III, $H_3BNHCH_3BH_2NHCH_3BH_2NH_2CH_3$, the only postulated intermediate which was not isolated. It is apparently unstable with respect to the trimer under the conditions of the pyrolysis. Some experimental evidence which might be consistent with the presence of III is the formation of $H_3BNH_2CH_3$ from the reaction of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$ with $NaBH_4$ in a dilute monoglyme solution. Compound III should be soluble in monoglyme and could dissociate[13] to form, under dilute conditions, $H_3BNH_2CH_3$ and $(H_2BNHCH_3)_x$ polymer, the observed products. However, under very concentrated conditions, monoglyme solution or pyrolysis of II, the six-membered ring is formed by an intramolecular dehydrogenation reaction (eq 4) and disproportionation is averted.

In contrast to the ionic and polymeric type of intermediates, which characterized the formation of $(H_2BNHCH_3)_3$, the mechanism for the pyrolysis of $H_3BN(CH_3)_2H$ probably involves only neutral species. There was no experimental evidence for the cation $H_2B(N(CH_3)_2H)_2^+$ during the pyrolysis of $H_3BN(CH_3)_2H$ or the reaction of $NaBH_4$ and $(CH_3)_2NH_2Cl$ in etherated solvents. Similarily, the cation $[H(CH_3)_2NBH_2N(CH_3)_2BH_2N(CH_3)_2H]^+$ could not be prepared. Even though no intermediates could be isolated during the partial pyrolysis of $H_3BN(CH_3)_2H$, the experimental evidence is consistent with neutral monomeric species, $H_2BN(CH_3)_2$, which associate to give the dimer. The dimer is also in equilibrium with the proposed monomeric species. The association of monomers[14] was originally suggested to account for the formation of all aminoboranes.

The most likely route to the monomer $H_2BN(CH_3)_2$ is an intramolecular dehydrogenation of $H_3BN(CH_3)_2H$. Another possible route might be related to the initial formation of $H_3BN(CH_3)_2BH_2N(CH_3)_2H$ by the intermolecular dehydrogenation of two $H_3BN(CH_3)_2H$ molecules followed by either dissociation to give $H_3BN(CH_3)_2H$ and the monomer $H_2BN(CH_3)_2$ or an intramolecular ring-closure reaction by dehydrogenation. However, the observation that 2 moles of H_2 is formed for every mole of $(H_2BN(CH_3)_2)_2$ in the quenching experiment suggests that $H_3BN(CH_3)_2BH_2N(CH_3)_2H$ either is not a primary intermediate or is too unstable for a measurable quantity to be present under the pyrolytic conditions. It should be noted that the dimer has been prepared from $H_3BN(CH_3)_2BH_2N(CH_3)_2H$, but pyrolytic conditions[15] of 200° were used.

In conclusion, the most significant factor for the determination of the degree of association of aminoboranes appears to be the intermediates in their formation. All aminoboranes cannot be considered to be formed by the association of monomeric species. Therefore, steric effects should not be used as the only factor to explain the change in the degree of association with the substituents on the boron and nitrogen atoms. The differences in the intermediates might be related to steric effects, but the basicity of the amine and the strengths of the N–H bonds should also be considered.

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Molecular and Crystal Structure of *m*-$B_{10}Br_2H_8C_2H_2$

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The product of dibromination of *m*-$B_{10}H_{10}C_2H_2$ in the presence of $AlBr_3$ is shown to be a derivative with Br atoms substituted on B atoms 9 and 10, those farthest from the C atoms and the most negative B atoms in nonempirical molecular orbital studies of *m*-$B_{10}H_{10}C_2H_2$. There are four molecules in a unit cell having parameters a = 13.14, b = 7.08, and c = 12.64 A. The space group is Pnam. A tentative assignment of the ^{11}B nuclear magnetic resonance spectrum is proposed.

The charge distribution[1] in *o*-$B_{10}C_2H_{12}$, as computed by molecular orbital theory, gives a reasonable account of some simple electrophilic free radical and electrophilic reactions which occur at various B atoms. Thus the icosahedral $B_{10}C_2$ framework is strongly polarized by the C atoms to give ground-state charges of −0.16 at B(8) and B(10), of −0.16 at B(9) and B(12), of −0.03 at B(4), B(5), B(7), and B(11), and of +0.08 at B(3) and B(6). Hitherto unpublished studies by less empirical procedures,[2] in which parameters were taken from B_4H_4[3] for B atoms and in which one- and two-center zero overlap matrix elements have been included, yield −0.29, −0.27, −0.02, and +0.22, in the order listed above. Where the charges are similar, for B(8)

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[1] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

[2] M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966).

