As further chemical and molecular structural studies of substituted carboranes become available, the nature of electronic and steric effects may become clearer in substitution reactions on the carboranes. In particular, models for activated complexes may be guessed, and the relevance of ground-state electronic structure gauged. This study indicates clearly that Cl substitution did not occur on the two most positively charged B atoms which were identified in both the molecular orbital and resonance studies.[3,4] Further studies are in progress.

Acknowledgment.—The Fourier maps were calculated using Sly, Shoemaker, and Van den Hende's ERFR2 program, the least-squares refinements using G. S. Pawley's rigid body least-squares program, which is a special case of a more general treatment of rigid body motion in a crystal developed independently by V. Schomaker. We acknowledge support of this research by the Office of Naval Research, the National Science Foundation, and the U. S. Army Research Office (Durham). We wish to thank Dr. H. Schroeder for providing us with the sample.

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Molecular Structure of Carboranes. A 1,2-Dicarbaclovododecaborane Derivative, $B_{10}H_{10}(CCH_2Br)_2$

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A three-dimensional X-ray diffraction study of single crystals of 1,2-bis(bromomethyl)carborane has proved the icosahedral structure of the $B_{10}C_2$ unit. The covalently linked ethylenedecaborane $B_{10}C_2$ unit is not correct, and the C–C distance of 1.64 Å. within the $B_{10}C_2$ icosahedron is not abnormally short. The space group is $P2_12_12_1$, and there are four molecules in a unit cell having dimensions of $a = 9.46$, $b = 10.12$, and $c = 13.78$ Å.

The carboranes,[1,2] $B_{10}C_2H_{12}$, their isomers,[3-5] and their derivatives form an unusually thermally stable group of compounds. The probable isoelectronic relation to the regular icosahedral $B_{12}H_{12}^{-2}$ ion[6] led to the detailed prediction[7-9] of a near-icosahedral geometrical and valence structure, in which the C atoms of the $B_{10}C_2$ unit participate in the electron deficiency of the assumed near-icosahedral framework. A detailed X-ray diffraction study became desirable when a distorted icosahedral structure was proposed[3] in which a short C–C bond about 1.54 Å. in length was assumed to distinguish one isomer, carborane, from a regular icosahedral isomer, neocarborane. Then, a detailed study became urgent when Zakharkin, *et al.*,[10] published the results of an X-ray diffraction study which indicated that the $B_{10}C_2$ unit of $B_{10}H_{10}(CCH_2Br)_2$ had not a near-icosahedral structure, but an ethylenedecaborane covalent unit in which the two C atoms are joined to the outermost 6, 9 B atoms of the B_{10} cage.

We show in the present study that the $B_{10}C_2$ unit in $B_{10}H_{10}(CCH_2Br)_2$ has a near-icosahedral structure in which the C–C distance of 1.64 Å. indicates not a single bond, but an electron-deficient type of bonding similar to that of the B atoms.

Structure Determination

1,2-Bis(bromomethyl)carborane was prepared by the method of Heying, *et al.*,[1] and then purified by vacuum sublimation at 100°. The melting point of 65–66.5° is comparable with published values of[2] 68–69.5° and of[10] 66°. Also the infrared absorption spectrum of our sample was identical with that of a sample of the same material kindly supplied to us by Dr. H. Schroeder.

Single crystals were grown by sublimation at 60° onto a glass surface at room temperature. Two nearly spherical crystals, each about 0.2 mm. in diameter, were sealed into capillaries and aligned by X-ray diffraction methods along the *a* and *c* axes, respectively. These methods also established the reciprocal lattice symmetry as D_{2h}, the space group of $P2_12_12_1$, and the unit cell dimensions of $a = 9.46 \pm 0.02$, $b = 10.12 \pm 0.02$, and $c = 13.78 \pm 0.05$ Å.: systematic extinctions of $h00$ when h is odd, of $0k0$ when k is odd, and of $00l$ when l is odd were noted on the zero level Weissenberg photographs, which were calibrated with an Al powder diffraction pattern. The reasonable assumption of four molecules per unit cell leads to the calculated density of 1.64 g. cm.$^{-3}$, in essential agreement with a very rough value of 1.5 g. cm.$^{-3}$ found by flotation methods.

