such as $[B(ONO_2)_4]^-$, should be isolable in view of recent work.[12] We did find that when $(CH_3)_4NNO_3$ is treated with BF_3 at room temperature for 0.5 hr and then the excess BF_3 is pumped off, the solid gave a spectrum (Irtran plates) which had absorptions in the covalent nitrate region[12] (1582–1626 and 1297–1311 cm^{-1}).

Similarly, the reaction between $NaNO_2$ and BF_3, where the amount of BF_3 is less than the stoichiometric quantity, can be visualized as taking place in the following manner

$$\begin{aligned} 8NaNO_2 + 8BF_3 &\longrightarrow 8Na[F_3BNO_2] \\ 8Na[F_3BNO_2] &\longrightarrow 6NaBF_4 + 2Na[B(NO_2)_4] \\ 2Na[B(NO_2)_4] &\longrightarrow 2NaNO_2 + 2B(NO_2)_3 \\ 2B(NO_2)_3 &\longrightarrow B_2O_3 + 3N_2O_3 \\ 3N_2O_3 &\longrightarrow 3NO + 3NO_2 \\ 3NO_2 + 3NaNO_2 &\longrightarrow 3NaNO_3 + 3NO \\ \hline 9NaNO_2 + 8BF_3 &= 6NaBF_4 + 3NaNO_3 + 6NO + B_2O_3 \end{aligned}$$

The above equation is identical with the one proposed by Scott and Shriver for the above reaction conditions.

Scott and Shriver obtained $NOBF_4$, NO, $NaBF_4$, and small amounts of a noncondensables (not identified) when BF_3 (excess) reacted with $NaNO_2$ (heated to 180°). In this reaction the quantities of the individual gaseous products were not given. This observation can also be explained by the reaction scheme for nitrite (where it was in excess). In this case after the decomposition of N_2O_3 into NO and NO_2, the NO_2 will react with BF_3 forming $NOBF_4$, B_2O_3, and O_2 according to the equation proposed for the reaction between N_2O_4 and BF_3. It can be seen easily that all of the NO formed in the decomposition of N_2O_3 will not be converted into NO_2 as sufficient oxygen is not available. Hence, a trace of oxygen together with NO (major) will be the only gaseous products of this reaction.

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Molecular and Crystal Structure of $B_7C_2H_{11}(CH_3)_2$

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A three-dimensional X-ray diffraction study has yielded a structure of C_s symmetry for $B_7C_2H_{11}(CH_3)_2$ in which the B_7C_2 unit is an icosahedral fragment. In the open face of this fragment there are two adjacent bridge H atoms and two $CH(CH_3)$ groups, as was suggested from chemical and spectroscopic studies. Molecular orbital studies of the analogous $B_7C_2H_{13}$ molecule suggest that axial methylene hydrogen atoms are more positive than equatorial methylene hydrogen atoms. There are four molecules of $B_7C_2H_{11}(CH_3)_2$ in a unit cell having parameters $a = 10.56$, $b = 17.35$, $c = 5.57$ A, and $\beta = 82.4°$. The space group is $P2_1/n$, and the value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.08 for the 1146 observed reflections.

The compound $B_7C_2H_{13}$ is produced[1] by oxidation of $B_9C_2H_{11}$ by $K_2Cr_2O_7$ in acetic acid solution. Spectroscopic and chemical evidence suggests[1] that there are two bridge H atoms and two CH_2 groups. In the C,C′-dimethyl derivative, $B_7C_2H_{11}(CH_3)_2$, easily exchanged BHB bridges and CH′ units have been identified by Tebbe, Garrett, and Hawthorne, who have combined this chemical evidence with topological theory and steric information to suggest[1] that these CH′ units are axial. The molecular structure tentatively suggested by them has been confirmed for $B_7C_2H_{11}(CH_3)_2$ as described below. In addition, we have applied a new nonempirical (no experimental parameters) molecular orbital theory[2,3] to $B_7C_2H_{13}$, in which the axial hydrogen atoms are shown to be substantially more positively charged than the equatorial hydrogen atoms of the CH_2 groups in the ground electronic state. Since both CH units of a CH_2 group are terminal, this result may provide a basis for understanding the readily exchangeable axial protons in this molecular species.

