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# Molecular Structure of Carboranes. Molecular and Crystal Structure of $o$-$B_{10}Br_4H_6C_2(CH_3)_2$

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Bromination of $o$-$B_{10}H_{10}C_2(CH_3)_2$ in the presence of $AlCl_3$ is shown to yield 8,9,10,12-tetrabromo-C,C′-dimethyl-$o$-carborane. These four B atoms (8,9,10,12) are furthest removed from C atoms of the icosahedral cage and are the most negative B atoms in nonempirical molecular orbital studies of both $o$-$B_{10}H_{10}C_2H_2$ and $o$-$B_{10}H_{10}C_2(CH_3)_2$. These studies also confirm the increased electron density of the latter, which can be tetrabrominated, as compared with the former, which can only be tribrominated. Thus, the position of halogenation of this cage, in regions where steric and other effects are not selective, appear to have their transition states dominated by the initial ground-state charge distribution. There are four molecules in a unit cell having parameters $a = 13.18$, $b = 14.49$, $c = 8.20$ A, and $\beta = 96.3°$. The space group is $P2_1/n$.

Previous studies of halogenated carboranes have shown the first proof of the icosahedral $B_{10}C_2$ unit[1] in $o$-$B_{10}Cl_{10}C_2Cl_2$, the substitution under photochemical conditions of Cl on all B atoms except 3 and 6 in[2] $o$-$B_{10}Cl_8H_2C_2H_2$, and bromination catalyzed by $AlCl_3$ first at B atoms 9 and 12 in[3] $o$-$B_{10}Br_2H_8C_2H_2$ and then at B atom 8 (or 10) in[4] $o$-$B_{10}Br_3H_7C_2H_2$. Molecular orbital predictions of ground-state charge distributions had earlier indicated[5] that B atoms 3 and 6 nearest carbon atoms were the most positive and that B atoms 8, 9, 10, and 12 not attached to C were most negative in $o$-$B_{10}C_2H_{12}$. Qualifications of the relevance of ground-state charge distributions to transition states exist in our earlier papers.[1,3,5]

Chemical proof has been given[6] for the identity of the dibromo product, $o$-$B_{10}H_8Br_2C_2(CH_3)_2$, with that obtained from C,C′-methylation of the now established 9,12-$o$-$B_{10}H_8Br_2C_2H_2$ structure. The structure established here[7] of 8,9,10,12-$o$-$B_{10}Br_4H_6C_2(CH_3)_2$ also clearly infers the identity of positions 9, 12, and 8 (or 10) in $o$-$B_{10}Br_3H_7C_2(CH_3)_2$ with those known[4] in $o$-$B_{10}Br_3H_7C_2H_2$. Thus, the sequential order of bromination is the same in $o$-$B_{10}C_2H_{12}$ and $o$-$B_{10}H_{10}C_2(CH_3)_2$, to the extent that Br, can, so far, be substituted for H on the polyhedron.

Zakharkin and Kalinen found that $o$-$B_{10}H_{10}C_2HCH_3$ gives two monobromo, one dibromo, one tribromo, and one tetrabromo product under Friedel–Crafts conditions. From these results and the assumptions that atoms 3 and 6 are not involved[2,5] and that the sequential order of substitution is the same for $o$-$B_{10}C_2H_{12}$, $o$-$B_{10}H_{10}C_2HCH_3$, and $o$-$B_{10}H_{10}C_2(CH_3)_2$, they concluded that B atoms 9 and 12 are substituted first, followed by 8 and 10. Our results prove that their assumptions and conclusions are correct.

We also present results of a new nonempirical molecular orbital theory[8,9] which indicate that the C-methyl groups cause a rather uniform increase in electron density on the B atoms, in qualitative agreement with the observations that the sequence of substitution is not changed by C-methylation and that $o$-$B_{10}H_{10}C_2(CH_3)_2$ can be tetrabrominated[6] but $o$-$B_{10}C_2H_{12}$ can only be tribrominated.

## Structure Determination

A single crystal 0.6 mm long and 0.05 mm in a nearly square cross section was mounted on the needle axis $c$. A second crystal was cut to a cube about 0.05 mm on edge and then mounted on the symmetry axis $b$. Reciprocal lattice symmetry is $C_{2h}$, and unit cell parameters are $a = 13.18 \pm 0.02$, $b = 14.49 \pm 0.02$, $c = 8.20 \pm 0.02$ A, and $\beta = 96.3 \pm 0.3°$. Extinctions of $h0l$ when $h + l$ is odd and of $0k0$ when $k$ is odd lead to the space group $P2_1/n$.

Data from the needle crystal were collected for levels $0 \leqslant l \leqslant 6$ photographically with the use of Weissenberg geometry and Cu K$\alpha$ radiation. A standard scale prepared from timed exposures of a representative $hk3$ reflection was used for visual estimates of the multiple films. These data were correlated within each level by methods described elsewhere[10] but were scaled by times of exposure between different levels. Three of the four Br atoms were located unambiguously in symmetry sections of the three-dimensional Patterson function computed from these 1378 independent reflections. The fourth Br was found in an electron density map phased by these three Br atoms. At this stage the value of $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.32 from Br contributions only. The electron density map based upon phases from these four Br atoms showed 24 peaks higher than about 40% of the height expected for a B atom. Nevertheless, it was easy to locate the 14 peaks for the expected icosahedral cage structure in which two methyl carbons were already known from chemical evidence to be attached to C

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[1] J. A. Potenza and W. N. Lipscomb, unpublished studies. See W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 26.

[2] J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964).

[3] J. A. Potenza and W. N. Lipscomb, *ibid.*, **5**, 1471 (1966).

[4] J. A. Potenza and W. N. Lipscomb, *ibid.*, **5**, 1478 (1966).

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

[6] H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

[7] J. Potenza, W. N. Lipscomb, H. Schroeder, and G. D. Vickers, *J. Am. Chem. Soc.*, **88**, 628 (1966).

[8] F. P. Boer, M. D. Newton and W. N. Lipscomb, *ibid.*, **88**, 2353 (1966).

[9] F. P. Boer, J. Potenza, and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1301 (1966).

[10] P. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 2339 (1963).

