1.1)		
4-8-Cl	114.2 (1.3)	114.9 (1.5)		$B_e-B_e-B_{eCl}'$			
5-8-Cl	105.5 (1.4)	119.4 (1.6)	2-3-6	55.3 (1.5)	59.1 (1.2)		
	$B_e'-B_e'-Cl$		3-2-6	61.0 (1.5)	61.8 (1.2)		
7-6-Cl	129.5 (2.0)	132.9 (1.6)	4-5-8	55.0 (1.2)	62.6 (1.2)		
9-6-Cl	129.8 (1.6)	131.8 (1.6)	5-4-8	62.4 (1.4)	54.7 (1.1)		
7-8-Cl	138.1 (1.8)	127.1 (1.5)		$B_e'-B_{eCl}'-B_e'$			
9-8-Cl	122.0 (1.5)	135.6 (1.5)	3-6-7	59.4 (1.3)	59.8 (1.3)		
	$B_e-B_e'-Cl$		2-6-9	60.6 (1.5)	58.9 (1.2)		
10-6-Cl	119.7 (1.6)	124.1 (1.8)	4-8-7	61.0 (1.4)	57.0 (1.1)		
10-8-Cl	123.4 (1.4)	128.4 (1.5)	5-8-9	55.7 (1.2)	61.1 (1.3)		
	$B_e-B_{eH}-B_e$			$B_e-B_{eH}'-B_{eCl}'$			
6-10-7	63.4 (1.4)	66.9 (1.5)	3-7-6	59.1 (1.3)	60.2 (1.3)		
7-10-8	60.5 (1.4)	68.7 (1.6)	4-7-8	61.1 (1.4)	60.4 (1.2)		
8-10-9	71.7 (1.7)	64.0 (1.5)	2-9-6	53.8 (1.3)	59.8 (1.2)		
9-10-6	68.1 (1.7)	65.6 (1.5)	5-9-8	61.9 (1.3)	56.9 (1.2)		
	$B_e-B_{eCl}-B_e$			$B_{eCl}'-B_e-B_{eH}'$			
2-1-3	64.3 (1.5)	68.6 (1.3)	9-2-6	65.6 (1.5)	61.4 (1.2)		
4-1-5	67.4 (1.4)	63.7 (1.2)	6-3-7	61.5 (1.4)	60.0 (1.3)		
	$B_e-B_{eCl}-B_e$		7-4-8	57.9 (1.5)	62.6 (1.3)		
	H		8-5-9	62.4 (1.3)	61.9 (1.3)		
2-1-5	68.3 (1.3)	66.8 (1.3)		$B_e-B_{eCl}'-B_e$			
3-1-4	65.8 (1.4)	65.7 (1.3)	2-6-3	63.6 (1.5)	59.2 (1.2)		
	$B_e-B_e-B_e$		4-8-5	62.7 (1.3)	62.8 (1.1)		
2-3-4	88.8 (1.5)	92.1 (1.4)		$B_e-B_{eH}'-B_e$			
3-4-5	92.9 (1.5)	88.9 (1.3)	3-7-4	63.6 (1.4)	60.6 (1.2)		
4-5-2	84.6 (1.4)	89.8 (1.2)	2-9-5	65.0 (1.3)	62.5 (1.2)		
5-2-3	93.6 (1.4)	89.2 (1.3)		$C-N-C$			
	$B_{eCl}-B_e-B_{eCl}$			Molecule 1	Molecule 2	Molecule 3	Molecule 4
8-7-6	87.2 (1.8)	87.0 (1.5)	1-N-2	111.4 (1.7)	108.8 (1.4)	77.3 (3.9)	111.9 (1.5)
6-9-8	79.6 (1.5)	90.4 (1.4)	1-N-3	116.2 (1.8)	110.5 (1.4)	110.8 (3.8)	107.8 (1.7)
			1-N-4	105.3 (1.9)	110.4 (1.4)	100.1 (3.9)	111.5 (1.6)
			2-N-3	107.5 (1.6)	109.4 (1.5)	131.7 (2.8)	107.9 (1.6)
			2-N-4	107.3 (1.7)	106.8 (1.4)	112.2 (2.3)	113.5 (1.7)
			3-N-4	107.1 (1.9)	110.9 (1.6)	112.8 (2.8)	103.1 (1.8)
			1-N-5			148.1 (4.1)	
			2-N-5			71.0 (2.3)	
			3-N-5			89.0 (2.8)	
			4-N-5			94.4 (2.6)	

^a See Table V, footnote a.

is a projection of the asymmetric unit onto the $h0l$ plane, showing the two symmetry-independent boron cages and the four tetramethylammonium cations. Atomic coordinates of Table III give the bond distances and angles of Tables V-VIII. The closest approaches between atoms of different molecules are 2.47 (methyl $H \cdots$ cage H), 3.06 (methyl $H \cdots Cl$), and 3.64 Å (cage $H \cdots Cl$). These distances indicate reasonably normal van der Waals contacts expected in a molecular crystal.