Structure Determination

A needlelike crystal, about 0.2 mm in diameter and 0.7 mm in length, was grown by slow sublimation under vacuum near room temperature and was then sealed into a thin-walled glass capillary tube in a drybox. Weissenberg and precession photographs taken with the long axis (c) mounting indicated reciprocal lattice symmetry of C_{2h}, and Al-powder diffraction calibration established unit cell parameters of $a = 10.56 \pm 0.02$, $b = 17.35 \pm 0.02$, $c = 5.57 \pm 0.01$ A, and $\beta = 82.4 \pm 0.2°$. Extinctions of $0k0$ when k is odd and of $h0l$ when $h + l$ is odd indicate the space group $P2_1/n$. If four molecules are placed in the unit cell, the reasonable calculated density of 0.92 g cm^{-3} is obtained.

Relative intensities of 1823 independent reflections were measured on levels hkL for $0 \leqslant L \leqslant 6$ on the Buerger automated X-ray diffractometer. The ω scan

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[1] F. N. Tebbe, P. N. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 607 (1966).

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

[3] F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966).

TABLE I

LIST OF OBSERVED F_{hkl} VALUES[a]

```
L=0(K)(H) ( 0)( 0, 12)6398,,2222,,237,,348,,590,,277,,99+,( 1)( -1, 12)U,,
1467,3197,1806,996,0+,352,85+,577,44+,272,64+,35+,( 2)( 0, 12)2495,3358,713,
953,585,1230,853,853,308,92+,0+,150,81+,( 3)( 0, 12),1793,1754,1687,768,160,
58+,111,686,110,76+,121,113,( 4)( 0, 12)1619,1540,383,754,2075,782,1326,491,
138,214,88+,116,89+,( 5)( 0, 12),769,549,413,616,279,80+,196,405,198,118,140,
51+,( 6)( 0, 12)1777,1168,95+,1348,129,1042,126,659,415,231,117,304,29+,
( 7)( 0, 12),581,810,631,394,457,245,681,180,130,53+,167,109,( 8)( 0, 11)
797,1764,81+,789,421,101,222,166,74+,65+,230,0+,( 9)( 0, 11),1345,714,315,
248,431,153,251,266,67+,36+,89+,(10)( 0, 11)276,974,380,98+,1473,123,186,104,
60+,36+,162,153,(11)( 0, 10),414,863,234,464,290,88+,229,137,62+,105,
(12)( 0, 10)347,46+,157,915,469,304,185,153,22+,91+,63+,(13)( 0, 10),94+,
90+,315,240,0+,261,33+,50+,64+,61+,(14)( 0, 9)84+,567,352,17+,43+,135,72+,
143,114,30+,(15)( 0, 9),278,144,226,49+,118,246,26+,21+,59+,(16)( 0, 8)
137,71+,0+,48+,217,129,156,116,34+,(17)( 0, 7),30+,91+,83+,149,0+,150,66+,
(18)( 0, 6)174,53+,56+,72+,32+,53+,126,(19)( 0, 5),60+,132,120,140,105,
(20)( 0, 4)136,92+,90+,18+,28+,(21)( 1, 1)21+
L=1(K)(H) ( 0)(-12, 11),113,,320,,94+,,388,,231,,4703,,5915,,723,,842,,915,,
412,,50+,( 1)(-12, 12)130,79+,135,489,203,992,109,1161,60+,0+,548,2664,276,
3070,875,106,96+,391,443,640,189,55+,148,136,66+,( 2)(-12, 12)68+,85+,76+,
95+,454,973,234,650,1324,1495,2347,1683,4084,97+,2364,310,841,506,475,124,554,
69+,100,165,61+,( 3)(-12, 12)19+,92+,45+,257,244,358,250,0+,1160,794,108,595,
2924,46+,1348,287,84+,158,238,130,63+,135,193,0+,152,( 4)(-12, 12)21+,91+,
79+,318,205,326,546,1375,823,1938,601,204,1275,149,239,919,1527,126,351,894,
402,97+,304,228,0+,( 5)(-12, 11)130,42+,99+,123,486,531,86+,358,526,1051,217,
468,539,914,406,558,854,490,600,135,355,163,64+,111,( 6)(-12, 11)0+,115,76+,
210,305,254,200,268,1518,323,193,452,1603,413,234,95+,0+,96+,639,197,106,198,
169,101,( 7)(-12, 11)127,49+,0+,0+,613,103,555,0+,56+,0+,519,1311,1379,472,
537,348,40+,331,651,76+,267,91+,68+,44+,( 8)(-11, 11)255,82+,48+,166,175,335,
146,642,691,895,326,1802,339,367,84+,766,130,48+,468,168,73+,46+,185,