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The relative intensities of 1423 independent diffraction maxima were measured on levels Hkl for $0 \leqslant H \leqslant 9$ and hkL for $0 \leqslant L \leqslant 13$ on the Buerger automated X-ray diffractometer at a scan rate[11] of 1°/min. and with the use of a Xe proportional counter. Background corrections, and then Lorentz-polarization corrections, $(LP)^{-1} = 2\cos^2\mu \sin \Upsilon/(1 + \cos^2 2\theta)$, were made in order to obtain the observed F_{hkl} (Table I). All final parameters were obtained from data correlated to a single scale, but the structure was solved from the a axis data which were assumed (justifiably, we later established) to be correlated by the instrument.

TABLE I

LIST OF OBSERVED F_{hkl} VALUES[a]

```
H=0 (K)(L),( 0)(0,16),632,U,21,U,110,U,47,U,5,U,37,U,*,U,10,U,10,( 1)(0,16),U,
46,169,26,34,23,56,46,27,24,33,14,2,15,7,13,3,( 2)(0,16),86,86,24,113,52,74,
4,26,61,22,5,12,20,10,*,*,*,( 3)(0,16),U,33,155,11,85,16,19,15,15,20,8,12,
22,11,3,*,16,( 4)(0,15),42,7,30,36,37,49,3*,32,39,13,17,37,15,*,8,8,
( 5)(0,15),U,72,28,19,34,58,37,22,24,10,17,5,7,12,*,*,( 6)(0,14),84,19,33,
28,24,15,34,17,15,21,20,7,*,*,7,( 7)(0,13),U,13,16,30,*,9,11,34,15,26,15,4,
8,14,( 8)(0,12),16,33,12,44,7,9,8,16,15,6,12,3,*,( 9)(0,11),U,14,25,13,17,
0,12,14,1,*,16,11,(10)(0, 9),14,4,8,9,6,27,15,9,5,7,(11)(0, 7),U,20,3,15,11,
10,3,*,(12)(0, 3),8,17,7,9
H=1 (K)(L),( 0)(0,16),U,49,95,89,79,4,81,8,7,5,59,6,17,*,6,3,*,( 1)(0,16),
24,40,60,91,92,36,25,29,14,28,15,14,14,9,6,7,4,( 2)(0,16),32,70,119,55,29,
42,35,64,16,27,*,11,8,11,4,*,6,( 3)(0,16),13,72,65,31,40,57,69,14,53,12,14,
7,18,5,3,*,*,( 4)(0,15),13,96,75,13,31,47,25,9,28,22,5,8,14,11,7,7,
( 5)(0,15),43,19,49,40,40,43,11,12,10,33,8,13,6,8,13,8,( 6)(0,14),33,33,12,
40,61,20,35,15,21,9,28,6,11,8,7,( 7)(0,13),42,29,17,55,35,9,15,10,5,10,8,7,
11,4,( 8)(0,12),35,10,27,15,14,13,10,29,6,14,*,11,8,( 9)(0,11),22,12,24,11,*,
11,18,11,17,9,5,*,(10)(0, 9),7,25,13,4,12,15,*,8,9,6,(11)(0, 7),5,3,6,4,7,
8,4,0,(12)(0, 3),*,5,5,*