The B_{10} cage is a bicapped square antiprism as shown in previous X-ray studies.^{1,19} Three chlorines are substituted in the 1,6,8 positions, *i.e.*, at one apical boron and two opposite equatorial positions, giving the anion C_{2v} symmetry.

Careful study of the plane containing three chlorines attached to a boron cage reveals that the Cl atoms lie at the vertices of a nearly equilateral triangle. This introduces the possibility of a threefold orientational disorder of the boron cage, permuting the Cl positions. Such a disorder could conceivably be one cause for the poor quality of the data. However, a Fourier map of the

electron density computed in the plane of the three chlorines attached to one anion (Figure 3) clearly shows only one boron (B-10) outside of the boundaries of the hypothetical equilateral triangle. Electron density in equivalent regions between chlorines 1 and 6 and between 1 and 8 would be expected if the threefold disorder existed.

Even though the precision and accuracy of the molecular structure are somewhat low, the isomeric positions of the chlorines have been established conclusively. This was the main point of the study. The Cl atoms within the ion are as clearly far apart as possible, but we are unable to say, in the absence of information relating to intermediates or the activated complex, whether this substitution reaction really is governed primarily by steric factors, cooperative effects, or primarily electronic factors. The occurrence of single apical and double equatorial substitution suggests that, if steric factors are not responsible, the unknown sequential order of substitution of these three Cl atoms is associated with modification of the electronic structure of the B_{10} unit as substitution proceeds. Clearly one does not have a consistent preference for substitution at both apices before some equatorial substitution occurs, nor does one find consistent equatorial

(19) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).

TABLE VIII
ANGLE SUMMARY^a

Angle	Symmetry-related angles	Deg			Std dev of mean
		Mean value	Av dev	Max dev	
2-1-Cl	3-1-Cl, 4-1-Cl, 5-1-Cl	129.2	2.5	6.6	1.4
2-6-Cl	3-6-Cl, 4-8-Cl, 5-8-Cl	114.8	2.5	9.3	1.5
7-6-Cl	9-6-Cl, 7-8-Cl, 9-8-Cl	130.9	3.8	8.9	1.9
10-6-Cl	10-8-Cl	121.9	1.9	2.2	1.3
6-10-7	7-10-8, 8-10-9, 9-10-6	66.1	2.7	5.6	1.3
2-1-3	4-1-5	65.9	2.1	2.8	1.5
2-1-5	3-1-4	66.7	0.9	1.6	0.7
2-3-4	3-4-5, 4-5-2, 5-2-3	90.0	2.2	5.4	1.1
7-6-9	7-8-9	93.8	2.7	4.5	2.0
8-7-6	6-9-8	86.1	3.3	6.5	2.7
4-3-7	3-4-7, 2-5-9, 5-2-9	58.5	1.0	3.1	0.5
2-3-6	3-2-6, 4-5-8, 5-4-8	59.0	3.0	4.3	1.3
3-6-7	2-6-9, 4-8-7, 5-8-9	59.2	1.5	3.5	0.7
3-7-6	4-7-8, 2-9-6, 5-9-8	59.2	1.9	5.3	1.0
9-2-6	6-3-7, 7-4-8, 8-5-9	61.7	1.5	4.0	0.8
2-6-3	4-8-5	62.1	1.5	2.9	1.1
3-7-4	2-9-5	63.0	1.2	2.5	1.1
C-N-C	6 equiv bonds				
	Molecule 1	109.4	2.9	6.8	1.7
	Molecule 2	109.5	1.2	2.7	0.7
	Molecule 3	107.5	12.6	30.0	8.0
	Molecule 4	109.4	3.1	6.3	1.7

^a The average deviation of all angles (comparing symmetry-related bonds in both molecules) is 3.0°. The average deviation if the disordered tetramethylammonium is not considered is 2.2°. The average deviation of B-B-Cl angles is 2.8°; B-B-B angles, 2.0°; C-N-C angles, 4.9°; C-N-C angles if the disorder is not considered, 2.4°.

substitution here. Studies of other substituted products are desirable in order further to elucidate this sequence. The Cl atom at only one apex does indeed agree with the results of the nmr study,³ which did not yield the positions for the other two Cl atoms of this B₁₀H₇Cl₃²⁻ ion.

