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

Molecular Structure of Carboranes. Molecular and Crystal Structure of o-$B_{10}Br_3H_7C_2H_2$

BY JOSEPH A. POTENZA AND WILLIAM N. LIPSCOMB

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The bromination of o-$B_{10}H_{10}C_2H_2$ in the presence of $AlCl_3$ produces o-$B_{10}Br_3H_7C_2H_2$ in which the Br atoms are at the 8 (or 10), 9, and 12 positions of the $B_{10}C_2$ polyhedron. These results are consistent with the structure of the 9,12-dibrominated compound, o-$B_{10}Br_2H_8C_2H_2$, and with the correlation of reactivity with ground-state charge distribution obtained earlier from extended Hückel theory and here from a new nonempirical molecular orbital theory. The space group is C2/c, and there are eight molecules in a unit cell having parameters $a = 12.28$, $b = 8.54$, $c = 23.42$ A, and $\beta = 90.3°$.

Introduction

The elucidation of the structure of o-$B_{10}Br_3H_7C_2H_2$,[1] the final product of stepwise substitution of unsubstituted o-carborane with Br_2 in the presence of $AlCl_3$, completes structural work on the known Br derivatives of o-carborane. The 9,12 substitution of Br in o-$B_{10}Br_2H_8C_2H_2$, established in the preceding paper,[2] implies the structure of o-$B_{10}BrH_9C_2H_2$. It seems probable to us that this reaction of Br_2 is electrophilic and that the ground-state charge distribution in the parent o-$B_{10}H_{10}C_2H_2$ determines the charge distribution of the transition state well enough to indicate the major features of sequential substitution. We are well aware of the qualifications[2] of this idea but are interested in its limitations and whether exceptions are primarily those of complex reactions for which the initial steps, when not sterically controlled, also follow this pattern.

Here we show that the three Br atoms attached in o-$B_{10}Br_3H_7C_2H_2$ are in a very nearly equilateral triangular arrangement, which, together with the structure of o-$B_{10}Br_2H_8C_2H_2$, is sufficient to prove that the halogens are in the 8 (or 10), 9, and 12 positions. Our failure to distinguish between C and B, however, suggests that the $B_{10}C_2$ cage is disordered in all senses in which the three Br atoms of the triangle can be permuted. Finally, we compare the experimental results with aspects of the ground-state charge distribution[3,4] in o-$B_{10}H_{10}C_2H_2$ and establish the assignment of peaks in the ^{11}B 64.2-Mc nuclear magnetic resonance (nmr) spectra[5,6] of these compounds.

Structure Determination

A large single crystal of o-$B_{10}Br_3H_7C_2H_2$, from acetone solution, was cut into cubes 0.03 mm on edge. Two crystals, one mounted on the b axis and one on the c axis, were used for data collection. Reciprocal lattice symmetry of 2/m and unit cell parameters of $a = 12.28 \pm 0.02$, $b = 8.54 \pm 0.02$, $c = 23.42 \pm 0.02$ A, and $\beta = 90.3 \pm 0.4°$ were established from photographs. The assumption of eight molecules in the unit cell led to the reasonable calculated density of 2.06 g cm^{-3} for the crystals. Extinctions of hkl when $h + k$ is odd and of $h0l$ when l is odd lead to possible space groups Cc or C2/c. The Br arrangement found as described below established C2/c as the correct space group.

The three-dimensional data were collected with the use of an Xe proportional counter on the Buerger automated X-ray diffractometer, using a scan time which was proportional to the Lorentz factor. Within each level one reflection was chosen as a monitor and measured after each group of 15 reflections. After each level was completed, a set of six zero-level reflections was measured. Equivalent reflections agreed to within $2\sigma_c$, where σ_c is the square root of the total number of counts. A total of 2172 independent reflections was recorded for levels $0 \leqslant k \leqslant 8$ and $0 \leqslant l \leqslant 7$. After correction for Lorentz and polarization factors, the data were correlated to a single scale with the use of weights which were inversely proportional to the net number of counts for $F_o^2 \geqslant \bar{\sigma}_c$ and which were inversely proportional to $\bar{\sigma}_o$ for $F_o^2 \leqslant \bar{\sigma}_c$. Here σ_c is the square root of the counts in background plus scan for a reflection having zero net count, and the average $\bar{\sigma}_c$ is taken over all σ_c in the sphere of reflection. The correlated F_o are shown in Table I. Of the 2172 measured values of F_o^2, 1132 were greater than $1.5\bar{\sigma}_c$ after background corrections, and all reflections less than $1.5\bar{\sigma}_c$ ($F_o < 75$ on the scale of those in Table I) were excluded from final refinements and discrepancy factors.