( 9)(-11, 11)158,144,107,125,515,84+,923,132,658,171,98+,14+,0+,457,249,361,
647,0+,42+,83+,66+,63+,40+,(10)(-11, 10)34+,130,45+,27+,205,479,568,332,476,
204,132,568,0+,0+,1179,175,993,90+,63+,65+,168,35+,(11)(-10, 10)59+,0+,0+,
77+,505,123,602,1128,373,476,477,655,0+,786,187,379,74+,137,0+,0+,28+,
(12)(-10, 10)92+,0+,49+,166,102,145,597,471,604,610,77+,478,0+,678,675,281,
179,46+,48+,77+,95+,(13)(-10, 9)149,82+,74+,30+,95+,91+,48+,109,357,720,271,
675,248,358,192,95+,305,91+,0+,39+,(14)( -9, 9)88+,0+,74+,0+,61+,83+,475,
65+,467,485,147,164,117,214,180,123,154,146,112,(15)( -9, 8)83+,60+,0+,86+,
115,181,175,281,192,256,145,99+,118,154,332,291,189,156,(16)( -8, 7)117,0+,
84+,97+,135,68+,121,118,103,104,0+,171,96+,253,25+,195,(17)( -7, 7)70+,89+,
92+,164,160,168,148,115,176,86+,57+,0+,359,128,167,(18)( -6, 6)0+,84+,154,
150,81+,0+,0+,0+,108,18+,232,42+,39+,(19)( -5, 5)0+,120,136,31+,242,76+,0+,
60+,97+,62+,94+,(20)( -3, 3)75+,205,176,62+,138,16+,0+
L=2(K)(H) ( 0)(-12, 10)147,,239,,255,,755,,779,,1471,,U,,345,,346,,109,,644,,
51+,( 1)(-12, 11)38+,56+,46+,0+,613,851,147,110,55+,425,1659,334,1760,884,502,
135,683,39+,673,310,65+,62+,150,39+,( 2)(-12, 11)50+,164,54+,0+,169,0+,644,
428,1266,1193,1205,922,48+,528,1591,1705,437,336,489,192,214,120,162,34+,
( 3)(-12, 11)53+,93+,0+,79+,139,737,488,200,145,1651,468,939,865,1386,190,737,
1261,318,278,248,138,123,113,87+,( 4)(-12, 11)148,92+,150,211,110,288,575,
57+,198,250,330,177,869,138,326,392,61+,933,278,126,33+,100,80+,198,
( 5)(-12, 11)69+,29+,111,123,250,142,174,206,208,236,586,606,677,990,1021,786,
492,188,217,0+,221,0+,208,56+,( 6)(-12, 11)89+,87+,134,260,102,406,0+,595,322,
679,480,374,890,1476,341,42+,33+,726,34+,226,208,132,41+,128,( 7)(-11, 10)106,
116,0+,79+,397,32+,621,53+,482,268,88+,237,1135,99+,357,619,17+,102,295,225,
183,0+,( 8)(-11, 10)0+,89+,0+,218,92+,729,295,144,190,83+,337,768,113,939,
0+,156,539,45+,291,43+,0+,48+,( 9)(-11, 10)50+,0+,0+,95+,148,592,243,1204,1191,
60+,80+,102,243,228,531,33+,324,438,71+,24+,60+,70+,(10)(-11, 10)39+,43+,0+,
191,159,0+,119,267,0+,502,597,489,655,218,298,898,123,274,0+,6+,34+,78+,
(11)(-10, 9)35+,116,151,31+,312,603,664,350,273,165,563,347,582,413,96+,207,
198,134,0+,62+,(12)(-10, 9)53+,156,237,73+,100+,132,171,347,1015,372,61+,
91+,414,239,543,279,184,111,97+,90+,(13)( -9, 8)135,112,87+,216,143,0+,240,
369,247,820,257,478,236,107,229,62+,142,150,(14)( -9, 8)114,186,48+,0+,99+,
177,82+,442,0+,148,0+,203,70+,121,225,117,0+,70+,(15)( -8, 7)50+,0+,33+,78+,
320,153,102,103,355,190,95+,146,136,273,324,228,(16)( -7, 6)104,134,109,150,
213,191,80+,118,59+,0+,134,325,80+,38+,(17)( -6, 5)78+,0+,170,215,149,200,
146,34+,38+,60+,119,81+,(18)( -5, 4)93+,21+,84+,278,21+,74+,61+,0+,151,0+,
(19)( -4, 3)0+,105,183,88+,182,126,86+,0+,(20)( -1, 0)46+,137
L=3(K)(H) ( 0)(-11, 9)420,,408,,66+,,115,,194,,527,,1316,,105,,86+,,138,,
93+,( 1)(-12, 10)50+,228,0+,141,378,552,971,0+,314,1661,44+,1294,910,1323,510,
942,429,221,122,155,0+,38+,0+,( 2)(-11, 10)149,412,0+,231,212,702,573,438,1211,
897,209,153,626,194,591,139,628,346,227,102,137,67+,( 3)(-11, 10)26+,103,113,
231,771,552,690,618,552,752,372,487,528,396,1174,101,419,117,101,166,62+,0+,
( 4)(-11, 10)36+,0+,153,124,41+,168,1058,387,700,500,79+,350,741,176,383,420,
549,166,263,126,143,0+,( 5)(-11, 10)100+,170,127,46+,168,317,227,134,350,60+,
477,753,618,113,158,816,400,101,78+,285,249,0+,( 6)(-11, 9)65+,0+,36+,142,
210,733,29+,669,150,146,77+,582,61+,512,144,279,214,228,144,280,0+,