H=2 (K)(L),( 0)(0,16),150,6,19,68,52,24,34,76,*,28,20,18,10,12,*,6,5,
( 1)(0,16),88,100,38,89,46,28,49,45,30,22,18,17,4,19,7,*,7,( 2)(0,16),11,95,
34,91,50,48,26,24,37,11,16,17,14,2,9,7,6,( 3)(0,15),*,30,80,14,44,81,18,10,
17,37,7,13,10,9,7,8,( 4)(0,15),9,54,56,46,38,53,22,25,23,17,8,23,12,6,8,*,
( 5)(0,14),17,48,17,36,32,37,32,15,25,18,13,6,10,13,3,( 6)(0,14),58,19,30,
23,16,16,38,33,14,15,6,9,10,7,*,( 7)(0,13),31,28,22,23,21,5,10,23,7,16,11,
7,7,*,( 8)(0,12),15,31,9,28,14,*,18,10,14,11,10,10,9,( 9)(0,10),10,8,14,8,
21,14,*,*,11,8,4,(10)(0, 9),13,5,20,5,11,19,12,8,*,*,(11)(0, 6),*,11,*,12,
5,11,6,(12)(0, 1),11,7
H=3 (K)(L),( 0)(0,16),U,118,18,129,41,41,14,26,7,11,16,*,*,8,*,6,4,
( 1)(0,16),19,37,43,114,47,21,30,59,10,44,26,14,11,11,6,6,*,( 2)(0,15),94,
47,40,25,39,86,38,46,16,32,5,24,*,*,1,6,( 3)(0,15),22,85,53,39,17,65,21,*,
16,12,14,12,7,4,*,8,( 4)(0,15),13,43,44,*,26,57,16,23,44,25,13,10,12,6,10,*,
( 5)(0,14),7,4,68,51,39,9,15,39,16,18,12,4,*,4,*,( 6)(0,13),38,25,23,45,35,
10,12,1,20,4,7,12,10,7,( 7)(0,12),6,13,13,17,23,10,32,24,8,8,21,8,10,
( 8)(0,11),52,18,13,13,27,19,13,11,6,0,7,6,( 9)(0,10),11,16,17,8,8,6,7,6,3,
7,6,(10)(0, 8),*,9,12,10,11,9,7,8,13,(11)(0, 5),*,5,14,6,*,6
H=4 (K)(L),( 0)(0,15),29,27,34,32,54,12,9,72,34,26,7,16,6,21,4,*,( 1)(0,15),
66,56,55,71,21,13,51,24,20,17,17,*,*,8,*,10,( 2)(0,15),33,70,31,27,53,38,37,
12,34,13,22,9,10,6,8,*,( 3)(0,15),10,26,24,21,29,63,25,4,16,31,15,16,8,6,0,
7,( 4)(0,14),43,63,58,30,38,32,13,12,15,5,17,*,10,5,7,( 5)(0,14),7,40,31,32,
32,11,39,14,27,10,8,10,14,11,*,( 6)(0,13),5,23,30,21,10,11,28,28,12,10,6,8,
4,8,( 7)(0,12),46,30,15,17,20,11,16,12,5,7,8,10,8,( 8)(0,11),*,18,*,11,15,
15,17,7,4,11,13,6,( 9)(0, 9),17,8,*,15,19,17,*,6,11,10,(10)(0, 6),7,11,15,
8,8,8,6,10,(11)(0, 4),10,6,2,9,4
H=5 (K)(L),( 0)(0,14),U,50,57,83,7,8,33,4,10,12,12,7,*,11,10,( 1)(0,14),67,
11,28,38,60,13,17,28,14,9,15,14,15,7,12,( 2)(0,14),46,13,78,8,21,31,40,10,
27,19,13,9,7,7,2,( 3)(0,14),33,52,12,12,48,34,23,16,20,8,6,7,5,10,*,
( 4)(0,13),14,15,28,13,7,26,24,11,20,16,9,11,10,8,( 5)(0,13),16,1,30,18,34,