[3] W. E. Palke and W. N. Lipscomb, *J. Chem. Phys.*, **45**, 3945 (1966).

and B(9), those electrons on B(9) appear to be more polarizable than those on B(8). Friedel–Crafts bromination,[4–6] photochemical chlorination,[7] and withdrawal of B by ethoxide ion[8,9] are all in agreement with the hypothesis that these ground-state charges are preserved to a large extent in the transition states and that the usual qualifications[6] apply to these reactions.

In the expectation that these results may be more general, we have proposed a simple inductive rule[10] which indicates clearly that simple electrophilic attack should take place at B(9) and B(10) in m-$B_{10}C_2H_{12}$. We show here from the results of a three-dimensional X-ray diffraction study that this is indeed so in m-$B_{10}Br_2H_8C_2H_2$, which had been prepared[11] by a Friedel–Crafts reaction. Thus the early predictions[1] of molecular orbital theory are supported. On the basis of this theory, and isomer counts for unsubstituted, C-methyl, and C,C′-dimethyl m-$B_{10}C_2H_{12}$, Zakharkin and Kalinin[12] have also concluded that B(9) and B(10) are the first to be attacked by electrophilic reagents.

These results also make possible a tentative experimental assignment of the ^{11}B nuclear magnetic resonance spectrum, as described below. We now turn to the crystal structure determination.

Structure Determination

Single crystals, about 0.5 × 0.04 × 0.04 mm, were mounted along the long dimension onto fine capillaries for photographic collection of X-ray data. Reciprocal lattice symmetry of mmm and unit cell dimensions (calibrated by Al powder diffraction lines) of $a = 13.14 \pm 0.01$, $b = 7.08 \pm 0.03$, and $c = 12.64 \pm 0.04$ A were established. Extinctions of $0kl$ when $k + l$ is odd and $h0l$ when h is odd left the space group ambiguous, either as $Pna2_1$ or Pnam. Later work showed that Pnam is most probably correct. Weissenberg levels hKl for $0 \leqslant K \leqslant 5$ were taken with Cu Kα radiation, and precession levels 0 and 1 about the [100], [101], and [001] axes were taken with Mo Kα radiation. After the usual Lorentz-polarization corrections, these data were correlated to a single scale, and the Patterson function[13] was then computed from sharpened coefficients. The clear Br···Br interaction indicated the space group Pnam for these heavy atoms, and yielded $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.33$ for Br contributions only. Phases computed from Br then yielded 31 peaks greater than about one-third the height expected for B, from which an icosahedral arrangement was easily located, bisected by the crystallographic mirror plane and chemically reasonably located relative to the Br atoms. Inclusion of these atoms as boron, four on the mirror plane and four off this plane, yielded $R_F = 0.25$ after two cycles of position and anisotropic thermal parameters.

Meanwhile, back at the laboratory, levels hKl including $0 \leqslant K \leqslant 4$ were taken from a crystal, 0.5 × 0.04 × 0.04 mm, on the Buerger automated diffractometer with the use of Cu Kα radiation and a Xe proportional counter. Also diffractometer data hkL for $0 \leqslant L \leqslant 3$ were taken from a cube, about 0.04 mm on edge, which had been cut from a needlelike crystal. After Lorentz and polarization corrections these nine levels were correlated and merged with the photographic data (Table I). A value of $R_F = 0.113$ was then achieved after (a) two cycles of least-squares refinement of position and anisotropic temperature parameters of Br, (b) two cycles of least-squares refinement of position and isotropic temperature parameters of cage atoms, and (c) three cycles of least-squares refinement of position and anisotropic temperature parameters for all atoms (except H) and the scale factor.