( 7)(-11, 9)164,185,0+,33+,0+,100+,283,627,542,275,286,0+,437,423,103,492,
313,207,281,0+,50+,( 8)(-10, 9)130,148,115,236,123,502,565,152,573,75+,197,
1138,490,274,0+,168,170,0+,155,81+,( 9)(-10, 9)64+,45+,62+,205,172,492,629,
648,1030,401,450,82+,427,223,93+,55+,132,88+,109,10+,(10)(-10, 8)111,63+,
93+,119,133,76+,325,249,405,96+,531,329,809,161,170,108,85+,100+,0+,
(11)( -9, 8)16+,126,445,61+,63+,301,703,127,179,136,155,159,33+,257,232,71+,
0+,38+,(12)( -9, 7)55+,137,141,236,186,158,313,114,152,151,62+,99+,194,92+,
65+,131,149,(13)( -8, 7)167,261,162,205,69+,196,195,402,275,44+,0+,0+,44+,
50+,101,135,(14)( -8, 6)0+,221,0+,129,65+,168,55+,57+,39+,192,0+,124,0+,0+,
62+,(15)( -7, 6)108,160,80+,38+,146,61+,57+,63+,178,110,66+,148,138,92+,
(16)( -6, 5)105,185,0+,52+,171,195,67+,101,95+,74+,37+,119,(17)( -5, 3)0+,
70+,164,195,102,71+,61+,66+,0+,(18)( -3, 2)178,94+,157,71+,76+,29+
L=4(K)(H) ( 0)(-10, 8)549,,77+,,116,,604,,382,,U,,864,,111,,117,*,69+,
( 1)(-11, 9)108,96+,95+,79+,433,108,474,758,188,769,144,939,958,308,524,263,
95+,56+,29+,96+,60+,( 2)(-11, 9)82+,227,290,106,28+,101,109,785,332,326,484,
150,177,446,220,305,159,217,82+,96+,31+,( 3)(-10, 8)0+,71+,56+,184,798,90+,
278,533,920,463,189,978,473,62+,839,54+,56+,91+,192,( 4)(-10, 8)39+,61+,159,
104,87+,162,753,568,356,693,156,448,12+,183,191,306,109,0+,245,( 5)(-10, 8)
190,53+,0+,66+,322,370,359,40+,17+,117,344,42+,150,373,201,273,309,398,79+,
( 6)(-10, 8)137,90+,84+,193,256,335,155,622,306,102,299,566,388,85+,264,192,
94+,83+,48+,( 7)(-10, 8)138,169,130,113,269,211,51+,318,339,149,672,144,145,
92+,181,218,183,352,242,( 8)( -9, 7)68+,23+,186,79+,82+,155,0+,133,194,269,
256,602,227,0+,167,160,33+,( 9)( -9, 7)69+,188,38+,105,272,0+,796,69+,446,
254,426,176,207,90+,144,199,134,(10)( -9, 7)61+,70+,92+,498,267,75+,80+,129,
126,327,449,52+,216,154,80+,141,0+,(11)( -8, 6)196,56+,127,44+,0+,86+,128,
92+,428,357,254,33+,226,0+,0+,(12)( -8, 6)88+,168,113,180,148,0+,147,96+,497,
108,65+,202,0+,62+,35+,(13)( -7, 5)233,171,98+,60+,179,330,103,79+,88+,444,
102,0+,84+,(14)( -6, 4)108,24+,22+,0+,89+,132,412,157,86+,144,68+,
(15)( -5, 3)214,89+,68+,33+,72+,66+,39+,90+,55+,(16)( -3, 1)23+,100,102,107,
140
L=5(K)(H) ( 0)( -9, 5)181,*,174,,348,,101,,64+,,265,,0+,*,28+,( 1)( -9, 6)
58+,53+,0+,43+,0+,290,472,155,197,0+,312,287,99+,159,73+,4+,( 2)( -9, 6)105,
80+,84+,121,168,270,226,171,50+,444,222,21+,60+,96+,140,43+,( 3)( -9, 6)74+,
90+,60+,220,254,119,125,124,325,256,0+,268,317,33+,72+,37+,( 4)( -9, 6)59+,
127,61+,118,73+,355,405,272,126,452,75+,118,11+,136,93+,0+,( 5)( -8, 6)187,
75+,50+,36+,217,89+,261,40+,0+,43+,142,88+,146,89+,85+,( 6)( -8, 6)31+,66+,
278,76+,42+,111,277,190,169,351,97+,108,80+,90+,27+,( 7)( -8, 5)78+,220,138,
281,87+,200,40+,144,0+,60+,126,75+,9+,0+,( 8)( -7, 5)101,283,383,55+,48+,173,
79+,0+,200,84+,0+,0+,24+,( 9)( -7, 4)214,169,42+,31+,127,41+,49+,217,96+,
40+,55+,65+,(10)( -6, 4)16+,251,270,57+,13+,147,217,35+,51+,51+,25+,
(11)( -6, 3)68+,186,42+,70+,134,35+,105,227,150,50+,(12)( -5, 2)45+,84+,146,
0+,304,146,174,24+,(13)( -3, 1)58+,0+,156,48+,118
L=6(K)(H) ( 0)( -6, 2)118,*,53+,*,199,*,U,*,253,( 1)( -5, 2)90+,52+,19+,
50+,188,281,151,51+,( 2)( -5, 2)12+,23+,27+,113,0+,120,116,141,( 3)( -5, 2)
150,70+,90+,158,73+,33+,52+,65+,( 4)( -5, 2)0+,67+,99+,23+,0+,77+,153,75+,
( 5)( -4, 1)107,100,36+,87+,43+,126,( 6)( -4, 1)25+,0+,76+,66+,64+,115,
( 7)( -3, 0)33+,28+,109,82+
```