15,7,19,16,11,4,7,12,*,( 6)(0,11),12,11,14,22,*,13,13,13,4,13,12,7,
( 7)(0,11),15,16,*,13,20,9,13,11,*,9,14,8,( 8)(0,10),27,10,15,11,12,11,11,
10,6,3,*,( 9)(0, 8),6,15,4,6,4,10,4,13,6,(10)(0, 6),*,11,*,5,4,5,5,

(11)(0, 1),4,5
H=6 (K)(L),( 0)(0,14),87,23,7,6,44,15,7,9,24,12,9,9,*,10,7,( 1)(0,14),31,15,
49,21,10,20,41,19,11,16,20,10,7,6,3,( 2)(0,13),44,24,15,19,37,10,3,12,31,*,
7,5,15,8,( 3)(0,13),17,24,51,22,22,11,14,13,*,14,9,6,7,*,( 4)(0,13),45,23,
24,12,28,22,7,18,17,14,11,6,8,4,( 5)(0,12),17,37,31,18,12,19,23,5,15,6,7,12,
4,( 6)(0,12),32,29,3,15,16,16,7,16,9,15,9,4,2,( 7)(0,10),14,14,11,18,5,12,
13,10,4,8,8,( 8)(0, 9),3,18,*,13,12,*,10,9,*,5,( 9)(0, 7),7,11,10,7,4,8,5,
10,(10)(0, 3),*,7,7,5
H=7 (K)(L),( 0)(0,13),U,27,26,14,15,13,33,13,2,14,18,6,10,*,( 1)(0,13),45,
45,19,24,45,24,8,*,15,6,*,6,*,*,( 2)(0,12),8,28,46,24,6,7,23,13,14,11,3,6,
5,( 3)(0,12),12,6,23,17,31,*,21,19,22,8,6,13,*,( 4)(0,11),27,26,24,23,16,17,
17,7,7,12,8,5,( 5)(0,11),16,15,8,6,15,16,10,11,*,11,15,9,( 6)(0,10),11,13,*,
6,13,16,13,4,5,12,8,( 7)(0, 8),13,15,11,13,10,7,7,7,7,( 8)(0, 7),9,3,8,11,
5,*,7,9,( 9)(0, 4),11,8,1,11,1
H=8 (K)(L),( 0)(0,11),33,22,4,23,13,18,9,14,0,8,7,7,( 1)(0,11),5,20,5,12,14,
24,16,11,12,11,6,*,( 2)(0,11),7,18,11,20,10,11,7,16,13,6,*,4,( 3)(0,11),8,
25,15,15,15,13,7,8,8,9,4,5,( 4)(0,10),4,9,13,17,12,13,13,12,9,*,1,( 5)(0, 9),
21,14,9,10,17,9,10,7,9,7,( 6)(0, 8),10,10,16,6,5,10,9,*,5,( 7)(0, 7),5,8,7,
6,13,5,8,3,( 8)(0, 4),*,4,12,3,7
H=9 (K)(L),( 0)(0,10),U,20,3,13,6,18,6,10,6,16,5,( 1)(0,10),4,19,7,17,4,16,
5,13,7,4,5,( 2)(0, 9),6,17,*,14,4,15,6,9,7,8,( 3)(0, 9),12,12,12,11,7,7,11,
13,9,12,( 4)(0, 8),14,13,9,8,15,9,*,5,8,( 5)(0, 7),*,12,10,14,4,1,10,9,
( 6)(0, 6),16,11,4,1,13,10,6,( 7)(0, 3),6,5,11,*
H=10 (K)(L),( 0)(0, 7),9,15,7,*,13,11,6,3,( 1)(0, 7),4,17,5,8,4,9,8,3,
( 2)(0, 7),18,14,6,*,9,9,3,6,( 3)(0, 6),11,15,*,*,11,*,12,( 4)(0, 5),10,9,
4,10,7,6,( 5)(0, 4),9,*,6,*,10
H=11 (K)(L),( 0)(0, 4),U,4,5,8,4,( 1)(0, 4),10,3,*,*,12,( 2)(0, 3),6,4,7,10,
( 3)(0, 2),19,4,*
```