Analysis of the three-dimensional Patterson function yielded a near-equilateral triangular arrangement for the three Br atoms if the space group C2/c was assumed. Peak heights at all positions for Br···Br interactions were 1200 ± 100 on an arbitrary scale. No such internally consistent interpretation was possible in the space group Cc. These Br contributions gave a value of $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.36. A three-dimensional electron density map based upon signs for the Br contributions showed 52 candidates for light atoms in the range from 30 to 60% of the height of a B atom, but 12 of these formed an icosahedral structure appropriately

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TABLE I

LIST OF OBSERVED F_{hkl} VALUES[a,b]

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L= 0 (K)(H)( 0)(  0,14)4804,427,515,551,377,73,78,0,( 1)(  1,13)508,866,487,
112,232,62,116,( 2)(  0,14)650,479,931,0,79,55,104,32,( 3)(  1,13)475,45,615,
313,190,214,27,( 4)(  0,12)255,46,302,261,87,118,35,( 5)(  1,13)143,33,88,251,
220,0,0,( 6)(  0,12)149,208,276,259,58,52,31,( 7)(  1,11)99,160,25,114,0,20,
( 8)(  0, 8)387,224,58,54,58,( 9)(  1, 7)120,170,68,43,(10)(  0, 4)66,69,53
L= 1 (K)(H)( 1)(-13,13)65,54,195,389,200,176,392,335,637,153,348,342,103,20,
( 2)(-14,14)44,136,77,0,476,715,691,751,166,220,362,275,267,119,0,( 3)(-13,13)
0,231,69,338,139,217,31,634,77,792,69,184,57,30,( 4)(-12,12)97,214,451,206,
292,390,205,550,565,465,433,76,59,( 5)(-13,13)34,139,181,237,41,50,197,268,
335,759,139,181,79,33,( 6)(-12,12)78,50,37,249,257,262,360,21,306,285,114,118,
0,( 7)(-11,11)0,68,218,0,0,19,381,204,50,248,241,0,( 8)( -8, 8)0,85,0,23,226,
44,117,105,27,( 9)( -7, 7)0,51,0,130,50,87,118,24,(10)( -4, 4)129,137,31,6,
48
L= 2 (K)(H)( 0)(-14,14)65,146,47,59,1500,899,108,U,351,277,50,253,680,87,37,
( 1)(-13,13)53,206,317,709,521,1252,767,615,486,244,445,380,211,91,
( 2)(-14,14)56,0,320,481,429,167,1092,164,276,0,473,363,178,93,87,( 3)(-13,13)
51,224,0,588,65,127,848,792,460,596,177,79,163,37,( 4)(-12,12)81,77,120,79,
61,269,145,87,218,120,80,68,0,( 5)(-13,13)43,0,74,99,83,212,197,378,465,176,
75,91,59,34,( 6)(-12,12)91,159,92,119,179,181,239,37,279,259,105,112,37,
( 7)(-11,11)0,65,72,73,156,0,128,133,23,110,75,8,( 8)( -8, 8)113,280,201,42,
0,74,32,0,88,( 9)( -7, 7)86,89,208,95,83,134,36,39,(10)( -4, 4)20,92,23,10,
57
L= 3 (K)(H)( 1)(-13,13)79,57,0,286,646,761,62,466,913,182,72,38,67,73,
( 2)(-14,14)12,94,182,179,430,331,614,126,359,630,650,259,194,39,0,
( 3)(-13,13)40,56,91,76,158,63,853,394,446,64,356,24,35,38,( 4)(-12,12)79,121,
164,83,474,657,617,1033,26,185,324,101,104,( 5)(-13,13)28,33,78,258,192,97,
880,537,374,55,254,108,47,0,( 6)(-12,12)40,29,85,193,0,437,201,201,499,244,
44,56,36,( 7)( -9, 9)90,0,339,373,27,109,472,118,78,25,( 8)( -8, 8)48,142,18,
203,0,51,206,82,43,( 9)( -7, 7)121,74,66,214,122,63,140,45,(10)( -2, 2)30,23,
70
L= 4 (K)(H)( 0)(-14,14)110,256,295,494,310,75,491,U,414,2565,981,583,69,174,
0,( 1)(-13,13)110,91,558,107,247,354,327,623,957,402,672,191,88,82,
( 2)(-14,14)125,95,105,447,198,180,187,691,712,460,197,721,33,99,31,
( 3)(-13,13)63,90,76,432,434,265,539,236,415,127,176,354,174,0,( 4)(-12,12)
47,65,205,120,169,118,109,164,140,25,209,81,52,( 5)(-11,11)34,113,151,366,481,
204,11,199,70,63,57,33,( 6)(-12,12)30,61,95,101,105,292,264,236,141,155,146,
108,20,( 7)( -9, 9)75,28,84,140,31,156,107,35,94,39,( 8)( -8, 8)55,70,71,74,
81,217,339,191,26,( 9)( -7, 7)85,23,55,57,108,50,175,101,(10)( -2, 2)16,81,
110
L= 5 (K)(H)( 1)(-13,13)103,189,325,170,308,606,300,148,423,392,267,96,94,69,
( 2)(-14,14)31,99,80,373,177,144,461,858,549,429,158,158,0,0,0,( 3)(-13,13)
40,83,90,556,346,624,298,453,67,145,105,278,61,48,( 4)(-12,12)0,27,315,260,
981,290,51,385,318,200,197,80,118,( 5)(-11,11)69,67,384,314,294,213,208,224,
67,69,290,32,( 6)(-10,10)31,300,59,293,284,468,169,117,82,115,64,( 7)( -9, 9)