[a] The value of k and the range of h are given in parentheses. For each observed reflection the value of $10|F_o|$ is listed followed by a comma. Absent reflections are indicated by an asterisk, experimentally unobserved reflections by a U, and systematically extinct reflections by an extra comma. Those reflections not used in the final refinement are followed by a plus sign. No absorption or extinction corrections were made. The scaled value of $F(000)$ is given as a reference point. It is summed over the entire unit cell. Scale factors: $L = 0, 6.6556$; $L = 1, 6.8627$; $L = 2, 6.8070$; $L = 3, 7.0782$; $L = 4, 7.5214$; $L = 5, 6.4049$; $L = 6, 4.0975$.

time was proportional to the Lorentz factor, at rates of 1°/min and also at 4°/min. The radiation was Cu Kα, filtered through Ni foil, and the counter was a Xe-filled proportional counter which fed into a pulse-height analyzer. Background readings were consistent with minimum standard deviations of about 200 at small angles and 50 at higher angles. Lorentz-polarization factors, $(\mathrm{LP})^{-1} = 2\cos^2\mu \sin \Upsilon/(1 + \cos^2 2\theta)$, were applied *after* backgrounds were subtracted, and all reflections at different scan rates were correlated to a single relative scale. Only those 1146 reflections in the range 100–350,000 were used in the final refinements (Table I).