[a] The value of k and the range of l are given in parentheses. Unobserved reflections are indicated by an asterisk, and space group extinctions by an extra comma. All reflections are on the same scale as F_{000}, which is given as a reference point. No extinction or absorption corrections were made.

Solution of the structure presented no difficulties. The Br atoms were readily found in the sharpened three-dimensional Patterson function, and a three-dimensional electron density map based upon phases of these Br atoms yielded fourteen peaks in the range of 210 to 329 units on an arbitrary scale on which Br atoms were 4668 and 4384. The highest false peak was 154. Thus the complete arrrangement of all B and C atoms was found without chemical assumptions, and it was immediately clear that twelve of these atoms were at the corners of a very nearly regular icosahedron.

We did not solve the absolute configuration of the crystal, but only record here that the positions of the two symmetry unrelated Br atoms, as found from the Patterson function, have a sixteenfold ambiguity associated with the arbitrary eightfold choice of the origin of the unit cell and the twofold choice of the enantiomorph. Thus our choice of enantiomorph is arbitrary.

Refinement of the structure proceeded rapidly. Values of $R_F = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$ for the 1353 a axis reflections were 0.35 for Br atoms only and 0.29 when the fourteen peaks were initially given scattering amplitudes of B atoms. A new three-dimensional electron density map yielded the expected C atoms at heights of 445 to 520 and B atoms between 383 and 448 in height. Two cycles were carried out of least-squares refinement of the single scale factor, the 48 atomic position parameters, and the six translational, six rotational, and three center of rotational thermal parameters.[12] Then separate scale factors were assigned to each level of reciprocal lattice data about the a axis, and two more cycles of three-dimensional least-squares refinement reduced R_F to 0.165. No further improvement was obtained by assigning separate anisotropic thermal parameters to each Br atom.

The data about the c axis became available, and a single scale of all reflections was then established. The 1239 reflections having $|F_o| > 4$ and $|F_c| > 4$ were used, and the 47 reflections having $|F_o| < 4$ and $|F_c| > 4$ were assigned $F_o = 2$ in the final refinements, which yielded $R = 0.132$ after three cycles (Table II). All parameter shifts at this stage were less than 0.7σ, where σ is the standard deviation. Weighting factors were $w = 1$ for $|F_o|^2 \leqslant 300$ and $w = |F_o|^2/300$ for $|F_o|^2 \geqslant 300$ where $\sqrt{w}$ is the weighting factor in the equations of condition of the least-squares treatment.

TABLE II

FINAL VALUES FOR $R_F = (\Sigma||F_o| - |F_c||)/|\Sigma|F_o|)$

hkl	R	Range of $\sin\theta$	R
All	0.13	0.00 to 0.40	0.09
h even	0.14	0.40 to 0.50	0.07
h odd	0.12	0.50 to 0.60	0.09
k even	0.13	0.60 to 0.65	0.12
k odd	0.13	0.65 to 0.70	0.11
l even	0.13	0.70 to 0.75	0.14
l odd	0.13	0.75 to 0.80	0.20
$k + l$ even	0.13	0.80 to 0.85	0.28
$k + l$ odd	0.13	0.85 to 0.90	0.29
$h + l$ even	0.13	0.90 to 1.00	0.43
$h + l$ odd	0.13		
$h + k$ even	0.13		
$h + k$ odd	0.13		
$h + k + l$ even	0.13		
$h + k + l$ odd	0.13		

---

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TABLE III

FINAL ATOMIC COORDINATES IN FRACTIONS OF CELL LENGTHS AND THERMAL PARAMETERS[a]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
1	0.265	0.569	0.839	108	95	33	−7	12	5
2	0.360	0.457	0.894	96	97	28	−10	7	−1
3	0.208	0.522	0.949	124	109	33	−10	20	13
4	0.088	0.554	0.857	105	123	50	−8	13	21
5	0.172	0.506	0.745	119	121	36	−8	−3	22
6	0.344	0.450	0.770	100	96	27	−5	12	2
7	0.245	0.342	0.950	123	106	33	−1	25	6
8	0.076	0.403	0.922	105	126	61	−5	35	2
9	0.053	0.401	0.793	90	141	68	−19	−4	4
10	0.211	0.339	0.744	103	114	38	−17	−5	2
11	0.324	0.304	0.837	90	92	28	−7	10	−3
12	0.151	0.267	0.850	97	109	59	−11	19	−16
13	0.336	0.706	0.823	157	92	57	−6	24	−1
14	0.493	0.482	0.947	119	126	47	−25	−13	1
15	0.305	0.834	0.929	223	101	81	−29	19	4
16	0.665	0.476	0.871	93	153	97	−29	−3	−17

[a] The thermal parameters are in the form

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$$

Results and Discussion

Final parameters are given in Table III, distances in Table IV, and angles in Tables V and VI. The atomic numbering system is shown in Fig. 1. Corrections for molecular thermal oscillations are only about one-tenth of the standard deviations of the bond distances (footnotes, Table IV). Bond angles are listed in a form suitable for construction of a model.