227,20,0,358,94,232,0,162,245,0,( 8)( -8, 8)90,58,65,112,170,51,68,54,44,
( 9)( -7, 7)118,132,18,69,68,117,81,0,(10)( -2, 2)131,136,182
L= 6 (K)(H)( 0)(-14,14)103,107,103,206,138,73,1577,1478,984,214,365,275,94,
90,53,( 1)(-13,13)131,83,155,149,218,986,397,1382,194,643,555,189,53,0,
( 2)(-14,14)30,47,120,143,347,654,246,218,929,393,422,68,62,105,36,
( 3)(-13,13)61,162,107,211,101,514,200,293,610,735,58,177,124,7,( 4)(-12,12)
43,67,116,134,373,48,98,342,42,192,117,72,35,( 5)(-11,11)87,194,121,94,46,145,
267,145,195,321,135,47,( 6)(-10,10)23,190,300,130,46,182,199,144,46,122,75,
( 7)( -9, 9)25,41,129,95,52,146,27,107,34,0,( 8)( -8, 8)50,81,183,354,283,0,
0,53,19,( 9)( -5, 5)70,112,115,258,122,0,(10)( -2, 2)0,29,110
L= 7 (K)(H)( 1)(-13,13)0,0,183,182,210,533,638,768,285,116,451,219,0,62,
( 2)(-12,12)53,0,155,448,175,181,89,382,15,241,332,268,0,( 3)(-13,13)8,141,
94,288,16,83,124,79,741,422,239,58,172,10,( 4)(-12,12)40,325,149,0,191,160,
221,377,286,844,42,0,112,( 5)(-11,11)94,118,284,91,68,151,61,585,407,216,138,
104,( 6)(-10,10)105,65,194,87,121,74,293,30,258,158,118,( 7)( -9, 9)35,65,165,
119,249,346,113,102,284,53
L= 8 (K)(H)( 0)(-14,14)0,61,60,392,743,566,777,584,151,810,199,375,285,53,0,
( 1)(-13,13)30,73,253,68,784,308,587,147,340,0,425,54,256,0,( 2)(-12,12)81,
248,122,353,535,466,642,447,144,604,113,89,182,( 3)(-13,13)0,0,201,252,81,340,
770,183,264,392,114,73,0,36,( 4)(-12,12)0,87,51,119,118,100,258,136,0,120,14,
0,52,( 5)(-11,11)0,U,65,255,312,311,438,246,64,95,69,0,( 6)(-10,10)18,0,71,
37,100,36,268,286,156,44,85,( 7)( -9, 9)52,0,141,33,110,49,37,136,61,41
L= 9 (K)(H)( 1)(-13,13)0,89,124,349,457,187,191,411,286,245,141,129,122,20,
( 2)(-12,12)30,0,69,141,304,149,358,449,805,322,0,22,0,( 3)(-13,13)37,61,0,
71,68,408,524,223,408,444,173,111,0,0,( 4)(-12,12)0,48,51,80,204,117,923,427,
167,266,241,0,0,( 5)(-11,11)0,25,79,70,435,449,321,281,294,75,187,0,
( 6)(-10,10)0,12,0,201,129,281,96,452,0,34,63,( 7)( -9, 9)74,99,256,101,55,
240,183,234,86,0
L=10 (K)(H)( 0)(-14,14)52,68,99,355,37,34,372,320,1057,1227,361,362,255,0,0,
( 1)(-13,13)0,171,187,276,63,241,88,347,54,926,231,225,114,68,( 2)(-12,12)0,
93,107,74,248,234,411,0,317,476,272,280,0,( 3)(-13,13)27,0,51,368,228,0,132,
201,214,136,221,400,36,0,( 4)(-12,12)25,0,0,99,97,0,280,135,270,86,96,108,0,
( 5)(-11,11)16,45,133,215,169,154,139,68,160,119,0,81,( 6)(-10,10)14,0,72,213,
234,172,76,118,121,77,0,( 7)( -9, 9)18,38,31,0,143,107,59,70,0,67
L=11 (K)(H)( 1)(-13,13)27,0,37,72,79,111,330,642,399,395,200,22,91,39,
( 2)(-12,12)80,143,120,134,108,567,441,83,93,0,153,91,0,( 3)(-13,13)0,36,117,
187,151,425,117,244,151,0,200,196,0,0,( 4)(-12,12)0,0,0,426,278,191,140,327,
80,0,82,236,10,( 5)(-11,11)58,0,204,98,399,57,186,224,152,103,151,35,
( 6)(-10,10)0,109,103,0,374,118,0,159,44,80,55,( 7)( -9, 7)0,83,62,143,190,
241,60,215,139
L=12 (K)(H)( 0)(-12,12)0,20,118,98,514,883,185,989,481,255,342,0,0,
( 1)(-13,13)0,64,0,0,226,109,863,377,551,0,378,95,0,55,( 2)(-12,12)64,110,99,
96,0,343,266,637,470,432,67,101,70,( 3)(-11,11)0,37,0,255,334,53,177,782,295,
75,179,0,( 4)(-12,12)0,0,0,67,108,140,25,0,245,77,85,42,0,( 5)(-11,11)23,0,
104,80,86,229,297,124,177,156,18,33,( 6)(-10,10)53,131,87,0,90,128,70,44,110,
145,13,( 7)( -7, 7)81,86,73,156,0,93,0,0
L=13 (K)(H)( 1)(-13,13)53,61,0,156,286,287,466,204,123,116,24,0,76,0,
( 2)(-12,12)0,42,146,170,0,148,125,231,140,101,362,100,0,( 3)(-11,11)0,139,
0,88,68,47,314,390,90,226,80,43,( 4)(-10,10)69,0,104,109,142,16,79,512,275,
71,42,( 5)(-11, 9)29,84,62,69,160,84,173,442,47,251,72,( 6)( -8, 8)109,116,
30,0,45,85,76,0,153,( 7)( -7, 7)45,140,56,149,164,46,100,62
L=14 (K)(H)( 0)(-12,12)62,76,205,0,639,175,335,499,347,226,290,47,0,
( 1)(-13,11)61,90,61,296,228,438,332,499,21,234,175,132,25,( 2)(-12,12)36,37,
102,0,U,110,412,0,141,171,143,0,82,( 3)(-11,11)0,133,45,54,421,337,145,81,0,
215,0,6,( 4)(-10,10)52,42,0,80,95,200,52,0,181,0,50,( 5)( -9, 9)40,0,168,150,
115,109,119,111,31,0,( 6)( -8, 8)0,47,0,100,180,217,118,0,88,( 7)( -7, 7)22,