The structure was solved by application of Sayre's method[4] with the use of a modified form of Long's program[5] for the IBM 7094. First, the scaled structure factors F_{hkl} are normalized to $E_{hkl}^2 = 1$, where (Table II)

$$E_{hkl}^2 = F_{hkl}^2[\epsilon \sum_{j=1}^{N} f_j^2\,(hkl)]^{-1}$$

TABLE II

EXPERIMENTAL[a] AND THEORETICAL[b] VALUES OF NORMALIZED STRUCTURE FACTORS

	Exptl	Centrosym	Noncentrosym
$\langle \lvert E \rvert \rangle$	0.760	0.798	0.886
$\langle E^2 - 1 \rangle$	1.029	0.968	0.736
$\lvert E \rvert \geqslant 3.0$	0.5%	0.3%	
$\lvert E \rvert \geqslant 2.0$	5.3%	5.0%	
$\lvert E \rvert \geqslant 1.0$	30.2%	32.0%	

[a] For the 1336 reflections contained in levels hkl, $0 \leqslant L \leqslant 3$.
[b] For structures with randomly distributed atoms.

TABLE III

DISAGREEMENT FACTORS[a] BASED ON F

Sin θ	R	Class	hkl
0.00–0.40	0.09	All	0.079
0.40–0.50	0.08	$H = 2N$	0.080
0.50–0.60	0.06	$H = 2N + 1$	0.078
0.60–0.65	0.05	$K = 2N$	0.082
0.65–0.70	0.06	$K = 2N + 1$	0.076
0.70–0.75	0.09	$L = 2N$	0.082
0.75–0.80	0.11	$L = 2N + 1$	0.077
0.80–0.85	0.13	$K + L = 2N$	0.079
0.85–0.90	0.12	$K + L = 2N + 1$	0.080
0.90–1.00	0.10	$L + H = 2N$	0.079
		$L + H = 2N + 1$	0.079
		$H + K = 2N$	0.078
		$H + K = 2N + 1$	0.081
		$H + K + L = 2N$	0.078
		$H + K + L = 2N + 1$	0.080

$R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0794$

$R_{F^2} = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2 = 0.165$

$R_{wF} = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w F_o^4]^{1/2} = 0.165$

[a] Based on the 1146 reflections with $I_{hkl} \geqslant 100$.

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[4] D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

[5] R. E. Long, Ph.D. Thesis, UCLA, 1965, part III.

TABLE IV

FINAL ATOMIC PARAMETERS

Atomic Positions in Fractions of a Unit Cell Edge

Atom	x	y	z
B(1)	0.8251	0.2169	0.0692
B(2)	0.9234	0.1359	0.0299
B(3)	0.7592	0.1268	0.0644
B(4)	0.7181	0.1949	0.2686
C(5)	0.8506	0.2481	0.3554
B(6)	0.9807	0.2133	0.2358
B(7)	1.0240	0.1122	0.2878
B(8)	0.8711	0.0625	0.2999
C(9)	0.7435	0.1002	0.3480
C(10)	0.6299	0.0479	0.3760
C(11)	0.8376	0.3350	0.3880
H(12)	1.0321	0.1676	0.4235
H(13)	0.9670	0.0724	0.4084
H(14)	0.8101	0.2567	−0.0676
H(15)	0.9530	0.1298	−0.1409
H(16)	0.6975	0.1024	−0.0799
H(17)	0.6240	0.2202	0.2521
H(18)	0.8644	0.2217	0.5051
H(19)	1.0510	0.2522	0.2025
H(20)	1.1171	0.0867	0.2752
H(21)	0.8692	0.0027	0.1795
H(22)	0.7911	0.1127	0.5097
H(23)	0.7769	0.3557	0.2880
H(24)	0.8874	0.3537	0.5405
H(25)	0.8886	0.3554	0.2930
H(26)	0.5777	0.0725	0.4507
H(27)	0.6000	0.0235	0.2062
H(28)	0.6517	0.0074	0.4966