Until this point in the refinement, all cage atoms were assumed to be boron atoms. The smaller radius found[6] for C in o-$B_{10}Br_2H_8C_2H_2$ proved to be the most reliable basis for location of C atoms in the framework. Hence, the *meta* and *para* distances of cage atoms were computed (Table II), from which we note that the 1–7 *meta* distance (Figure 1) is shorter than any other *meta* distance by four standard deviations. Thus atoms 1 and 7 are assigned as C atoms. This conclusion is also supported by the *para* distances, for which 1–12 and 7–5 are shorter than 2–9 and 4–11. Introduction of a scattering curve for C for atoms 1 and 7, followed by two cycles of least-squares refinement of position and anisotropic temperature parameters of Br, B, and C atoms, yielded $R_F = 0.103$. The H atoms were not found uniquely in a difference electron density map, but they were introduced at expected terminal positions. A final cycle of refinement of position and anisotropic temperature parameters of Br, B, and C then yielded $R_F = 0.105$ for the 685 observed reflections. Values of $R_{F^2} = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2 = 0.142$ and $R_{wF^2} = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2} = 0.085$ were also obtained. No unusual problems of pseudo-symmetry are suggested by the values of R_F for different classes of reflections (Table III).

Results and Discussion

In the numbering scheme (Figure 1) the C atoms are at positions 1 and 7, as compared with 1 and 2 in o-$B_{10}C_2H_{12}$. The crystal structure (Figure 2) diagram includes an indication of the crystallographic mirror plane which passes through the m-$B_{10}Br_2H_8C_2H_2$ molecule. Atomic parameters (Table IV) include standard deviations computed from the full-matrix least-squares refinements. No corrections of bond dis-