61,0,84,0,67,18,37
L=15 (K)(H)( 1)(-11,11)56,0,82,47,73,63,0,218,325,93,58,55,( 2)(-12,12)0,0,
65,90,145,58,51,537,352,0,0,87,42,( 3)(-11,11)26,0,0,141,217,93,402,0,249,141,
0,6,( 4)(-10,10)0,0,0,0,372,392,171,76,254,29,23,( 5)( -9, 9)0,39,118,243,74,
344,0,150,106,56,( 6)( -8, 8)0,0,123,37,55,278,140,82,75,( 7)( -7, 7)53,59,
64,20,124,90,198,0
L=16 (K)(H)( 0)(-12,12)30,89,0,0,195,274,300,513,183,343,0,0,56,( 1)(-11,11)
71,0,173,134,219,66,95,388,288,202,54,0,( 2)(-10,10)68,0,146,87,72,117,78,49,
305,54,158,( 3)(-11,11)23,48,108,0,35,138,356,113,58,262,143,28,( 4)(-10,10)
46,33,45,38,17,103,71,128,34,39,33,( 5)( -9, 9)50,37,47,41,145,46,36,147,0,
26,( 6)( -8, 8)43,30,148,69,65,0,75,0,0,( 7)( -5, 5)0,21,40,26,83,37
L=17 (K)(H)( 1)(-11,11)0,0,83,0,62,422,237,0,143,47,0,0,( 2)(-10,10)56,0,0,
201,169,65,54,0,99,85,0,( 3)(-11,11)0,12,0,158,66,201,100,149,34,103,23,0,
( 4)(-10,10)18,103,136,10,116,207,102,80,24,89,67,( 5)( -9, 9)0,0,164,110,114,
69,191,54,79,25,( 6)( -8, 6)0,0,125,165,56,46,20,0,( 7)( -5, 5)37,0,138,70,
18,113
L=18 (K)(H)( 0)(-10,10)0,0,71,156,0,551,140,250,177,135,0,( 1)(-11,11)0,78,
0,0,176,335,176,235,198,43,79,0,( 2)(-10,10)45,0,42,91,69,385,0,391,71,50,101,
( 3)( -9, 9)22,0,81,103,0,241,244,92,0,53,( 4)( -8, 8)0,0,10,60,77,28,116,0,
55,( 5)( -7, 7)45,44,21,151,139,87,74,0,( 6)( -6, 6)29,30,38,0,59,67,80,
( 7)( -5, 3)0,79,19,0,59
L=19 (K)(H)( 1)(-11,11)0,0,0,112,110,79,0,54,0,74,51,0,( 2)(-10,10)0,37,0,108,
99,105,79,25,160,108,67,( 3)( -9, 9)23,32,0,0,99,135,0,120,0,40,( 4)( -8, 8)
0,0,63,0,57,159,233,0,0,( 5)( -7, 7)53,37,0,0,65,42,109,0,( 6)( -6, 6)0,52,
68,46,60,44,72,( 7)( -3, 3)0,39,44,44
L=20 (K)(H)( 0)(-10,10)43,0,92,114,88,100,307,0,0,54,0,( 1)( -9, 9)39,116,60,
182,122,234,126,47,0,0,( 2)( -8, 8)31,34,63,168,140,11,99,108,32,( 3)( -9, 9)
29,0,0,113,0,139,54,102,48,23,( 4)( -8, 8)0,0,56,109,34,48,0,58,41,
( 5)( -7, 7)24,0,0,0,0,60,0,12,( 6)( -4, 4)24,50,96,41,187,( 7)( -1, 1)0,0
L=21 (K)(H)( 1)( -9, 9)35,0,83,0,0,61,109,62,0,0,( 2)( -8, 8)21,86,37,0,161,
216,90,0,0,( 3)( -9, 7)21,27,120,0,102,55,134,70,41,( 4)( -8, 8)0,0,82,101,
21,112,68,73,42,( 5)( -5, 5)0,0,0,38,45,34,( 6)( -4, 4)0,0,0,81,0
L=22 (K)(H)( 0)( -8, 8)58,0,102,124,50,0,141,0,70,( 1)( -9, 9)0,59,61,0,0,96,
138,0,0,46,( 2)( -8, 8)38,20,0,0,50,81,76,0,38,( 3)( -7, 7)29,0,69,49,78,0,
24,44,( 4)( -6, 6)24,38,58,0,16,0,0,( 5)( -5, 5)0,46,17,0,0,0,( 6)( -2, 2)0,
34,0
L=23 (K)(H)( 1)( -7, 7)0,39,0,0,0,79,30,40,( 2)( -6, 6)16,75,101,88,0,0,0,
( 3)( -7, 7)17,49,29,0,73,0,45,36,( 4)( -6, 6)59,48,35,27,36,72,25,
( 5)( -3, 3)28,0,47,33
L=24 (K)(H)( 0)( -8, 8)0,53,0,78,43,68,0,32,0,( 1)( -7, 7)0,81,0,0,88,74,24,
26,( 2)( -6, 6)54,0,0,17,63,110,46,( 3)( -5, 5)38,43,20,74,26,38,( 4)( -4, 4)
48,0,24,0,0,( 5)( -3, 1)40,42,0
L=25 (K)(H)( 1)( -7, 7)29,34,54,0,0,40,0,8,( 2)( -6, 6)0,0,0,0,0,0,45,
( 3)( -5, 5)43,18,0,17,0,34,( 4)( -4, 2)40,0,0,0
L=26 (K)(H)( 0)( -6, 6)56,38,0,47,87,0,27,( 1)( -5, 5)31,0,41,0,46,0,
( 2)( -4, 4)42,0,44,40,0,( 3)( -3, 3)28,13,29,33,( 4)(  0, 0)29
L=27 (K)(H)( 1)( -3, 3)26,14,66,27,( 2)( -2, 2)23,23,0,( 3)( -1, 1)0,0
L=28 (K)(H)( 0)( -2, 2)0,0,42,( 1)( -1, 1)74,0
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[a] F_{hkl} is listed followed by a comma. The general extinction (hkl, $h + k = 2n + 1$) is not indicated; account must be taken of this when reading the table. Unobserved reflections are indicated by a zero, and experimentally unobserved reflections by a U. All reflections are on the same scale as F_{000}, given as a reference point. The summation for F_{000} is for the entire unit cell. All F_{hkl} values are included for which F_o as measured by the diffractometer was greater than zero (however, see text for those F_{hkl} values used in the refinement). [b] Scattering factors were used as obtained from the "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England, Vol. III, 1962, p 202 ff.