Comparison of the present B₁₀H₇Cl₃²⁻ ion with structures for Cu₂B₁₀H₁₀,¹⁹ the photoisomer of B₂₀H₁₈²⁻,²⁰ the "normal" isomer of B₂₀H₁₈²⁻,²¹ and B₂₀H₁₇NO³⁻²² indicates that the B₁₀ units in these species are very similar within the large standard deviations of all of these studies. Average distances are as follows: apex to edge: 1.69, 1.73, 1.68, 1.70, and 1.72 Å; edge to edge in the square pyramid: 1.85, 1.86, 1.83, 1.84, and 1.87 Å; edge to edge in the equatorial belt: 1.79, 1.82, 1.79, 1.81, and 1.82 Å in the B₁₀ units of these species in the order listed. Of course, these averages ignore distortions which arise from the strong bonding interactions in the local environments of the B₁₀ units. What is probably noteworthy is that fairly consistent average distances do occur in spite of these different environments. Moreover, the detailed distortions of chemical bonding of these B₁₀ units appear to be fairly small but will have to await X-ray studies at higher precision than those available so far.

Acknowledgment.—We wish to thank A. Kaczmarczyk for the sample and for informing us of the nmr results, and we acknowledge support by the Office of Naval Research.

(20) B. G. deBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **7**, 1085 (1968).

(21) C. H. Schwalbe and W. N. Lipscomb, *ibid.*, **10**, 151 (1971).

(22) C. H. Schwalbe and W. N. Lipscomb, *ibid.*, **10**, 160 (1971).

CONTRIBUTION NO. 3 FROM THE FASTBIOS LABORATORY,
DEPARTMENT OF CHEMISTRY, TEXAS CHRISTIAN UNIVERSITY, FORT WORTH, TEXAS 76129

The Molecular and Crystal Structure of Ethylenediamine-Bisborane, C₂H₁₄B₂N₂

BY HSING-YIE TING, WILLIAM H. WATSON,* AND H. C. KELLY

Received June 17, 1971

In the solid state ethylenediamine-bisborane is an open-chain molecule which exists in the trans conformation. The molecule contains a center of symmetry and all nonhydrogen atoms lie within 0.005 Å of a least-squares fitted plane. The compound crystallizes in the space group *Pbca* and the cell dimensions are $a = 10.761$ (3) Å, $b = 8.172$ (8) Å, and $c = 8.131$ (14) Å. The observed and calculated densities are 0.83 and 0.82 g cm⁻³, respectively. The intensities were collected by counter techniques and the model was refined to a conventional *R* factor of 0.062. The C-C distance is 1.514 (7) Å, the C-N distance is 1.477 (5) Å, and the N-B distance is 1.600 (7) Å. The molecule essentially has C_{2h} symmetry in the solid state.

Introduction

Ethylenediamine-bisborane has been shown to be a neutral monomer with a BH₃ group coordinated to each nitrogen atom of the diamine in an open-chain configuration.¹ In a previous study, the infrared spectrum of ethylenediamine-bisborane was compared with the spectra of selected ethylenediamine-metal complexes.² The gauche conformation was assigned to the ethylenediamine residue, and a cyclic structure was proposed. Although the molecule has been shown to be an open-chain configuration, the question remained whether ethylenediamine-bisborane exists in a gauche or trans conformation in the solid state. The present study was undertaken to resolve this question.

(1) H. C. Kelly and J. O. Edwards, *Inorg. Chem.*, **2**, 226 (1963).

(2) J. Goubeau and H. Schneider, *Ber.*, **94**, 816 (1961).

Experimental Section

Ethylenediamine-bisborane was synthesized¹ and the crystalline product recrystallized from distilled water. A single crystal with dimensions of 0.72 × 0.36 × 0.30 mm was chosen for study, and the crystal was mounted with the long edge (*c* axis) coincident with the rotation axis. Precession and Weissenberg photographs, calibrated with superimposed NaCl powder lines ($a = 5.6402$ Å), were used to determine the unit cell dimensions and space group. The errors in cell edges are the average deviations calculated from measurements of several higher angle reflections or layer lines. The density was determined by the flotation technique using a mixture of toluene and 1-hexene.

Crystal Data

C₂H₁₄B₂N₂, mol wt 87.77, has unit cell dimensions $a = 10.761$ (3) Å, $b = 8.172$ (8) Å, $c = 8.131$ (14) Å; systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; hko , $h = 2n + 1$; space group *Pbca* (*D*_{2h}¹⁶, no. 61); $Z = 4$; $V = 715$ Å³; $\mu = 0.51$ cm⁻¹ (Mo K α); $d_{\text{obsd}} = 0.83$ g cm⁻³; $d_{\text{calcd}} = 0.82$ g cm⁻³; λ (Cr K α) 2.2909 Å.