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TABLE I

LIST OF OBSERVED F_{hkl} VALUES

H	K	L	FOBS
0	2	0	69
0	4	0	86
0	6	0	50
0	1	1	98
0	3	1	26
0	5	1	48
0	0	2	61
0	2	2	23
0	4	2	33
0	1	3	167
0	3	3	31
0	7	3	12
0	0	4	168
0	2	4	35
0	4	4	82
0	3	5	11
0	0	6	139
0	2	6	39
0	4	6	28
0	1	7	102
0	3	7	21
0	5	7	50
0	0	8	52
0	1	9	57
0	3	9	6
0	0	10	61
0	2	10	33
0	4	10	43
0	1	11	29
0	3	11	13
0	0	12	31
0	2	12	18
0	1	13	40
0	3	13	7
0	0	14	31
0	2	14	11
1	1	0	82
1	2	0	70
1	3	0	124
1	4	0	33
1	5	0	10
1	6	0	14
1	7	0	31
1	8	0	11
1	1	1	70
1	2	1	108
1	3	1	11
1	4	1	28
1	6	1	16
1	1	2	58
1	2	2	19
1	3	2	51
1	7	2	13
1	1	3	47
1	2	3	153
1	3	3	53
1	4	3	64
1	7	3	11
1	1	4	79
1	2	4	43
1	3	4	92
1	4	4	16
1	1	5	16
1	2	5	8
1	3	5	11
1	4	5	13
1	1	6	69
1	2	6	39
1	3	6	86
1	1	7	22
1	2	7	108
1	3	7	48
1	4	7	42
1	1	8	16
1	2	8	8
1	3	8	23
1	1	9	28
1	2	9	37
1	3	9	6
1	4	9	28
1	1	10	47
1	2	10	26
1	3	10	54
1	4	10	10
1	1	11	13
1	2	11	30
1	3	11	10
1	4	11	11
1	1	12	8
1	2	12	8
1	3	12	13
1	1	13	10
1	2	13	32
1	3	13	6
1	4	13	16
1	1	14	15
1	2	14	8
1	3	14	15
2	1	0	112
2	2	0	46
2	3	0	17
2	4	0	50
2	5	0	62
2	6	0	31
2	0	1	156
2	1	1	84
2	2	1	38
2	3	1	13
2	4	1	45
2	5	1	42
2	0	2	106
2	1	2	42
2	2	2	41
2	5	2	11
2	6	2	15
2	7	2	14
2	0	3	139
2	1	3	123
2	2	3	18
2	4	3	55
2	5	3	46
2	6	3	27
2	7	3	14
2	0	4	105
2	1	4	88
2	2	4	57
2	3	4	10
2	4	4	35
2	5	4	41
2	1	5	11
2	2	5	23
2	4	5	10
2	0	6	106
2	1	6	48
2	2	6	29
2	3	6	17
2	4	6	39
2	0	7	80
2	1	7	62
2	2	7	20
2	3	7	13
2	4	7	34
2	0	8	14
2	2	8	9
2	3	8	4
2	4	8	18
2	0	9	37
2	1	9	46
2	2	9	17
2	3	9	6
2	4	9	18
2	0	10	70
2	1	10	50
2	2	10	20
2	3	10	16
2	4	10	23
2	0	11	19
2	1	11	24
2	3	11	7
2	4	11	13
2	0	12	11
2	1	12	17
2	0	13	29
2	1	13	29
2	2	13	12
2	3	13	5
2	4	13	14
2	0	14	17
2	2	14	4
2	3	14	9
3	1	0	60
3	2	0	152
3	3	0	89
3	4	0	33
3	5	0	15
3	6	0	13
3	8	0	10
3	1	1	71
3	2	1	43
3	3	1	72
3	4	1	28
3	7	1	16
3	1	2	22
3	2	2	59
3	4	2	28
3	6	2	21
3	8	2	13
3	1	3	101
3	2	3	48
3	3	3	93
3	4	3	39
3	6	3	17
3	7	3	20
3	1	4	62
3	2	4	105
3	3	4	28
3	4	4	21
3	6	4	27
3	1	5	10
3	3	5	12
3	4	5	10
3	1	6	5
3	2	6	97
3	3	6	37
3	4	6	51
3	1	7	58
3	2	7	29
3	3	7	68
3	4	7	16
3	1	8	9
3	2	8	39
3	3	8	10
3	4	8	7
3	1	9	24
3	2	9	28
3	3	9	39
3	4	9	13
3	1	10	20
3	2	10	48
3	3	10	20
3	4	10	23
3	1	11	20
3	2	11	17
3	3	11	16
3	4	11	7
3	1	12	20
3	2	12	10
3	3	12	7
3	4	12	14
3	1	13	19
3	2	13	19
3	3	13	29
3	4	13	7
3	2	14	14
4	0	0	25
4	1	0	150
4	2	0	19
4	3	0	35
4	5	0	60
4	0	1	129
4	1	1	19
4	2	1	11
4	4	1	37
4	5	1	21
4	6	1	27
4	8	1	9
4	0	2	7
4	1	2	47
4	2	2	4
4	3	2	10
4	5	2	16
4	0	3	157
4	1	3	18
4	2	3	75
4	4	3	68
4	6	3	30
4	0	4	22
4	1	4	92
4	2	4	10
4	3	4	33
4	5	4	43
4	0	5	22
4	1	5	14
4	2	5	12
4	3	5	21
4	4	5	6
4	1	6	94
4	2	6	12
4	3	6	13
4	5	6	48
4	0	7	109
4	1	7	40
4	2	7	19
4	3	7	8
4	4	7	44
4	0	8	14
4	1	8	22
4	2	8	4
4	3	8	14
4	0	9	53
4	1	9	18
4	2	9	27
4	3	9	12
4	4	9	23
4	0	10	6
4	1	10	53
4	2	10	10
4	3	10	14
4	4	10	5
4	0	11	24
4	3	11	4
4	4	11	20
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5	4	0	72
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5	2	2	31
5	4	2	19
5	7	2	15
5	1	3	74
5	2	3	36
5	3	3	92
5	4	3	4
5	6	3	10
5	7	3	15
5	1	4	26
5	2	4	75
5	3	4	4
5	4	4	59
5	1	5	7
5	2	5	8
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5	4	10	25
5	1	11	19
5	3	11	17
5	2	12	19
5	3	12	7
5	4	12	7
5	1	13	20
5	2	13	10
5	3	13	24
6	0	0	96
6	1	0	98
6	3	0	12
6	4	0	45
6	5	0	32
6	6	0	20
6	7	0	9
6	0	1	27
6	1	1	42
6	2	1	23
6	3	1	19
6	4	1	14
6	6	1	12
6	0	2	23
6	1	2	28
6	4	2	13
6	5	2	11
6	0	3	107
6	1	3	50
6	2	3	38
6	3	3	40
6	4	3	34
6	5	3	31
6	6	3	28
6	0	4	57
6	1	4	64
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6	3	5	19
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6	2	6	10
6	4	6	29
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6	4	9	8
6	0	10	29
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6	2	13	8
7	1	0	76
7	2	0	53
7	3	0	79
7	4	0	30
7	7	0	16
7	1	1	29
7	2	1	46
7	3	1	41
7	4	1	18
7	5	1	13
7	6	1	15
7	1	2	16
7	3	2	13
7	4	2	8
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7	6	2	14
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7	6	3	12
7	1	4	51
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7	3	4	43
7	4	4	11
7	1	5	18
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7	1	6	26
7	2	6	26
7	4	6	28
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7	3	7	27
7	4	7	12
7	1	8	5
7	2	8	18
7	4	8	7
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7	3	9	12
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7	1	10	25
7	2	10	18
7	3	10	29
7	4	10	14
7	1	11	11
7	2	11	13
7	3	11	10
7	4	11	3
7	1	12	7
7	3	12	15
7	1	13	6
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8	5	0	10
8	6	0	22
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8	1	1	36
8	2	1	16
8	3	1	11
8	5	1	25
8	6	1	12
8	7	1	10
8	0	2	39
8	2	2	26
8	3	2	9
8	4	2	21
8	0	3	19
8	1	3	72
8	2	3	11
8	5	3	33
8	0	4	45
8	1	4	20
8	2	4	32
8	3	4	15
8	4	4	35
8	0	5	12
8	1	5	9
8	4	5	7
8	0	6	75
8	1	6	7
8	2	6	10
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8	4	6	31
8	1	7	43
8	2	7	11
8	3	7	19
8	0	8	14
8	1	8	6
8	2	8	5
8	4	8	11
8	1	9	29
8	2	9	7
8	3	9	5
8	4	9	6
8	0	10	37
8	1	10	12
8	2	10	13
8	4	10	23
8	0	11	10
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8	4	11	8
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9	2	0	19
9	3	0	56
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9	4	1	20
9	1	2	14
9	3	2	18
9	6	2	11
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9	2	3	54
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9	1	4	32
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9	4	4	8
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14	0	1	11
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14	2	2	18
14	0	3	17
14	3	3	6
14	1	4	11
14	1	5	4
14	1	6	9
15	1	0	6
15	1	2	6
15	1	3	7