situated near the three Br atoms. Leat-squares refinement using anisotropic thermal parameters for these three Br and twelve light atoms yielded $R_F = 0.09$ for the 707 largest reflections, and two more cycles of anisotropic least-squares refinement led to $R_F = 0.12$ for the largest 1132 observed reflections. H atoms were added in expected (but not observed) positions, and a study was made of the possible disordering of B and C positions.

These studies, summarized in the present paragraph and in Tables II and III, suggest some disorder is likely. Atom numbers are shown in Figure 1, which shows the molecular structure. First, the *para* icosahedral distances were computed from the final X-ray structure assuming all icosahedral atoms to be B (column 2), after two cycles of refinement in which atoms 1, 2, and 6 are taken as $^2/_3$ C and $^1/_3$ B (a disorder produced by random permutation of triangle of Br_3 in positions 8, 9, and 12: column 3), and after two cycles in which atoms 1 and 2 are C and all others are taken as B (ordered structure: column 4). If one assumes B–B = 1.76, C–C = 1.64, and B–C = 1.70 A, one can calculate these *para* distances from an idealized model disordered as described above (column 5) and completely ordered (column 6). We see that the idealized disordered structure fits the X-ray results

TABLE II

para ICOSAHEDRAL DISTANCES

Atoms	12 B refined structure	Disordered[b]	Ordered[b]	Idealized disordered	Idealized ordered
1–12	3.17[a]	3.31 ± 0.038	3.30 ± 0.038	3.26	3.23
2–9	3.24	3.24 ± 0.036	3.24 ± 0.037	3.26	3.23
3–10	3.43	3.41 ± 0.042	3.41 ± 0.042	3.34	3.34
4–11	3.41	3.40 ± 0.035	3.40 ± 0.036	3.34	3.34
5–7	3.37	3.37 ± 0.035	3.37 ± 0.035	3.34	3.34
6–8	3.25	3.28 ± 0.047	3.27 ± 0.048	3.26	3.34

[a] The short 3.17 A is due to the fact that atom 12, owing to the proximity of the Br atom to which it is bonded, did not refine well until the C atoms were designated (as either ordered or disordered). [b] Standard deviations were obtained from the full variance–covariance matrix.