Temperature Factors^a (Anisotropic × 10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B(1)	129	48	335	11	45	23
B(2)	133	59	296	15	62	−3
B(3)	123	53	351	−4	34	15
B(4)	114	46	386	6	56	5
C(5)	142	36	386	4	65	8
B(6)	118	53	392	−3	55	14
B(7)	131	61	433	27	40	5
B(8)	179	40	426	10	60	−14
C(9)	140	40	412	−13	65	−13
C(10)	205	58	663	−40	97	−18
C(11)	223	37	748	−1	96	1

Temperature Factors (Anisotropic × 10^4)

Atom	B
H(12)	4.0
H(13)	4.1
H(14)	4.7
H(15)	3.8
H(16)	4.5
H(17)	4.7
H(18)	4.0
H(19)	4.3
H(20)	4.2
H(21)	6.9
H(22)	3.3
H(23)	10.1
H(24)	16.4
H(25)	10.5
H(26)	9.9
H(27)	8.1
H(28)	8.0

Maximum Value of σ for Atomic Positions in Fractions of the Unit Cell Edge

Atom type	x	y	z
B	0.0003	0.0002	0.0008
C (carborane)	0.0003	0.0001	0.0006
C (methyl)	0.0005	0.0002	0.0010
H (B terminal)	0.0041	0.0030	0.0101
H (bridge)	0.0029	0.0017	0.0075
H (methylene)	0.0029	0.0020	0.0081
H (methyl)	0.0102	0.0060	0.0254

Maximum Value of σ for Temperature Factors (Anisotropic × 10^4)

Atom type	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
B	4	1	50	2	6	4	
C (carborane)	3	1	49	1	5	2	
C (methyl)	5	1	53	2	8	4	
H (B terminal)							0.8
H (bridge)							0.6
H (methylene)							0.5
H (methyl)							3.0

[a] The thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ for anisotropic parameters and in the form $\exp[(-B \sin^2 \theta)/\lambda^2]$ for isotropic parameters.

in which in $P2_1/n$ the value of $\epsilon = 2$ for $0k0$ and $h0l$ reflections and $\epsilon = 1$ otherwise, and the sum over the squares of atomic scattering factors f_j extends over the N atoms of the unit cell. Second, the $E_{hkl} = E_h$ are ordered in decreasing size of $|E_h|\sum_{h'}|E_{h'}||E_{h+h'}|$, and the three largest which are linearly independent[6] are fixed in sign in order to determine the origin. Third, the next n (in our case, $n = 4$) reflections are given assumed signs, and each of the 2^n sets of assumed signs is then iterated by Sayre's equation through those reflections for which E_{hkl} is greater than some value, taken here as 1.5 (171 reflections). Fourth, after each iterative process produces no more sign changes, that consistency index

$$C = \frac{\langle|E_h\sum_{h'}E_{h'}E_{h+h'}|\rangle}{\langle|E_h|\sum_{h'}|E_{h'}||E_{h+h'}|\rangle}$$

which is highest is most probably correct. Of the 2^4 sets, the correct structure was that set which reached $C = 0.80$ in seven cycles, while the second highest value of $C = 0.64$ required nine cycles of iteration to reach self-consistency. In both of these iterations, and in only six others, the predicted signs of both the three origin-fixing and four arbitrarily signed reflections remained invariant. Thus spake the Computer!

A Fourier map in which the best E values were used as coefficients yielded the B_7C_4 framework as eleven peaks ranging from 438 to 264 on an arbitrary scale on which the next lowest peak was at 131. This unrefined B_7C_4 unit gave a value of $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.26 for those 974 reflections for which[7] sin

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(6) M. M. Woolfson, "Direct Methods in Crystallography," Oxford University Press, London, 1961.

(7) The atomic scattering factor tables were taken from the "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

$\theta \leqslant 0.75$. Full-matrix refinement[8] with standard errors σ was employed in subsequent work, with weights w related to total background B and scan S counts as

$$w^{-1/2} = \sigma = [0.01 + (S - B)/(S + B)^2]^{1/2}(S - B)$$

Essentially, these are fractional weights for refinement on F_{hkl}^2, because the term $(S - B)/(S + B)$,^{2} which accounts for some variation in counting statistics, is small compared with the constant 0.01 chosen for our particular set of data. Typical values for $||F_o| - |F_c||/\sigma(F_o)$ were of the order of 0.5.