TABLE II

meta and *para* DISTANCES IN 12 B REFINED STRUCTURE[a]

Atoms	Distance, A
meta Over-all $\sigma = 0.035$	
1–7	2.56
1–8	2.79
1–9	2.86
3–5	2.86
3–6	2.89
3–9	2.83
3–11	2.89
3–12	2.85
4–6	3.00
4–7	2.76
4–10	3.01
4–12	2.94
5–8	2.90
5–12	2.81
7–9	2.73
8–10	2.89
8–11	2.93
para Over-all $\sigma = 0.061$	
1–12	3.26
5–7	3.21
2–9	3.35
4–11	3.49

[a] Over-all standard deviations obtained by averaging equivalent distances and applying the formula $\sigma = [\sum_{i=1}^{n} (x_i - \bar{x})^2/(N - 1)]^{1/2}$.

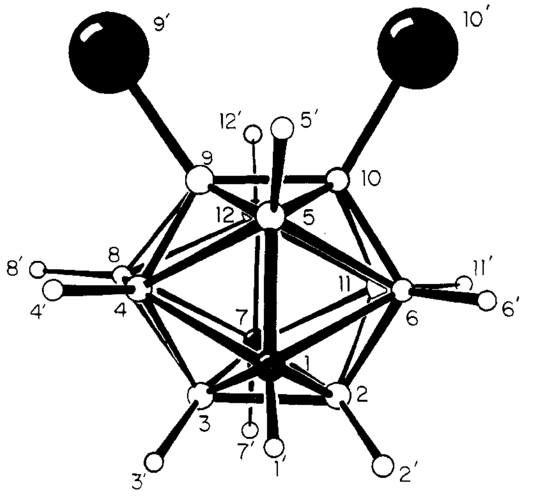

Figure 1.—The molecular structure and numbering scheme for m-$B_{10}Br_2H_8C_2H_2$. Atoms are designated as follows: H (1', 2', 3', 4', 5', 6', 7', 8', 11', 12'); C (1, 7); B (2, 3, 4, 5, 6, 8, 9, 10, 11, 12); Br (9', 10').