TABLE IV

BOND DISTANCES[a]

Bond	Corrected length,[b] Å.	Bond	Corrected length,[b] Å.
C–C		B–B	
1–2	1.64	3–4	1.74
1–13	1.55	3–7	1.86
2–14	1.49	3–8	1.78
C–Br		4–5	1.80
13–15	1.96	4–8	1.77
14–16	1.94	4–9	1.81
B–C		5–6	1.76
1–3	1.68	5–9	1.69
1–4	1.70	5–10	1.74
1–5	1.69	6–10	1.73
1–6	1.71	6–11	1.76
2–3	1.75	7–8	1.76
2–6	1.71	7–11	1.77
2–7	1.77	7–12	1.80
2–11	1.77	8–9	1.78
		8–12	1.84
		9–10	1.75
		9–12	1.81
		10–11	1.71
		10–12	1.72
		11–12	1.69

[a] Standard deviations (Å.) for the various types of bonds are: B–C, $\sigma = 0.037$; B–B, $\sigma = 0.033$; B–C(methyl), $\sigma = 0.045$; and C(methyl)–Br, $\sigma = 0.016$. The standard deviations were computed by averaging all bond lengths of the same type and applying the equation

$$\sigma = \left(\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}\right)^{1/2}$$

[b] Corrections for thermal vibrations were computed using the least-squares rotation tensor and were found to be small compared to the standard deviation in bond lengths. For B–B, B–C, B–C(methyl), and C(methyl)–Br bonds, the largest corrections were 0.0044, 0.0045, 0.0013, and 0.0017 Å., respectively.

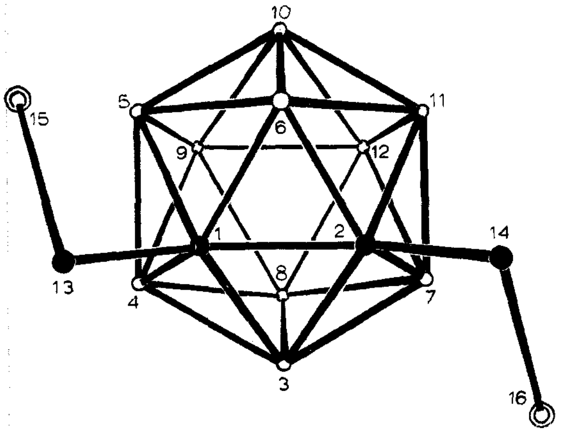

Fig. 1.—The molecular structure and numbering scheme for $B_{10}H_{10}(CCH_2Br)_2$. B atoms are designated as single circles, C atoms are filled circles, and Br atoms are double circles.

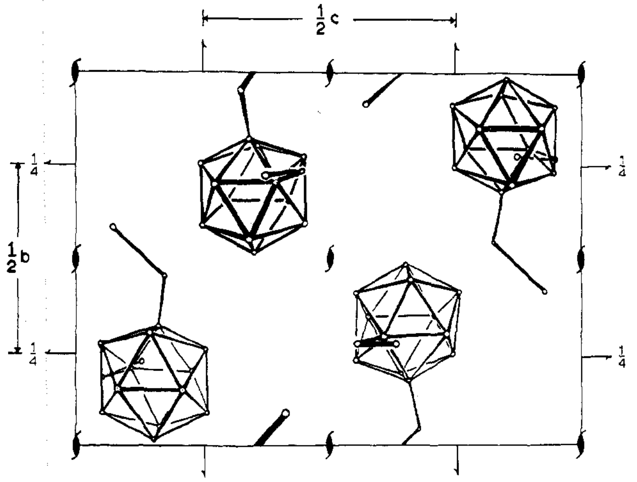

Fig. 2.—The molecular packing of $B_{10}H_{10}(CCH_2Br)_2$ as seen in the projection along the a axis.