### TABLE I

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

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L=0 (K)(H)( 0)(  0,14)3114,,261,,386,,69,,354,,145,,104,,
54,( 1)(  1,15)50,*,227,293,207,258,54,88,382,97,105,77,*,
66,49,( 2)(  0,15)307,510,114,600,327,284,91,501,92,*,67,*,
107,*,*,99,( 3)(  1,14)186,476,304,250,327,200,130,123,
120,218,*,164,*,36,( 4)(  0,14)715,241,108,648,95,168,206,
384,223,98,*,*,78,*,77,( 5)(  1,15)126,160,234,96,180,*,
71,289,301,128,*,141,*,*,52,( 6)(  0,12)1005,523,174,232,
294,56,72,169,171,76,110,*,87,( 7)(  1,14)262,110,137,*,
405,91,107,89,83,118,*,58,50,63,( 8)(  0,12)103,128,*,317,
271,324,180,174,66,112,*,*,75,( 9)(  1,12)193,*,201,80,
243,74,144,126,65,61,77,111,(10)(  0,10)59,258,329,255,
97,111,135,78,62,101,75,(11)(  4,11)141,134,*,110,165,*,
58,67,(12)(  0,  5)90,147,182,106,114,75,(13)(  1,  5)123,*,
*,131,124,(14)(  0,  9)111,82,*,*,72,138,*,*,*,51,
(15)(  7,  7)60,(16)(  0,  2)84,*,133
L=1 (K)(H)( 0)(-13,13)113,,*,,148,,274,,458,,686,,*,,264,,
807+,,133,,185,,271,,216,,221,( 1)(-14,12)103,84,*,184,
186,*,141,*,680,*,339,779,460,299,273,*,162,232,629,113,
68,*,*,*,126,*,133,( 2)(-14,14)81,*,181,79,72,130,*,150,*,
89,341,311,239,459,376,50,162,248,246,256,647,111,93,247,
199,*,*,*,153,( 3)(-13, 6)124,*,240,104,139,*,71,61,211,
312,1373+,534,56,167,877,127,233,156,173,189,( 4)(-13,13)
105,86,92,112,89,125,75,156,229,161,355,94,492,91,114,493,
410,142,99,497,123,*,132,103,144,108,118,( 5)(-14,12)78,*,
*,*,160,223,222,200,437,105,449,200,145,*,159,410,86,150,
481,312,*,108,*,*,103,90,112,( 6)(-12,13)88,*,*,*,99,144,
249,192,352,360,153,276,319,162,344,385,207,116,*,119,137,
225,*,159,*,115,( 7)(-14, 6)65,95,*,137,*,*,131,*,422,193,
*,333,530,311,292,55,126,254,184,195,204,( 8)(-11, 9)124,*,
85,*,113,*,96,104,100,75,73,*,91,192,72,216,371,325,157,
140,214,( 9)(-11, 7)90,81,127,*,*,*,*,270,295,482,193,231,
323,246,89,*,142,95,80,(10)( -8,11)115,*,178,*,112,102,*,*,
*,200,328,72,80,145,139,114,*,*,*,82,(11)( -9, 6)105,146,*,
114,108,175,*,*,*,89,267,136,87,*,146,109,(12)( -6, 9)104,
*,114,*,*,124,*,162,125,*,138,*,*,*,113,101,(13)( -6, 6)
79,160,*,*,192,196,82,*,*,85,*,*,82,(14)( -6, 9)75,*,*,*,*,
*,*,*,*,*,124,133,*,*,89,59,(15)( -2, 2)118,130,85,*,88,
(16)( -5, 5)64,*,*,*,*,*,85,*,*,*,62,(17)(  0, 2)60,59,
60
L=2 (K)(H)( 0)(-14,12)123,,*,,251,,107,,506,,406,,832,,
111,,78,,141,,61,,171,,137,,160,( 1)(-15,10)83,*,*,83,*,*,
123,246,331,264,382,244,193,31,*,732,258,*,786,74,125,*,
545,162,*,200,( 2)(-14,11)79,93,87,*,*,383,151,238,160,*,
256,230,344,282,176,632,241,495,69,*,108,*,78,222,*,96,
( 3)(-12,10)97,67,*,126,411,211,352,123,418,80,275,319,
1333,351,258,148,201,73,232,92,288,*,273,( 4)(-14,10)116,*,
*,*,127,202,*,*,290,501,114,109,243,442,158,211,323,168,
182,81,*,76,*,134,164,( 5)(-12,10)88,*,*,*,75,392,78,382,
146,*,267,166,218,320,72,632,292,219,354,409,137,*,159,
( 6)(-14,12)84,96,114,*,165,93,113,138,201,351,121,358,
438,401,86,139,144,152,*,*,101,*,116,119,89,*,170,
( 7)(-11,10)95,*,257,116,131,164,291,215,229,112,244,421,
102,261,517,101,132,*,213,148,*,113,( 8)(-12,10)92,88,*,
177,184,211,*,*,136,70,194,96,246,137,454,86,*,132,*,*,
178,101,108,( 9)( -7,10)129,*,*,154,83,271,255,312,308,
229,179,*,186,135,*,*,98,147,(10)(-12,10)80,*,*,*,91,*,*,
327,248,77,163,227,150,105,101,*,*,*,*,*,*,*,105,
(11)( -5, 9)130,*,80,161,*,*,111,97,179,207,204,184,*,*,
88,(12)(-11, 2)65,71,*,*,99,*,165,*,105,*,189,*,*,105,
(13)(-10, 3)76,89,*,*,*,94,*,*,146,*,*,*,191,121,
(14)( -8, 8)71,103,*,*,105,80,98,*,*,85,128,*,*,*,*,67,
103,(15)( -2, 6)92,*,*,*,95,*,*,*,102,(16)( -4, 0)131,66,
85,*,75,(17)(  1, 1)65
L=3 (K)(H)( 0)(-15,11)74,,*,,254,,92,,67,,58,,1072,,217,,
583,,186,,*,,326,,*,,91,( 1)(-12,13)98,*,*,198,*,239,87,
197,221,301,408,251,575,*,139,115,234,*,438,265,95,75,111,
102,120,91,( 2)(-11,12)120,201,*,199,*,275,176,631,266,
286,122,356,368,85,212,742,143,*,133,82,*,*,*,91,
( 3)(-13,13)96,*,*,78,93,209,285,191,325,185,281,*,226,
40,60,51,83,*,*,140,258,*,338,*,127,109,186,( 4)(-11,12)
148,79,80,251,100,267,75,172,670,325,189,477,66,59,199,
477,209,*,*,143,*,*,*,92,( 5)(-12, 9)106,108,*,*,*,*,105,*,
*,345,319,211,518,255,55,136,219,270,394,86,71,203,
( 6)(-11, 8)143,166,*,*,69,93,153,240,529,445,333,92,484,
126,*,*,117,*,205,112,( 7)( -9,12)73,166,*,251,*,295,*,
94,343,208,*,256,106,175,72,112,168,*,*,*,114,119,
( 8)(-10, 7)105,81,113,99,200,171,235,111,70,90,127,381,
175,288,246,313,131,124,( 9)(-12, 9)89,*,*,*,142,*,132,*,
231,125,*,*,94,135,97,*,*,83,84,77,97,184,(10)( -8, 8)146,
*,119,134,*,111,260,274,146,124,73,128,101,102,77,*,105,
(11)(-11, 9)111,*,*,*,80,*,*,*,138,*,165,*,120,112,119,
114,133,*,*,136,77,(12)(-10, 8)77,*,*,*,*,95,*,*,155,169,*,