TABLE III

FINAL VALUES OF R_F FOR 685 REFLECTIONS

hkl	R_F
All ($h, k, l \neq 0$)	0.109
h even	0.120
h odd	0.102
k even	0.109
k odd	0.110
l even	0.113
l odd	0.107
$k + l$ even	0.119
$k + l$ odd	0.100
$h + l$ even	0.104
$h + l$ odd	0.115
$h + k$ even	0.124
$h + k$ odd	0.096
$h + k + l$ even	0.113
$h + k + l$ odd	0.106

Range of sin θ	R_F	No. of reflections
0.00–0.40	0.087	89
0.40–0.50	0.068	71
0.50–0.60	0.080	109
0.60–0.65	0.097	56
0.65–0.70	0.140	63
0.70–0.75	0.129	69
0.75–0.80	0.203	64
0.80–0.85	0.144	74
0.85–0.90	0.203	64
0.90–1.00	0.212	26

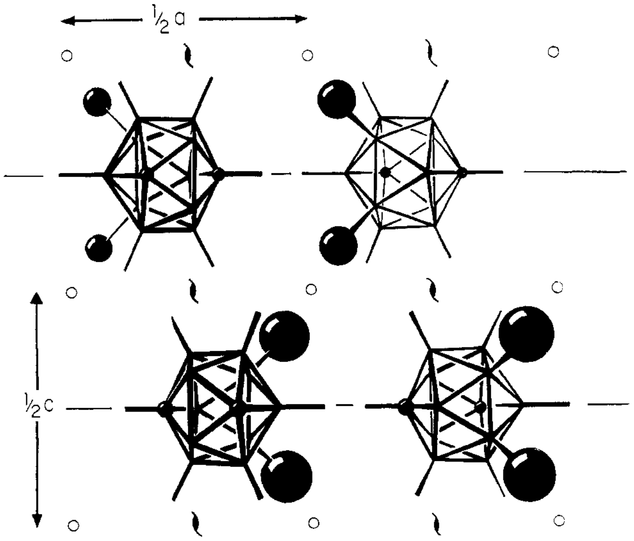

Figure 2.—The molecular packing as seen in $h0l$ projection. Only those symmetry elements necessary to generate the space group are shown. Hydrogen atoms are omitted where necessary for clarity.

tances (Table V) have been made for thermal motion, because the large standard deviations did not make a rigid body refinement seem worth the effort. In Table VI the bond distances are given on the assumption that the molecule has C_{2v} symmetry. Final *meta* distances are in Table VII.

The m-carborane framework has the C atoms nonadjacent, in disagreement with the adjacent-carbon model.[14] An electron diffraction study[15] of m-$B_{10}C_2H_{12}$ did not yield a unique result but supported a slightly distorted icosahedral model. Our results (Table VI) are in excellent agreement with the average distances B–C = 1.70 ± 0.11 and B–B = 1.75 ± 0.06 A, and consistent with the average B–Cl distance of 1.79 ± 0.05 A found in m-$B_{10}Cl_{10}C_2H_2$.[16] Thus the difference of 0.20 A between B–Br and B–Cl is exactly that observed in our studies[6,7] of derivatives of o-$B_{10}C_2H_{12}$. Here, as in o-$B_{10}C_2H_{12}$ derivatives, it seems clear that the C atoms share in the electron deficiency

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(14) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

(15) R. K. Bohn and M. D. Bohn, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(16) J. A. Potenza and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1917 (1966).

TABLE IV

FINAL POSITION PARAMETERS IN FRACTIONS OF CELL LENGTHS AND THERMAL PARAMETERS ($\times 10^4$)[a-c]

Atom	No.	x	σx	y	σy	z	σz
C	1	0.158	0.002	0.694	0.004	0.250	
B	3	0.256	0.002	0.674	0.004	0.325	0.001
B	4	0.143	0.001	0.594	0.003	0.367	0.001
B	5	0.070	0.001	0.511	0.003	0.250	
C	7	0.309	0.001	0.504	0.003	0.250	
B	8	0.252	0.001	0.436	0.003	0.366	0.001
B	9	0.135	0.001	0.346	0.003	0.320	0.001
B	12	0.242	0.001	0.289	0.004	0.250	
Br	9′	0.5815	0.0001	0.3465	0.0003	0.0987	0.0001
H	1′	0.130		0.865		0.250	
H	2′	0.301		0.790		0.376	
H	4′	0.107		0.651		0.451	
H	5′	0.976		0.523		0.250	
H	7′	0.396		0.501		0.250	
H	8′	0.293		0.380		0.448	
H	12′	0.273		0.123		0.250	