Our major conclusion is that both bond distances and

TABLE V

MODEL DRILLING ANGLES

Center atom	Coordinating atom	ϕ,[a] deg.	ρ,[a] deg.
1	2	90.0	0.0
	3	0.0	64.0
	4	322.5	114.2
	5	252.2	111.9
	6	214.4	61.5
2	1	90.0	0.0
	3	0.0	59.1
	6	145.6	61.5
	7	41.4	108.6
	8	41.1	70.6
3	1	90.0	0.0
	2	0.0	56.9
	4	219.0	59.8
	8	262.5	103.2
	9	259.3	67.1
4	1	90.0	0.0
	3	0.0	58.2
	5	218.1	57.6
	9	255.1	100.9
	10	255.1	66.5
5	1	90.0	0.0
	4	0.0	58.4
	6	215.3	59.5
	10	254.4	105.6
	11	254.6	70.5
6	1	90.0	0.0
	2	0.0	57.1
	5	140.0	58.3
	7	37.4	69.1
	11	40.2	104.9
7	2	90.0	0.0
	3	0.0	57.8
	8	38.9	103.5
	11	139.5	59.9
	12	103.2	104.0
8	3	90.0	0.0
	4	0.0	58.7
	7	140.7	63.2
	9	38.2	107.6
	12	101.8	110.1
9	4	90.0	0.0
	5	0.0	61.8
	8	136.1	59.1
	10	38.0	110.0
	12	99.6	109.8
10	5	90.0	0.0
	6	0.0	60.8
	9	139.8	57.9
	11	39.4	109.1
	12	102.3	109.5
11	2	90.0	0.0
	6	0.0	58.0
	7	217.2	60.0
	10	321.8	105.6
	12	257.8	109.2
12	7	90.0	0.0
	8	0.0	57.6
	9	35.1	105.4
	10	97.5	108.2
	11	136.1	61.0
13	1	90.0	0.0
	15	0.0	114.7
14	2	90.0	0.0
	6	0.0	115.8

[a] See ref. 4, p. 228, for definitions of ϕ and ρ. These are spherical coordinates in which ϕ is measured in the x, y plane, and ρ is measured from the z axis.

TABLE VI

AVERAGE BOND ANGLES (DEG.)[a]

No. of measurements	Bond type	Average angle	Largest angle	Smallest angle
36	B–B–B	60	63	56
12	B–B–C	59	61	58
6	B–C–B	62	64	60
4	B–C–C	62	64	59
2	C–B–C	57	57	57
8	B–C–C(methyl)	119	125	111
2	C–C–C(methyl)	121	125	117
2	C–C(methyl)–Br	115	116	115

[a] The bond angles were computed using values for the atomic positions which were corrected for thermal vibrations by means of the least-squares rotation tensor. These corrections were found to be small compared to the standard deviation of the bond angles, the largest correction being 0.10°. Estimated standard deviations of bond angles are about 3°.

angles clearly indicate the near-icosahedral geometry of the $B_{10}C_2$ unit, not the ethylenedecarborane structural unit (Fig. 2 of ref. 11b derived in the X-ray study reported by Zakharkin, *et al.*[10]).

Secondly, our results do not support the proposal[3] that the carborane cage has a 1.54 Å. C–C distance, which opens up to the regular icosahedral distance of 1.77 Å. in the transformation at about 470° to neocarborane. The C–C distances of 1.64 ± 0.40 Å. in this study, and of 1.67 ± 0.02 Å. in octachlorocarborane,[11] leave no physical basis for a high barrier between these proposed structures, and hence the proposal[13] of a rearrangement through a near-cuboctahedral intermediate (perhaps involving localized regions of expansion and contraction) seems most reasonable, at present, for the relation between carborane and neocarborane. An X-ray diffraction study of a neocarborane structure is under way. With almost improper respect for the observation that predictions in science are more difficult than in science fiction (which is limited to what we can imagine), we maintain[9,13] our present belief that neocarborane has its two C atoms in the *meta* positions, neither adjacent nor opposite in the icosahedron.

The crystal structure (Fig. 2) has only one feature of interest: a $Br_{15} \cdots Br_{16}$ contact of 3.72 Å. between different molecules. This is the only intermolecular distance which is less than the expected van der Waals contact, which is 3.9 Å. for $Br \cdots Br$. There are many similar examples in other crystal structures containing halogen atoms, including the crystals of the diatomics Cl_2, Br_2, and I_2, but not F_2. It may be that this particularly strong intermolecular interaction is responsible in part for the distortion of bond angles $C_2C_1C_{13}$ = 116.6° and $C_1C_2C_{14}$ = 125.0° from each other and from the value of 121.7° expected from a regular icosahedral structure. The implied easy bending of external bonds suggests that the nondirectional character of electron-deficient bonding already indicated by the bond distances produces little restoring torque for angular deformations. Further evidence for this lack of directionality of bonding within the polyhedral surface is sug-

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(13) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962).

gested by the rearrangements and by the great simplicity of molecular spectra found in these complex polyhedral molecular species.