154,142,*,100,*,*,*,77,(13)( -7, 2)107,*,76,76,73,*,100,*,
*,78,(14)(  1, 6)123,130,*,*,116,96,(15)( -4, 0)116,*,70,*,
71
L=4 (K)(H)( 0)(-14,10)100,,87,,120,,204,,348,,281,,182,,
465,,274,,192,,272,,157,,372,( 1)(-14,10)62,*,*,*,124,131,
*,338,265,*,*,*,166,320,101,494,29,289,*,178,*,*,*,*,112,
( 2)(-15,13)82,*,*,*,72,*,*,136,179,197,278,*,303,369,236,
126,519,90,537,64,184,234,306,80,*,156,*,*,93,( 3)(-14,10)
117,*,*,*,113,69,90,143,380,264,119,51,449,57,89,77,180,*,
51,107,234,*,61,99,109,( 4)(-10,10)79,108,170,*,202,354,
286,186,*,37,431,195,179,491,119,192,105,226,150,91,143,
( 5)(-13, 6)73,72,*,*,U,*,311,131,62,114,64,269,124,126,
350,428,230,155,*,110,( 6)(-11,11)95,*,141,75,209,213,85,
156,120,359,149,155,65,239,121,88,89,206,*,117,77,233,66,
( 7)(-11,10)101,*,*,*,112,190,287,196,69,75,280,215,216,
256,*,83,136,*,*,*,113,90,( 8)( -7,10)95,68,106,167,*,226,
98,145,222,*,256,126,167,187,135,*,*,86,( 9)(-13, 9)59,*,*,
68,77,*,88,*,180,90,*,184,127,85,*,202,69,*,183,84,*,*,
80,(10)(-11, 6)67,*,87,*,83,*,135,187,*,*,108,105,74,110,
141,79,114,*,70,89,(11)(-11, 6)68,*,*,*,81,91,*,*,*,143,
74,104,*,246,92,*,78,80,(12)( -9, 9)71,*,98,*,69,*,*,144,
71,*,*,79,*,*,68,72,*,72,59,(13)( -5, 8)109,145,*,77,*,
94,*,94,*,*,84,*,*,47,(14)( -4, 6)77,*,116,77,*,*,*,*,*,
96,63,(15)( -1, 5)83,65,*,*,66,*,80
L=5 (K)(H)( 0)(-15, 7)42,,125,,*,,136,,199,,190,,63,,109,,
44,,312,,121,,367,( 1)(-15, 8)43,*,*,*,121,145,93,210,92,
109,74,407,315,263,104,269,92,130,*,499,86,*,133,98,
( 2)(-12, 9)72,*,138,*,107,*,64,*,197,179,308,161,516,172,
*,212,162,49,169,111,*,80,( 3)(-12,11)86,166,118,134,*,
97,108,*,163,473,183,456,86,182,105,117,116,129,*,262,103,
*,63,143,( 4)(-13, 9)57,*,*,58,105,58,*,*,*,220,98,146,
400,367,197,49,57,157,*,*,176,*,85,( 5)(-10, 8)141,*,150,
130,60,322,314,107,186,174,305,247,201,189,357,184,63,150,
64,( 6)(-13, 9)54,65,*,64,*,139,68,80,76,146,118,123,144,
157,194,110,268,117,*,171,192,*,149,( 7)(-12, 8)65,65,*,*,
153,148,89,*,89,256,52,173,112,49,160,63,163,103,108,*,
125,( 8)(-10, 6)76,108,*,*,*,*,*,132,*,323,*,211,177,167,
94,90,86,( 9)(-10,10)94,*,*,*,*,193,*,78,104,228,92,118,*,
*,*,58,67,98,116,75,44,(10)( -8, 9)85,*,*,*,124,103,60,
148,92,*,*,*,118,55,71,64,*,64,(11)( -7, 7)97,87,118,*,
57,*,78,93,132,143,60,*,76,107,51,(12)( -9, 6)57,*,*,*,*,
87,*,*,34,104,*,134,*,*,79,71,(13)( -1, 2)72,*,*,77,
(14)( -2, 3)65,76,57,*,64,47
L=6 (K)(H)( 0)(-14, 8)98,,64,,*,,*,,222,,133,,76,,302,,
47,,*,,142,,103,( 1)(-12,10)54,93,85,*,78,61,*,192,206,
304,118,*,44,351,109,216,168,161,101,77,120,*,56,
( 2)(-13, 9)83,*,60,*,*,*,293,*,126,218,62,139,175,*,391,
188,53,116,81,115,*,74,73,( 3)(-11,11)66,98,86,87,88,202,*,
209,77,191,U,120,*,187,143,271,85,176,78,146,*,235,88,
( 4)(-11, 9)81,*,*,*,202,203,53,129,54,*,*,216,211,161,*,
58,177,77,*,*,79,( 5)(-11, 8)79,60,*,*,72,59,126,140,262,
310,86,92,225,*,252,*,153,126,*,72,( 6)( -7, 9)104,82,141,
172,81,99,*,190,143,147,60,*,156,103,*,65,70,( 7)( -9, 9)
55,*,*,*,62,225,78,*,*,108,282,*,57,90,157,80,*,86,65,
( 8)(-11, 9)55,75,*,69,106,138,*,136,56,118,*,58,73,247,
109,68,*,57,*,67,47,( 9)( -8, 9)67,*,*,*,*,*,152,94,*,71,*,
142,67,*,113,*,75,40,(10)( -7, 8)63,105,93,67,74,*,71,*,*,
*,63,*,122,*,*,48,(11)( -6, 5)52,*,100,*,115,97,*,*,*,76,*,
93,(12)( -4, 5)108,68,*,58,*,*,81,*,*,99,(13)( -4, 1)69,*,
*,*,65,78,(14)(  2, 2)60
L=7 (K)(H)( 0)( -9, 9)104,,126+,,*,,208,,302,,*,,105,,129,
,217,,74,( 1)(-10, 7)120,118,99,*,*,*,147+,101+,134+,*,
172,*,*,123,99,*,*,135,( 2)(-10, 7)85,*,96+,*,161,*,209,*,
241,232,221,*,*,107,*,179,*,119,109,( 3)(-10, 7)92,104,*,*,
83,*,*,*,116+,*,*,*,*,256,*,*,*,233,( 4)( -8, 7)97,132,*,*,
105,203,86+,190+,*,104,250,*,116,154+,114,89,( 5)( -1, 5)
175,132,*,*,173,*,108,( 6)( -6, 2)90,119,*,U,*,258,87+,*,
117
L=8 (K)(H)( 0)( -4, 8)177,,*,,115+,,*,,258,,*,,148,
( 1)( -4, 3)99,*,*,*,115,95,*,115,( 2)( -5, 4)89,*,248,*,*,
76,*,*,153,124,( 3)(-10, 0)86,*,*,*,*,*,U,78,*,*,185,
( 4)( -4, 4)165,104,*,*,*,142,136+,*,160,( 5)( -3,-3)83
L=9 (K)(H)( 0)( -5, 3)75,,177,,97,,*,,129,( 1)( -6, 2)106,
*,*,*,96,*,*,*,91,( 2)( -4,-4)106,( 3)( -7, 1)131,79,*,*,*,
79,112+,98,147
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[a] $F_{hkl}$ is listed followed by a comma. Unobserved reflections are indicated by an asterisk, experimentally unobserved reflections by a U, space group extinctions by an extra comma, and reflections not used in the refinement by $F_{hkl}$ followed by a plus sign. All reflections are on the same scale as $F_{000}$, which is given as a reference point. The summation for $F_{000}$ is over the entire unit cell.
[b] Scattering factors for all atoms were used as obtained from the "International Tables for X-ray Crystallography," The Kynoch Press, Birmingham, England, Vol. III, 1962, p 202 ff.