Atom	No.	β_{11}	$\sigma\beta_{11}$	β_{22}	$\sigma\beta_{22}$	β_{33}	$\sigma\beta_{33}$	β_{12}	$\sigma\beta_{12}$	β_{13}	$\sigma\beta_{13}$	β_{23}	$\sigma\beta_{23}$
C	1	280	26	1189	166	324	35	35	65	177	37	−415	87
B	3	90	17	519	89	46	7	−42	31	−11	9	−48	27
B	4	94	15	413	66	71	11	34	19	40	11	61	21
B	5	65	14	387	86	226	30	18	25	−17	35	−271	98
C	7	49	11	1580	134	282	25	−107	36	43	27	−555	68
B	8	48	8	364	80	46	8	49	16	13	7	14	21
B	9	65	7	223	58	21	6	−24	19	5	6	−44	15
B	12	203	21	481	88	204	23	46	27	162	25	64	62
Br	9′	91	1	297	6	60	1	−47	2	−10	1	−27	2

[a] The thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Standard deviations (σ) were obtained from the full least-squares matrix after the final refinement of all position and temperature parameters. [c] The H atom positions were not refined and are assigned no σ values. All the H atoms were given isotropic temperature factors $\beta = 3.30$.

TABLE V

BOND DISTANCES[a,b]

Bond	Length, A	σ
	Br–Br	
9′–10′	3.82	0.007
	B–Br	
9–9′	1.99	0.017
	C–B	
1–3	1.61	0.027
1–4	1.65	0.026
1–5	1.73	0.032
7–3	1.68	0.034
7–8	1.72	0.017
7–12	1.76	0.032
	B–B	
3–2	1.89	0.035
3–4	1.68	0.031
3–8	1.76	0.038
4–5	1.86	0.024
4–8	1.81	0.029
4–9	1.85	0.029
5–9	1.69	0.024
8–9	1.76	0.023
8–12	1.80	0.025
9–10	1.77	0.024
9–12	1.71	0.020

[a] Bond distances have not been corrected for thermal motion. [b] Standard deviations were computed from the full variance–covariance matrix calculated for all positions and temperature factors after the final refinement.

TABLE VI

AVERAGED DISTANCES[a]

Type	No. averaged	Length, A	σ
	Averaged to C_{2v}		
1–3	2	1.64	0.050
1–4	2	1.68	0.050
1–5	2	1.74	0.022
2–3	1	1.89	0.035
3–4	2	1.72	0.057
4–5	2	1.83	0.042
4–8	1	1.81	0.029
4–9	2	1.80	0.064
9–10	1	1.77	0.024
	Averaged Bond Types		
B–C	6	1.69	0.056
B–B	11	1.78	0.070
Br–Br	1	3.82	0.007
B–Br	1	1.99	0.017

[a] The standard deviations were obtained by averaging distances and applying the formula in footnote *a* of Table II except in single cases where standard deviations are from Table IV.

of bonding in the icosahedral cage. Of particular interest in m-$B_{10}Br_2H_8C_2H_2$ is the remarkably long B(2)–B(3) bond of 1.89 ± 0.04 A, indicative probably of the tendency of the C atoms to remove electrons preferentially from the vicinal B atoms. This same B(2)–B(3) length is 1.89 ± 0.06 A in m-$B_{10}Cl_{10}C_2H_2$.[16]

The position of attack in the Friedel–Crafts reaction is clearly B(9) and B(10) in m-$B_{10}C_2H_{12}$. The charge distribution as predicted in the early molecular orbital study is −0.16 for B(9) and B(10), −0.03 for B(5) and B(12), −0.03 for B(4), B(6), B(8), and B(11), and +0.10 for B(2) and B(3). Recent studies, which employ parameters for B from the self-consistent-field wave function[3] for B_4H_4, and which also employ two-

TABLE VII

FINAL *meta* DISTANCES[a]

Atoms	Length, A	σ
1–7	2.39	0.031
1–8	2.64	0.032
1–9	2.63	0.036
3–5	2.86	0.033
3–6	2.91	0.029
3–9	2.81	0.035
3–11	2.94	0.030
3–12	2.89	0.042
4–6	2.96	0.039
4–7	2.72	0.022
4–10	2.95	0.028
4–12	2.90	0.029
5–8	2.85	0.023
5–12	2.75	0.023
7–9	2.69	0.023
8–10	2.88	0.021
8–11	2.93	0.027