Table III
Evidence for the Inability to Determine C Atoms Unambiguously[a]

Atom	I[b]	II[c]	III[d]	IV[e]	V[f]
1	483	1.07 ± 0.09	1.01 ± 0.06	1.70	5.58
2	307	1.11 ± 0.05	1.06 ± 0.05	1.69	4.97
3	−42	1.03 ± 0.06	1.04 ± 0.06	1.73	5.56
4	−225	1.03 ± 0.05	1.01 ± 0.05	1.76	3.69
5	395	1.00 ± 0.07	1.02 ± 0.06	1.75	5.59
6	30[g]	1.06 ± 0.06	1.05 ± 0.05	1.71	6.26
7	56	1.06 ± 0.06	1.06 ± 0.06	1.74	4.49
8	461	0.99 ± 0.07	1.02 ± 0.07	1.75	5.74
9	240	1.02 ± 0.05	1.04 ± 0.05	1.80	4.69
10	110	1.00 ± 0.06	0.98 ± 0.06	1.78	5.82
11	9	1.01 ± 0.05	1.01 ± 0.05	1.77	4.05
12	193	1.01 ± 0.06	0.96 ± 0.05	1.73	2.93

[a] Standard deviations were calculated from the full least-squares matrix. [b] Three-dimensional linearly interpolated electron density at B positions from three-dimensional difference Fourier calculated on the basis of 12 B, 9 H, and 3 Br atoms with $R_F = 0.12$. One electron per cubic angstrom is 710 on this arbitrary scale. [c] The atom multipliers of the "12 B" atoms after two cycles of least-squares refinement of only the atom multipliers (from the $R_F = 0.12$ parameters). [d] The atom multipliers of the 12 cage atoms after two cycles of least-squares refinement of only the atom multipliers (from the parameters determined with 9 H, 3 Br, 9 B, and three $^2/_3$, $^1/_3$ B atoms, 1, 2, and 6). [e] The average nearest neighbor bond distances as calculated from the "12 B" $R_F = 0.12$ parameters. Standard deviations can be obtained from the average of the individual bond distances listed in Table V. [f] Average isotropic equivalents as calculated from the anisotropic temperature factors of the "12 B" $R_F = 0.12$ parameters. [g] This atom was 0.2 A from the highest (height 730) nonresidual peak in the map (one electron per cubic angstrom is 710).

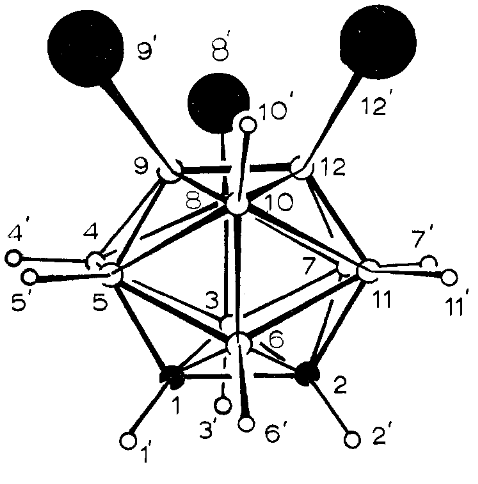

Figure 1.—The molecular structure and numbering scheme for o-$B_{10}Br_3H_7C_2H_2$. Atoms are designated as follows: H(1′,2′,3′,4′,5′,6′,7′,10′,11′); B(3,4,5,6,7,8,9,10,11,12); C(1,2); Br(8′,9′,12′).

slightly better than does the idealized ordered model, but the results are not conclusive. They do suggest that the disorder is most likely to involve atoms 1, 2, and 6. However, other possible choices, for example, of 1 and 6 for C and 2 for B, or of 2 and 6 for C and 1 for B, were expected to lead to similar results, but they were not refined. Other criteria for comparing ordered and disordered structures are summarized in Table III (see footnotes). In column 2 we see that the highest residual of electron density (possible C contribution) is at atoms 1, 2, 5, and 8, when the structure of 3 Br and 12 B is subtracted. Atom multipliers suggest atoms 1, 2, 6, and 7 (column 3) or atoms 2 and 6 (column 4) after refinement of the disordered structure. Closest bond distances (column 5) suggest atoms 1, 2, and 6 for shortening due to the smaller covalent radius of C as compared with B. The thermal parameters (column 6) are quite ambiguous as a criterion, most probably because absorption corrections were neglected. The R_F values of Table IV are simply not a local or detailed enough criterion for distinguishing between these models. Bond distances shown in Table V favor bond 1–2 as most nearly a C–C bond, but 1–6 and 2–6 cannot be excluded. One final, but somewhat negative, argument slightly in favor of some disorder is that our previous experience with comparable X-ray data from ordered crystals of comparable structures has led to more conclusive distinction between B and C than we have found here.

Table IV
Final Values For $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for 1132 of 2172 Reflections

	R_F Ordered	R_F Disordered
All (h, k, $l \neq 0$)	0.110	0.110
h even	0.110	0.109
h odd	0.110	0.110
k even	0.110	0.109
k odd	0.110	0.110
l even	0.116	0.116
l odd	0.105	0.104
$k + l$ even	0.111	0.111
$k + l$ odd	0.109	0.109
$h + l$ even	0.111	0.111
$h + l$ odd	0.109	0.109
$h + k$ even	0.110	0.110
$h + k + l$ even	0.116	0.116
$h + k + l$ odd	0.105	0.104
Over-all	0.1196	0.1194
R_{wF^2}[a]	0.302	0.301
R_{F^2}[b]	0.215	0.215

Range of sin θ	R_F Ordered	R_F Disordered	No. of reflections
0.00–0.40	0.101	0.102	161
0.40–0.50	0.108	0.108	152
0.50–0.60	0.125	0.125	205
0.60–0.65	0.121	0.121	124
0.65–0.70	0.120	0.119	127
0.70–0.75	0.146	0.146	115
0.75–0.80	0.156	0.155	111
0.80–0.85	0.149	0.149	78
0.85–0.90	0.202	0.202	40
0.90–1.00	0.163	0.163	19

[a] $R_{wF^2} = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4]^{1/2}$. [b] $R_{F^2} = \Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2$.