atoms of the cage. The inclusion of these 14 atoms followed by one cycle of refinement of position and anisotropic temperature parameters of Br, one cycle of position refinement of all atoms, one cycle of refinement of anisotropic temperature parameters for all atoms, and one cycle of all position and thermal parameters led, finally for these 1371 data, to $R_F = 0.118$.

Data from the second crystal were measured, at the time of the above refinements, for levels $0 \leqslant k \leqslant 6$ on the Buerger automated diffractometer with the use of Cu K$\alpha$ radiation and an Xe proportional counter. Check reflections were measured after each group of six reflections, and a set of six zero-level reflections was measured after completion of each level. Equivalent reflections all agreed to within $2\sigma_c$ where $\sigma_c$ is the square root of the counts in the scan and background. These new data were assigned standard deviations proportional to the total number of scan plus background counts and then correlated with the film data for which standard deviations proportional to the observed $F_{hkl}{}^2$ were assumed. The small size of the $b$-axis crystal led us to give the film data 1.5 times the average weight of the counter data. Of the 1574 reflections, an overlap of 620 between the two sets of data gave a correlation $\Sigma w|F(1)^2 - F(2)^2|/\Sigma w|F(1)^2 + F(2)^2|$ value of 0.11. The lowest 97 of these, which were very low values from counter data only, were eliminated from the list, and the remaining 1477 reflections (Table I) reduced $R_F$ to its final value of 0.100 after three cycles of refinement of distance and anisotropic temperature parameters.

TABLE II

FINAL VALUES FOR $R_F$ FOR 1477 REFLECTIONS

| $hkl$ | $R_F$ | $hkl$ | $R_F$ |
|---|---|---|---|
| All ($h, k, l \neq 0$) | 0.101 | $k + l$ odd | 0.098 |
| $h$ even | 0.102 | $h + l$ even | 0.099 |
| $h$ odd | 0.100 | $h + l$ odd | 0.103 |
| $k$ even | 0.104 | $h + k$ even | 0.098 |
| $k$ odd | 0.098 | $h + k$ odd | 0.104 |
| $l$ even | 0.100 | $h + k + l$ even | 0.103 |
| $l$ odd | 0.102 | $h + k + l$ odd | 0.099 |
| $k + l$ even | 0.104 | Over-all | 0.100 |

| Range of sin $\theta$ | No. of reflections | $R_F$ | Range of sin $\theta$ | No. of reflections | $R_F$ |
|---|---|---|---|---|---|
| 0.00–0.40 | 209 | 0.106 | 0.70–0.75 | 145 | 0.081 |
| 0.40–0.50 | 182 | 0.106 | 0.75–0.80 | 126 | 0.112 |
| 0.50–0.60 | 257 | 0.097 | 0.80–0.85 | 118 | 0.121 |
| 0.60–0.65 | 145 | 0.075 | 0.85–0.90 | 90 | 0.139 |
| 0.65–0.70 | 153 | 0.075 | 0.90–1.00 | 52 | 0.103 |

Values of $R_F$ for various classes of reflections and angle ranges are shown in Table II, and we add that $R_{F^2} = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$ is 0.17, and $R_{wF^2} = [\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^4]^{1/2}$ is 0.18. These criteria supplement the over-all $R_F$ values in evaluating the essential correctness of the crystal structure.

## Results and Discussion

The molecular structure, shown in Figure 1, clearly shows Br substitution at the 8, 9, 10, and 12 positions of the near-icosahedral $B_{10}C_2$ cage, and methyl substitution of the cage C atoms. Neglecting methyl H atoms, which were not found in the final difference Fourier, the point group symmetry of the molecule is very nearly $C_{2v}$; however, H atoms could distort this to $C_s$ or even to a structure with no symmetry elements at all. A projection of the molecular packing as seen along $d(001)$ is shown in Figure 2, where cones of electron density are used to indicate methyl H atoms.