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Geometrical Theory of Boron Hydrides

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Based upon the assumptions that in some probable new boron hydrides the geometrical and bonding environments of B atoms will be similar to those in known hydrides, that all stable boron hydride molecules encounter external H···H contacts only upon collision with other molecules of the same or similar type, and finally that all intramolecular H···H contacts are reasonable ($\geqslant$ about 2 Å.) it is shown here that only a very limited number of predicted new boron hydrides based upon a single icosahedral fragment can be expected. Geometrical structural predictions are given for these possible new boron hydrides.

The three-center resonance and molecular orbital theories[1] of boron hydrides take the steric properties of boron hydride structures into account in only a general and not very restrictive way. Accordingly, it seems appropriate to give specific attention to the problems of intramolecular and intermolecular steric requirements, within the framework of these valence theories, in the hope that only a limited number of predictions would result. This paper represents a first theory of this type and is restricted to neutral single icosahedral fragments for the boron arrangements. We have therefore specifically excluded boron hydride ions, fragments, or polyhedra joined by BBB or BB[2] bonds (*e.g.*, $B_{10}H_{16}$), by single or double hydrogen bridges[3] (*e.g.*, $B_{20}H_{19}^-$), by the sharing of two B atoms[1] (*e.g.*, $B_{18}H_{22}$ and *i*-$B_{18}H_{22}$) or of four B atoms (*e.g.*, $B_{20}H_{16}$), or fragments obtained from possible degradation of structures in such a way that these joinings are preserved. Equivalent theories of these additional kinds of molecules and ions can easily be derived by similar methods.

Accordingly, the assumptions and procedures are as follows. (1) Construct models of the known boranes, ions, and ligand derivatives from balls precisely drilled according to the internuclear straight lines between all nearest neighboring atoms. These angles have been listed[1,4] for all of the known compounds, including[5] B_8H_{12}. (2) Choose from these models all different types of balls (Table I), but, for the single icosahedral frameworks considered here, limit the choices to B atoms having at least one terminal H atom (H_t). (3) Construct all possible models with the use of B–B distances of about 1.8 Å., B–H_t distances of 1.2 Å., and B–H_b (bridge) distances of about 1.4 Å., on a scale of 1 Å. = 10 cm. (4) Reject all models which have intramolecular H···H contacts of less than about 2.0 Å. where these H atoms

TABLE I

NEAREST COORDINATION ENVIRONMENTS OF B ATOMS OF ALL TYPES

B	H_t[a]	H_b[a]	Example
2	2	1	$B_3H_8^-$, the symmetry related B atoms
2	2	2	$B_3H_8^-$, the unique B
3	1	1	B_6H_{10}, nonapical atoms joined with the short bond
3	1	2	B_4H_{10}, the inner pair
3	2	0	$C_2H_5NH_2B_8H_{12}NHC_2H_5$, B joined to $C_2H_5NH_2$
3	2	1	$B_9H_{13}NCCH_3$, the BH_2 groups
4	1	0	$B_9H_{13}NCCH_3$, the BH on the symmetry plane
4	1	1	B_9H_{15}, adjacent to the BH_2 group
4	2	0	B_5H_{11}, apex
5	1	0	B_6H_{10}, apex
(5	0	0)[b]	$B_{10}H_{16}$, atoms joining the B_5H_8 units
(5	0	2)[b]	*i*-$B_{18}H_{22}$, on the molecular twofold axis
(6	0	0)[b]	B (elementary), not yet found in the hydrides
(6	0	1)[b]	$B_{18}H_{22}$, nearest molecular center of symmetry
(7	0	0)[b]	*i*-$B_{18}H_{22}$, on the molecular twofold axis

[a] The subscripts t and b refer to terminal and bridge H atoms, respectively. [b] Atoms of types listed in parentheses are required for structure types not considered in this paper, *e.g.*, structures based upon polyhedra or fragments joined by boron–boron bonds, by one or more bridge H atoms, or by common B atoms.

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(1) W. N. Lipscomb, "Boron Hydrides," The W. A. Benjamin Co., New York, N. Y., 1963, p. 227 ff.

(2) R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 996 (1961).

(3) W. N. Lipscomb, *ibid.*, **47**, 1791 (1961).

(4) R. D. Dobrott, L. Friedman, and W. N. Lipscomb, *J. Chem. Phys.*, **40**, 866 (1964); see footnote 3.

(5) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1451 (1964); *Inorg. Chem.*, **3**, 1659 (1964).