In spite of the possible disorder, the molecular structure is certain. In particular, the 8 (or 10), 9, and 12 positions of the three Br seem to us to be unambiguously established, especially since this is the only way that a

TABLE V

BOND DISTANCES

Bond	Bond length,[a] A ordered	σ, A	Bond length,[a] A disordered	σ, A
	Br–Br		Br–Br	
8′–9′	3.90	0.007	3.90	0.004
8′–12′	3.88	0.006	3.88	0.006
9′–12′	3.91	0.006	3.91	0.004
	B–Br		B–Br	
8–8′	1.99	0.038	1.99	0.038
9–9′	1.94	0.024	1.94	0.024
12–12′	1.98	0.025	1.98	0.025
	C–C		($^2/_3$ C, $^1/_3$ B)–($^2/_3$ C, $^1/_3$ B)	
1–2	1.65	0.044	1.66	0.044
1–6			1.70	0.051
2–6			1.71	0.034
	B–C		($^2/_3$ C, $^1/_3$ B)–B	
1–3	1.74	0.042	1.74	0.042
1–4	1.68	0.041	1.68	0.041
1–5	1.76	0.036	1.77	0.036
1–6	1.68	0.051		
2–3	1.68	0.046	1.68	0.045
2–6	1.71	0.035		
2–7	1.66	0.035	1.66	0.035
2–11	1.75	0.037	1.75	0.037
5–6			1.65	0.047
6–10			1.72	0.034
6–11			1.81	0.037
	B–B		B–B	
3–4	1.76	0.038	1.75	0.038
3–7	1.72	0.043	1.73	0.042
3–8	1.74	0.041	1.74	0.041
4–5	1.76	0.036	1.77	0.039
4–8	1.80	0.039	1.80	0.039
4–9	1.80	0.032	1.80	0.032
5–6	1.66	0.047		
5–9	1.85	0.038	1.85	0.038
5–10	1.77	0.043	1.76	0.043
6–10	1.73	0.034		
6–11	1.82	0.038		
7–8	1.74	0.042	1.75	0.041
7–11	1.83	0.037	1.83	0.037
7–12	1.78	0.036	1.80	0.036
8–9	1.74	0.036	1.75	0.036
8–12	1.79	0.042	1.80	0.041
9–10	1.85	0.048	1.85	0.048
9–12	1.80	0.037	1.79	0.036
10–11	1.82	0.035	1.82	0.035
10–12	1.80	0.038	1.80	0.037
11–12	1.75	0.037	1.75	0.037

Standard Deviations

σ(Br–Br)	0.015[b]	σ(Br–Br)	0.015[b]
σ(C–C),		σ($^2/_3$ C, $^1/_3$ B)–($^2/_3$ C, $^1/_3$ B)	0.026
σ(B–C)	0.038	σ($^2/_3$ C, $^1/_3$ B)–B	0.052
σ(B–B)	0.047	σ(B–B)	0.038

[a] Bond distances have not been corrected for thermal motion.

[b] The over-all standard deviations included in the table were computed by averaging equivalent bond types and applying the equation

$$\sigma = \left[\left(\sum_{i=1}^{N}(X_i - \bar{X})^2\right)/(N - 1)\right]^{1/2}$$

Individual standard deviations were computed from the full variance–covariance matrix obtained after the final least-squares cycle of refinement of all temperature and position parameters.

triangular array of Br atoms can be formed from bromination of the 9,12-o-$B_{10}Br_2H_8C_2H_2$.

Results and Discussion

A projection of the crystal structure along the b axis is shown in Figure 2, where light atoms subject to the possible packing disorder are shaded. Bond distances and average deviations of various bond types (Table V) have not been corrected for thermal motion, in view of the possible disorder. Atomic parameters are given in Table VI.

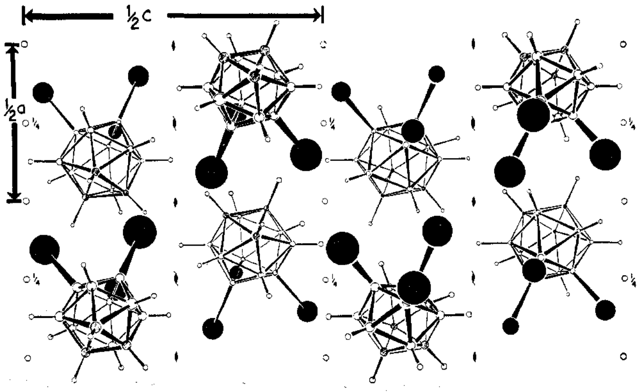

Figure 2. The molecular packing as seen in the projection along the b axis.