Final atomic parameters and anisotropic temperature factors are listed in Table III for all atoms except H, which were not found in the difference maps. Bond lengths and their standard deviations (Table IV) have not been corrected for rigid-body motion in view of their low accuracy. However, the objective of the study, to find the positions of substitution of Br, has been unambiguously achieved. Of course, the Br···Br distances are fairly precisely determined (±0.015 A). Intramolecular values of 3.90 A in $o$-$B_{10}Br_3H_7C_2H_2$ and 3.87 A in $o$-$B_{10}Br_4H_6C_2(CH_3)_2$ are perhaps significantly

TABLE III

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

| Atom | No. | $x$ | $\sigma_x$ | $y$ | $\sigma_y$ | $z$ | $\sigma_z$ |
|---|---|---|---|---|---|---|---|
| C | 1 | 0.175 | 0.002 | 0.293 | 0.002 | 0.539 | 0.002 |
| C | 2 | 0.134 | 0.002 | 0.211 | 0.001 | 0.655 | 0.002 |
| B | 3 | 0.068 | 0.002 | 0.226 | 0.002 | 0.460 | 0.003 |
| B | 4 | 0.164 | 0.002 | 0.251 | 0.003 | 0.338 | 0.003 |
| B | 5 | 0.285 | 0.002 | 0.255 | 0.002 | 0.462 | 0.003 |
| B | 6 | 0.260 | 0.002 | 0.231 | 0.002 | 0.673 | 0.003 |
| B | 7 | 0.095 | 0.002 | 0.116 | 0.003 | 0.558 | 0.004 |
| B | 8 | 0.116 | 0.002 | 0.133 | 0.002 | 0.342 | 0.003 |
| B | 9 | 0.246 | 0.002 | 0.155 | 0.002 | 0.345 | 0.004 |
| B | 10 | 0.307 | 0.002 | 0.144 | 0.002 | 0.559 | 0.003 |
| B | 11 | 0.213 | 0.002 | 0.119 | 0.002 | 0.682 | 0.003 |
| B | 12 | 0.202 | 0.002 | 0.072 | 0.002 | 0.481 | 0.003 |
| C | 13 | 0.158 | 0.003 | 0.393 | 0.002 | 0.570 | 0.004 |
| C | 14 | 0.077 | 0.002 | 0.239 | 0.002 | 0.802 | 0.003 |
| Br | 8′ | 0.0314 | 0.0002 | 0.0820 | 0.0002 | 0.1652 | 0.0003 |
| Br | 9′ | 0.3216 | 0.0003 | 0.1207 | 0.0003 | 0.1615 | 0.0003 |
| Br | 10′ | 0.4454 | 0.0002 | 0.0952 | 0.0003 | 0.6133 | 0.0004 |
| Br | 12′ | 0.2213 | 0.0003 | −0.0626 | 0.0002 | 0.4491 | 0.0003 |

| Atom | No. | $\beta_{11}$ | $\sigma\beta_{11}$ | $\beta_{22}$ | $\sigma\beta_{22}$ | $\beta_{33}$ | $\sigma\beta_{33}$ | $\beta_{12}$ | $\sigma\beta_{12}$ | $\beta_{13}$ | $\sigma\beta_{13}$ | $\beta_{23}$ | $\sigma\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | 73 | 19 | 34 | 13 | 55 | 38 | 5 | 12 | −2 | 18 | −10 | 15 |
| C | 2 | 39 | 16 | 23 | 12 | 128 | 42 | −1 | 11 | −15 | 17 | 24 | 14 |
| B | 3 | 63 | 21 | 47 | 16 | 12 | 38 | 5 | 15 | −3 | 19 | 7 | 17 |
| B | 4 | 40 | 21 | 43 | 23 | 195 | 65 | −29 | 18 | 22 | 26 | −27 | 26 |
| B | 5 | 63 | 19 | 39 | 15 | 43 | 39 | −16 | 13 | 37 | 20 | −17 | 17 |
| B | 6 | 42 | 17 | 29 | 13 | 96 | 49 | −1 | 12 | 11 | 20 | 3 | 17 |
| B | 7 | 26 | 19 | 161 | 38 | 121 | 58 | −8 | 20 | 7 | 23 | 112 | 38 |
| B | 8 | 38 | 19 | 51 | 18 | 96 | 47 | 6 | 14 | −5 | 20 | 12 | 20 |
| B | 9 | 45 | 19 | 42 | 18 | 133 | 62 | −14 | 15 | 29 | 25 | −16 | 23 |
| B | 10 | 54 | 20 | 44 | 16 | 44 | 38 | 8 | 13 | −2 | 18 | −9 | 16 |
| B | 11 | 35 | 17 | 27 | 15 | 107 | 46 | −1 | 13 | −6 | 18 | −4 | 18 |
| B | 12 | 44 | 20 | 32 | 16 | 164 | 55 | −9 | 14 | 23 | 22 | −33 | 20 |
| C | 13 | 97 | 28 | 25 | 18 | 243 | 66 | 17 | 18 | −10 | 31 | −9 | 24 |
| C | 14 | 76 | 20 | 74 | 19 | 83 | 39 | 12 | 16 | 54 | 21 | −4 | 20 |
| Br | 8′ | 84 | 2 | 61 | 2 | 93 | 4 | −25 | 2 | −30 | 2 | 6 | 2 |
| Br | 9′ | 88 | 2 | 91 | 3 | 113 | 5 | −20 | 2 | 55 | 3 | −44 | 2 |
| Br | 10′ | 52 | 2 | 85 | 3 | 231 | 6 | 19 | 2 | −13 | 3 | −44 | 3 |
| Br | 12′ | 103 | 3 | 35 | 1 | 156 | 5 | 9 | 2 | −6 | 3 | −15 | 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 ($\sigma$) were obtained from the full least-squares matrix after the final refinement of all position and temperature parameters.

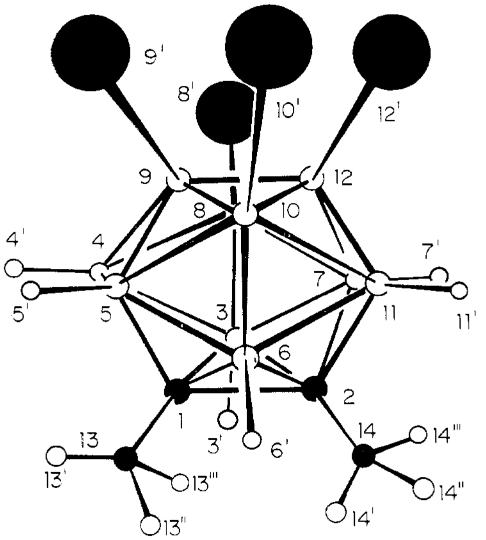

Figure 1.—The molecular structure and numbering scheme for $o\text{-}B_{10}Br_4H_6C_2(CH_3)_2$. Atoms are designated as follows: H(3′,4′,5′,6′,7′,11′,13′,13″,13‴,14′,14″,14‴); B(3,4,5,6,7,8,9,10,11,12); C(1,2,13,14); Br(8′,9′,10′,12′).