[a] Standard deviations obtained as in Table IV.

center zero overlap interactions as calibrated by total energy matrix elements[2] in B_4H_4, yield charges[17] of -0.25 for B(9) and B(10), -0.06 for B(5) and B(12), -0.03 for B(4), B(6), B(8), and B(11), and $+0.13$ for B(2) and B(3). Thus, the most negative B atoms of the ground state of m-$B_{10}C_2H_{12}$, namely B(9) and B(10), still survive improvements and elimination of arbitrary parameters in the molecular orbital methods. No doubt these charges are exaggerated by lack of self-consistency in these methods, but, where striking differences of charges occur, the results may be significant. Caution, however, should be applied when little difference occurs, for example between B(4) and B(5). If the reaction is indeed electrophilic, and if the transition state is influenced by the ground-state charge distribution, these charges given by molecular orbital theory do predict that Br substitution should take place, as observed, at B(9) and B(10).

It is also possible to assign some parts of the ^{11}B nuclear magnetic resonance spectrum. In Figure 3 we compare the ^{11}B nmr spectra of m-$B_{10}Br_2H_8C_2H_2$, m-$B_{10}H_{10}C_2H_2$, and m-$B_{10}Cl_{10}C_2H_2$. The most interesting aspect of these spectra is that the low-field component of the lowest field doublet of m-$B_{10}H_{10}C_2H_2$ appears to remain present when positions 9 and 10 are brominated. It is then probable that B(9) and B(10) are not the lowest field ^{11}B resonances, but are part of the group assigned to six B atoms in m-$B_{10}H_{10}C_2H_2$: a downfield shift, consistent with that found[5] in brominated o-$B_{10}H_{10}C_2H_2$, is also indicated by these assignments when H atoms on B(9) and B(10) are substituted by Br atoms. From these definite conclusions we then conjecture that the assignment is B(2), B(3) (35.4 ppm); B(4), B(6), B(8), B(11) (31.7 ppm); B(9), B(10) (29.1 ppm); and B(5), B(12) (25.1 ppm). For the last two peaks, this conjecture reverses the previous guess,[5] based upon a comparison with o-$B_{10}H_{10}C_2H_2$, and produces more scatter in the graph[18] of chemical shift *vs.* a function of overlap population. Nevertheless, the slope of the graph and the basic conclusions are substantially unchanged. Clearly, a systematic study of other B-substituted derivatives of m-$B_{10}H_{10}C_2H_2$ is desirable before any assignment of the ^{11}B nmr spectrum is to be considered as definite.

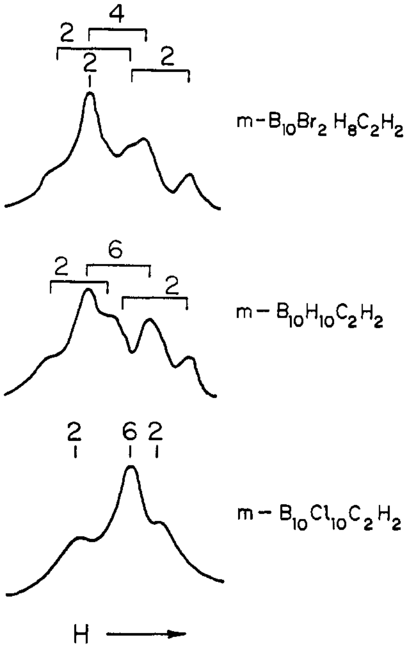

Figure 3.—The ^{11}B nuclear magnetic resonance spectra of m-$B_{10}Br_2H_8C_2H_2$ (15 Mc), m-$B_{10}H_{10}C_2H_2$ (19.3 Mc), and m-$B_{10}Cl_{10}C_2H_2$ (19.3 Mc). The magnetic field increases from left to right. Tentative groupings of symmetry equivalent ^{11}B resonances are indicated as singlets where B is halogenated and as (highly approximate) doublets for BH.

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(17) M. D. Newton and W. N. Lipscomb, unpublished results. A slight lack of rotational invariance in these wave functions has required an average at each B atom.

(18) F. P. Boer, R. A. Hegstrom, M. D. Newton, J. A. Potenza, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 5340 (1966).