The conclusion of these X-ray results on products of bromination in the presence of $AlBr_3$ is that 9,12 substitution is followed by 8 (10) substitution. These results also allow a unique identification[5] of the ^{11}B nuclear magnetic resonance spectrum of unsubstituted carborane. The 19.3-Mc/sec spectrum is thus assigned as B-9 and B-12 at 20.8 ppm, B-8 and B-10 at 28 ppm, four equivalent B atoms (4, 5, 7, 11) at 32.5 ppm, and B-3 and B-6 at 33.3 ppm. The sequential order of halogenation proved in this study has independently been suggested by Zakharkin and Kalinen,[7] who counted isomers of halogenation products from o-carborane, C-methyl-o-carborane, and C,C′-dimethyl-o-carborane. They assumed that the methyl groups on carbon did not influence the sequential ordering of substitution and that the 3 and 6 positions (last to be substituted[8] in photochemical chlorination) were too positively charged to be involved. Our results are not dependent upon these assumptions.

Further studies of the structures of sequentially substituted products are in progress. It is surely too much to expect that the apparently dominating effect of the C atoms of the framework will account for all substitution reactions in the carboranes. In particular, the order in which halogenation occurs at the 4, 5, 7, and 11 positions of o-carborane is very likely to depend upon other mechanistic effects of a steric or electronic nature. Also the study of other reactions which are more complex than halogenation, the study of sequen-

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(7) L. I. Zakharkin and V. N. Kalinen, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1311 (1965).

(8) J. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964).

TABLE VI

FINAL ATOMIC COORDINATES IN FRACTIONS OF CELL LENGTHS AND THERMAL PARAMETERS ($\times 10^4$)[a,b,c]

Type	Atom	x	σ_x	y	σ_y	z	σ_z
B–C	1	0.460	0.002	0.649	0.003	0.333	0.002
B–C	2	0.401	0.002	0.752	0.003	0.384	0.001
B	3	0.327	0.003	0.716	0.003	0.325	0.002
B	4	0.366	0.002	0.525	0.003	0.307	0.001
B	5	0.462	0.003	0.453	0.003	0.357	0.002
B–C	6	0.484	0.002	0.598	0.003	0.402	0.002
B	7	0.269	0.002	0.716	0.003	0.392	0.001
B	8	0.241	0.003	0.563	0.003	0.345	0.001
B	9	0.317	0.002	0.397	0.003	0.363	0.001
B	10	0.403	0.002	0.446	0.003	0.425	0.001
B	11	0.366	0.002	0.645	0.003	0.445	0.001
B	12	0.266	0.003	0.519	0.003	0.419	0.001
H	1′	0.530		0.694		0.302	
H	2′	0.430		0.884		0.395	
H	3′	0.300		0.813		0.288	
H	4′	0.364		0.485		0.258	
H	5′	0.530		0.359		0.343	
H	6′	0.572		0.612		0.423	
H	7′	0.198		0.809		0.405	
Br	8′	0.094	0.0002	0.539	0.0003	0.311	0.0002
Br	9′	0.276	0.0002	0.181	0.0003	0.351	0.0001
H	10′	0.432		0.353		0.462	
H	11′	0.367		0.683		0.494	
Br	12′	0.149	0.0003	0.443	0.0003	0.470	0.0002

Type	Atom	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}	$\sigma_{\beta_{23}}$
B–C	1	92	25	215	48	37	9	−11	27	−2	11	30	16
B–C	2	67	18	162	39	36	9	−33	19	−9	10	−29	14
B	3	124	27	120	31	29	8	21	25	−4	11	15	14
B	4	41	13	194	39	13	4	−1	18	13	6	14	11
B	5	89	26	139	40	31	8	−12	24	−13	11	−14	15
B–C	6	37	17	170	38	68	13	−5	20	13	12	−31	19
B	7	62	18	162	39	24	7	−27	22	17	9	−2	13
B	8	129	33	90	33	32	8	−3	24	5	14	19	13
B	9	50	16	77	28	43	9	4	16	−24	10	18	13
B	10	77	21	141	38	39	9	−5	22	−39	12	4	15
B	11	60	19	153	35	18	5	15	20	−2	8	−10	11
B	12	67	28	161	42	16	6	−20	27	−17	11	−5	13
H	1′	90		203		7		2		−3		−3	
H	2′	62		216		13		3		6		1	
H	3′	46		229		28		32		−6		−28	
H	4′	133		191		21		−38		−22		24	
H	5′	85		141		24		−35		14		−12	
H	6′	72		256		24		−13		−3		−22	
H	7′	26		184		15		7		−16		−21	
Br	8′	96	2	189	5	37	1	11	2	−23	1	−8	1
Br	9′	100	2	115	4	40	1	−6	2	−8	1	−8	1
H	10′	86		206		45		−20		−27		−13	
H	11′	99		236		24		−7		−22		3	
Br	12′	119	3	199	5	35	1	−31	3	4	1	0	1

[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] The nine hydrogen atoms were not unambiguously located on the final electron density map; their positions were calculated so as to place them 1.2 A from their respective $B_{10}C_2$ cage atoms and directed radially outward from the lines joining *para* atoms in the 12 B refined structure; the thermal parameters used for hydrogen were taken as equal to those of their corresponding B atoms before the designation of C atoms. [c] Standard deviations were obtained from the full least-squares matrix.

tial substitution on *m*-carborane and other carboranes, and detailed mechanistic studies would be of considerable interest.

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