TABLE IV

BOND DISTANCES,[a] AVERAGES, AND STANDARD DEVIATIONS[b]

| Bond | Length, A | $\sigma$ | Bond | Length, A | $\sigma$ |
|---|---|---|---|---|---|
| | Br–Br | | | B–B | |
| | | | 4–5 | 1.79 | 0.039 |
| 8′–9′ | 3.87 | 0.007 | 4–8 | 1.82 | 0.049 |
| 8′–12′ | 3.85 | 0.004 | 4–9 | 1.76 | 0.041 |
| 9′–10′ | 3.90 | 0.010 | 5–6 | 1.83 | 0.031 |
| 9′–12′ | 3.88 | 0.007 | 5–9 | 1.78 | 0.044 |
| 10′–12′ | 3.86 | 0.007 | 5–10 | 1.79 | 0.036 |
| | B–Br | | 6–10 | 1.73 | 0.036 |
| 8–8′ | 1.88 | 0.027 | 6–11 | 1.75 | 0.037 |
| 9–9′ | 1.96 | 0.027 | 7–8 | 1.84 | 0.036 |
| 10–10′ | 1.97 | 0.026 | 7–11 | 1.77 | 0.037 |
| 12–12′ | 1.99 | 0.031 | 7–12 | 1.73 | 0.044 |
| | C–C | | 8–9 | 1.74 | 0.041 |
| 1–2 | 1.65 | 0.028 | 8–12 | 1.76 | 0.038 |
| 1–13 | 1.48 | 0.038 | 9–10 | 1.85 | 0.037 |
| 2–14 | 1.54 | 0.031 | 9–12 | 1.78 | 0.041 |
| | C–B | | 10–11 | 1.72 | 0.038 |
| 1–3 | 1.77 | 0.037 | 10–12 | 1.79 | 0.041 |
| 1–4 | 1.75 | 0.038 | 11–12 | 1.77 | 0.038 |
| 1–5 | 1.73 | 0.036 | | | |
| 1–6 | 1.73 | 0.032 | | Av, A | Std dev |
| 2–3 | 1.75 | 0.030 | Br–Br | 3.87 | 0.021 |
| 2–6 | 1.67 | 0.035 | B–Br | 1.95 | 0.048 |
| 2–7 | 1.65 | 0.052 | C–B | 1.72 | 0.042 |
| 2–11 | 1.70 | 0.035 | B–B | 1.77 | 0.040 |
| | B–B | | | | |
| 3–4 | 1.73 | 0.039 | | | |
| 3–7 | 1.81 | 0.046 | | | |
| 3–8 | 1.81 | 0.039 | | | |

[a] Bond distances have not been corrected for thermal motion. [b] Over-all standard deviations were computed by averaging equivalent bond types and applying the equation

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

Individual standard deviations were computed from the full variance–covariance matrix calculated for all positions and temperature factors after the final refinement.

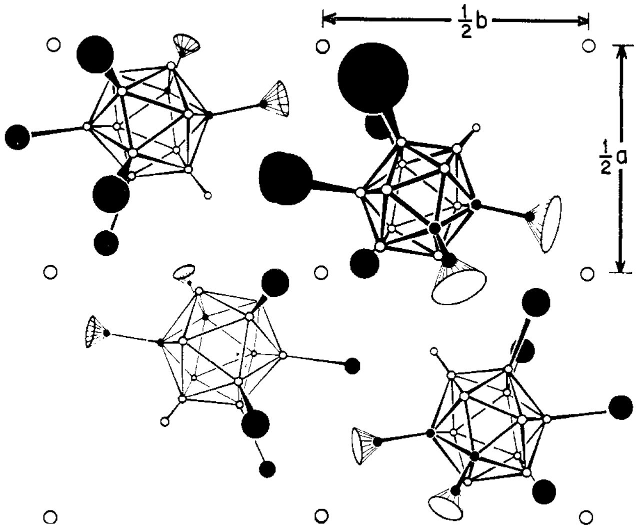

Figure 2.—The molecular packing as seen along *d*(001). Methyl hydrogens are indicated by circles of electron density; cage hydrogen atoms are omitted where necessary for clarity. Only centers of symmetry at $^1/_2$ along *c* are present; other symmetry elements are omitted for clarity.

longer than the 3.80 A Br· · ·Br distance in $o\text{-}B_{10}Br_2H_8C_2H_2$ and perhaps indicate some slight effect of Br· · ·Br repulsions. These distances are compatible with usual van der Waals contacts of about 3.9 A and with the contact of 3.8 A expected from a regular icosahedron. No significant distortions of B–B–Br angles from the regular icosahedral value of 121.7° occur (Table V). It therefore seems possible that substitution of more than three Br on $B_{10}C_2H_{12}$ or more than four Br on $B_{10}H_{10}C_2(CH_3)_2$ is primarily a question of electron availability, although other effects, such as steric influences, may play some role.

TABLE V

B–B–Br BOND ANGLES[a] IN $o\text{-}B_{10}Br_4H_6C_2(CH_3)_2$

| Atoms | Angle, deg | $\sigma^b$ | Av |
|---|---|---|---|
| 4–8–8′ | 122.4 | 1.6 | 121.7 |
| 7–8–8′ | 123.3 | 2.0 | |
| 5–10–10′ | 121.8 | 1.8 | |
| 11–10–10′ | 119.5 | 1.6 | |
| 4–9–9′ | 122.6 | 1.8 | 120.7 |
| 5–9–9′ | 118.6 | 1.8 | |
| 7–12–12′ | 122.0 | 2.1 | |
| 11–12–12′ | 119.7 | 1.6 | |
| 8–9–9′ | 121.8 | 2.0 | 120.6 |
| 10–9–9′ | 120.0 | 1.6 | |
| 8–12–12′ | 119.6 | 1.9 | |
| 10–12–12′ | 121.0 | 1.8 | |
| 9–8–8′ | 125.6 | 1.7 | 124.0 |
| 12–8–8′ | 125.7 | 2.0 | |
| 9–10–10′ | 122.8 | 1.5 | |
| 12–10–10′ | 121.9 | 1.8 | |
| 3–8–8′ | 119.7 | 1.7 | 120.5 |
| 6–10–10′ | 121.3 | 1.5 | |
| 12–9–9′ | 122.5 | 1.9 | 122.1 |
| 9–12–12′ | 121.8 | 1.8 | |

[a] The angle for a regular icosahedron is 121.7°. [b] Standard deviations were obtained from the full variance–covariance matrix after the last complete cycle of refinement of all position and temperature factors.

Table VI

Atomic Coordinates Used foe MO Calculations (A)[a] (in Orthogonal Coordinates)

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| C(1) | 0.000 | 1.335 | 0.825 | H(1) | 0.000 | 2.262 | 1.398 |
| C(2) | 0.000 | 1.335 | −0.825 | H(2) | 0.000 | 2.262 | −1.398 |
| B(3) | 1.432 | 0.885 | 0.000 | H(3) | 2.461 | 1.521 | 0.000 |
| B(4) | 0.885 | 0.000 | 1.432 | H(4) | 1.521 | 0.000 | 2.461 |
| B(5) | −0.885 | 0.000 | 1.432 | H(5) | −1.521 | 0.000 | 2.461 |
| B(6) | −1.432 | 0.885 | 0.000 | H(6) | −2.461 | 1.521 | 0.000 |
| B(7) | 0.885 | 0.000 | −1.432 | H(7) | 1.521 | 0.000 | −2.461 |
| B(8) | 1.432 | −0.885 | 0.000 | H(8) | 2.461 | −1.521 | 0.000 |
| B(9) | 0.000 | −1.432 | 0.885 | H(9) | 0.000 | −2.461 | 1.521 |
| B(10) | −1.432 | −0.885 | 0.000 | H(10) | −2.461 | −1.521 | 0.000 |
| B(11) | −0.885 | 0.000 | −1.432 | H(11) | −1.521 | 0.000 | −2.461 |
| B(12) | 0.000 | −1.432 | −0.885 | H(12) | 0.000 | −2.461 | −1.521 |
| Methyl C(1) | 0.000 | 2.645 | 1.635 | Methyl H(1) | 0.000 | 2.414 | 2.700 |
| Methyl C(2) | 0.000 | 2.645 | −1.635 | Methyl H(2) | 0.890 | 3.224 | 1.389 |
| | | | | Methyl H(3) | −0.890 | 3.224 | 1.389 |
| | | | | Methyl H(4) | 0.000 | 3.494 | −0.952 |
| | | | | Methyl H(5) | 0.890 | 2.684 | −2.263 |
| | | | | Methyl H(6) | −0.890 | 2.684 | −2.263 |

[a] Assumed bond distances in $o$-$B_{10}H_{10}C_2(CH_3)_2$ are B–B = 1.770, B–C = 1.713, C–C = 1.650, C–$CH_3$ = 1.540, B–H = 1.210, and C–H = 1.090 A.

Table VII

Net Mulliken Charges for $o$-$B_{10}H_{10}C_2H_2$ and Methyl Derivatives[a]

| Atom | $o$-$B_{10}H_{10}C_2H_2$ | 1-Methyl derivative $o$-$B_{10}H_{10}C_2H(CH_3)$ | 1,2-Dimethyl derivative $o$-$B_{10}H_{10}C_2(CH_3)_2$ |
|---|---|---|---|
| C(1) | 0.303 | 0.625 | 0.598 |
| C(2) | 0.303 | 0.267 | 0.590 |
| B(3) | 0.483 | 0.480 | 0.461 |
| B(4) | 0.216 | 0.196 | 0.179 |
| B(7) | 0.216 | 0.200 | 0.188 |
| B(8) | −0.038 | −0.057 | −0.072 |
| B(9) | 0.007 | −0.007 | −0.026 |
| B(12) | 0.007 | −0.011 | −0.031 |
| Methyl C(1) | | −0.539 | −0.539 |
| Methyl C(2) | | | −0.549 |
| H(1) | 0.035 | | |
| H(2) | 0.035 | 0.032 | |
| H(3) | −0.260 | −0.265 | −0.267 |
| H(4) | −0.243 | −0.246 | −0.247 |
| H(7) | −0.243 | −0.243 | −0.247 |
| H(8) | −0.234 | −0.235 | −0.235 |
| H(9) | −0.243 | −0.243 | −0.244 |
| H(12) | −0.243 | −0.244 | −0.245 |
| Methyl H(1) | | 0.158 | 0.158 |
| Methyl H(2) | | 0.151 | 0.153 |
| Methyl H(4) | | | 0.154 |
| Methyl H(5) | | | 0.154 |

[a] The point group symmetry of all the idealized methyl derivatives treated here is $C_s$, while that of $o$-$B_{10}H_{10}C_2H_2$ is $C_{2v}$; therefore, this table contains only entries for atoms which are not equivalent to $C_s$ symmetry. Equivalent atoms can be determined from Table VI, which lists the atomic coordinates used to calculate these charges.

Table VIII

Boron Framework Charges for $o$-$B_{10}H_{10}C_2H_2$ and Methyl Derivatives[a]

| Atom pair | $o$-$B_{10}H_{10}C_2H_2$ | 1-Methyl derivative $o$-$B_{10}H_{10}C_2H(CH_3)$ | 1,2-Dimethyl derivative $o$-$B_{10}H_{10}C_2(CH_3)_2$ |
|---|---|---|---|
| B(3)–H(3) | 0.223 | 0.215 | 0.194 |
| B(4)–H(4) | −0.027 | −0.050 | −0.068 |
| B(7)–H(7) | −0.027 | −0.043 | −0.059 |
| B(8)–H(8) | −0.272 | −0.292 | −0.307 |
| B(9)–H(9) | −0.236 | −0.250 | −0.270 |
| B(12)–H(12) | −0.236 | −0.255 | −0.276 |

[a] Entries have been included for atoms nonequivalent to $C_s$ symmetry, the lowest symmetry of all species.

These electronic effects were studied by the nonempirical molecular orbital method[8] in which atomic parameters were taken from self-consistent field results on diborane and ethane. The $B_{10}C_2$ cage was puckered to the geometry found in X-ray studies, methyl carbon atoms were placed radially outward, and methyl hydrogens were tetrahedrally arranged about C in molecular symmetry $C_s$ for both $B_{10}H_{10}C_2HCH_3$ and $B_{10}H_{10}C_2(CH_3)_2$ (Table VI). Two different orientations of hydrogen atoms on the monomethyl derivative produced no significant differences in the results. In addition, the results (Table VII) show that, as $CH_3$ is substituted for H on C, each B atom becomes more negative (by about 0.04 electron in the dimethyl derivative) largely at the expense of the cage C atom. Most important is the result that the order of charges on various types of B atoms is the same on the methyl derivatives as on the parent carborane, and a secondary result is that the charge distributions on B (Tables VII and VIII) have very nearly the $C_{2v}$ symmetry of the $B_{10}C_2$ unit even though the assumed molecular symmetry is only $C_s$. Thus, the factors governing electronic aspects of charge distribution in $o$-$B_{10}C_2H_{12}$ should also hold for the C-methyl and the C,C′-dimethyl derivatives. Finally we note that the slight increase in electron densities produced by C-methylation are in qualitative agreement with the experimental result that one more Br can be substituted on the C,C′-dimethyl derivative beyond the present limit of three Br on the parent carborane. These results support one of the assumptions which allowed Zakharkin and Kalinen[11] to reach correct conclusions on the order of

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

TABLE IX

OVERLAP POPULATIONS AND ENERGIES FOR $o$-$B_{10}H_{10}C_2H_2$ AND METHYL DERIVATIVES

| Bond | $o$-$B_{10}H_{10}C_2H_2$ | 1-Methyl derivative $o$-$B_{10}H_{10}C_2H(CH_3)$ | 1,2-Dimethyl derivative $o$-$B_{10}H_{10}C_2(CH_3)_2$ |
|---|---|---|---|
| C(1)–C(2) | 0.645 | 0.612 | 0.575 |
| C(1)–B(3) | 0.419 | 0.405 | 0.435 |
| C(1)–B(4) | 0.559 | 0.534 | 0.523 |
| C(2)–B(3) | 0.419 | 0.449 | 0.438 |
| C(2)–B(7) | 0.559 | 0.554 | 0.520 |
| B(3)–B(4) | 0.299 | 0.338 | 0.299 |
| B(3)–B(7) | 0.299 | 0.263 | 0.292 |
| B(3)–B(8) | 0.400 | 0.366 | 0.328 |
| B(4)–B(5) | 0.338 | 0.375 | 0.372 |
| B(4)–B(8) | 0.482 | 0.450 | 0.475 |
| B(4)–B(9) | 0.410 | 0.371 | 0.362 |
| B(7)–B(8) | 0.482 | 0.509 | 0.480 |
| B(7)–B(12) | 0.410 | 0.404 | 0.362 |
| B(8)–B(9) | 0.435 | 0.454 | 0.444 |
| B(8)–B(12) | 0.435 | 0.427 | 0.446 |
| B(9)–B(12) | 0.383 | 0.369 | 0.346 |
| C(1)–methylC(1) | | 0.912 | 0.916 |
| C(2)–methylC(2) | | | 0.918 |
| $\Sigma\epsilon_i$ | −114.502 | −127.743 | −140.984 |
| KE[a] | 326.607 | 365.396 | 404.182 |
| HFMO[b] | −0.382 | −0.381 | −0.378 |

[a] Kinetic energy in atomic units. [b] Highest filled molecular orbital in atomic units.

electrophilic attack on $o$-$B_{10}C_2H_{12}$ and its C-methyl derivatives.

Overlap populations (Table IX) are reasonable except for the values for C–$CH_3$ bonds of 0.91 to 0.92, which are to be compared with 0.71 for alkanes.[12] Of course, bond distances do not support partial double-bond character in these C–$CH_3$ bonds, so we believe that the problem is associated with the $K$ value[8] for $2p\pi$–$2p\pi$ overlap. Perhaps this same problem produces the lowered C–C overlap as carborane is methylated. Even so, the B–C overlap populations seem to be unaffected by this symptom, which may be cured when self-consistent field results are available on more appropriate model compounds. Values are also given in Table IX for $\Sigma\epsilon_i$, for the kinetic energy, and for the eigenvalue of the highest filled molecular orbital as an estimate of the vertical ionization potential.

Experimental and theoretical studies of these types are being carried out for other carboranes.

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(12) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2367 (1966).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING,
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# The Crystal Structure of Neodymium Telluride[1]

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The crystal structure of $NdTe_3$ has been determined from $h0l$ and $0kl$ electron density projections and by a least-square refinement of these structure factors. All other reported lanthanide tritellurides are isostructural with it. The crystal is orthorhombic, pseudo-tetragonal, with $a_0 = b_0 = 4.35$ A and $c_0 = 25.80$ A, space group Bmmb, with four molecules per unit cell. All four crystallographically independent atoms are in position 4(c), 0, $^1/_4$, $z$, of Bmmb. The $z$ parameters are 0.8306 (Nd), 0.0705 (Te), 0.4294 (Te), and 0.7047 (Te). The structure is closely related to that of $LaTe_2$. The lanthanide atoms in both structures have identical coordination. The $NdTe_3$ structure may be viewed as a stacking of $NdTe_2$ unit cells with additional Te layers between cells and with alternate cells shifted by $a_0/2$.

## Introduction

The rare earth lanthanides form a series of isostructural compounds of composition $LnTe_3$. Pardo, *et al.*,[2] report that Chirazi first prepared $CeTe_3$ by allowing $CeCl_3$ to react with $H_2$ and Te. The product consisted of $CeTe_2$ and golden, easily cleavable flakes. Carter[3] showed that these crystals had 1:3 stoichiometry, and he prepared also the tritellurides of La and Pr. He noted that their X-ray powder patterns were identical except for small differences in their cell parameters and from a single-crystal pattern of a disordered $LaTe_3$ crystal deduced that it was tetragonal, $a = 4.38$ A, $c = 26.10$ A, with 3 formula weights in the cell. Ramsey, *et al.*,[4] prepared $LaTe_3$ from the elements and obtained very good, ordered, single-crystal X-ray patterns. The diffraction photographs could be indexed on a tetragonal cell, with four formula weights in the unit cell, but nonspace-group extinctions were observed: *i.e.*, if $h + k = 2n + 1$, then reflections with all values of $l$ were present; if $h$ and $k$ were both even, then $l = 2n$ were present; and if $h$ and $k$ were both odd, $l = 2n$

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[2] M. Pardo, O. Gorochev, J. Flahaut, and L. Domange, *Compt. Rend.*, **260**, 1666 (1965).

[3] F. N. Carter, "Metallurgy of Semiconductor Materials," Interscience Publishers, Inc., New York, N. Y., p 260.

[4] T. H. Ramsey, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 1154 (1965).