Hydrogen atoms were located in difference electron density maps. The first difference map, which followed two cycles of scale factors (one for each level), position, and isotropic thermal parameter refinement to $R_F = 0.22$ was made from the 1823 reflections; it yielded very clearly resolved BH (terminal) hydrogen atoms at heights from 0.34 to 0.21 e A^{-3}, partially resolved bridge and CH (methylene) hydrogens from 0.32 to 0.25 e A^{-3}, boron and carbon residuals from 0.55 to 0.22 e A^{-3}, a recognizable smear in expected planes for CH_3 hydrogens, and no false peak higher than 0.10 e A^{-3}. Only the BH (terminal) hydrogens were added, followed by one cycle of anisotropic thermal parameter refinement of B and C atoms in which R_F dropped to 0.16 for reflections for which $\sin \theta \leqslant 0.75$. Well-resolved peaks were then found for both bridge and CH (methylene) hydrogens in the next difference map, but CH_3 hydrogens remained smeared in appropriate planes. Several refinements were then made of the seven scale factors and the appropriate anisotropic boron and carbon parameters, alternated with these parameters fixed and with isotropic and position refinement of hydrogen atoms ($R_F = 0.15$ for all data). Another difference map showed poorly resolved CH_3 hydrogen atoms, which were included in further alternating refinements to yield $R_F = 0.11$ for all 1823 reflections. For those intensities less than 50 on our original unscaled list, for which σ values ranged from 50 to 200, R_F was 0.78, and for those less than 100 the value of R_F was 0.33, but for those 1146 reflections greater than 100 the value of R_F was 0.083. Hence, the final refinements were made on this list of 1146 data which yielded $R_F = 0.079$ (Table III). A final difference electron density map showed no peaks higher than 0.18 e A^{-3}. All of the 171 signs which had been determined originally agreed with those computed after final refinement of the structure.

TABLE V

BOND DISTANCES AND STANDARD DEVIATIONS IN ANGSTROMS

Bond	Uncor	Cor[a]	σ[b]
B(2)–B(1)	1.779	1.776	0.005
B(2)–B(3)	1.777	1.777	0.006
B(2)–B(6)	1.817	1.816	0.005
B(2)–B(8)	1.825	1.830	0.006
B(2)–B(7)	1.719	1.725	0.006
B(7)–B(6)	1.826	1.819	0.005
B(7)–B(8)	1.821	1.819	0.006
B(6)–B(1)	1.778	1.775	0.006
B(8)–B(3)	1.789	1.783	0.005
B(1)–B(3)	1.710	1.714	0.005
B(1)–B(4)	1.729	1.728	0.006
B(3)–B(4)	1.735	1.732	0.005
B(4)–C(5)	1.693	1.692	0.004
B(4)–C(9)	1.713	1.716	0.004
B(6)–C(5)	1.714	1.711	0.004
B(8)–C(9)	1.706	1.700	0.005
B(3)–C(9)	1.674	1.673	0.006
B(1)–C(5)	1.671	1.670	0.005
C(9)–C(10)	1.529	1.559	0.006
C(5)–C(11)	1.526	1.558	0.004
B(7)–H(20)	1.09	1.06	0.03
B(2)–H(15)	1.04	1.01	0.04
B(3)–H(16)	1.05	1.05	0.04
B(1)–H(14)	1.03	1.02	0.04
B(4)–H(17)	1.08	1.08	0.03
B(8)–H(21)	1.07	1.08	0.05
B(6)–H(19)	1.04	1.02	0.03
C(5)–H(18)	0.95	0.93	0.04
C(9)–H(22)	1.00	0.98	0.04
B(6)–H(12)	1.37	1.36	0.03
B(8)–H(13)	1.33	1.33	0.04
B(7)–H(13)	1.18	1.16	0.03
B(7)–H(12)	1.22	1.20	0.03
C(11)–H(23)	0.87	0.94	0.07
C(11)–H(24)	0.88	0.90	0.07
C(11)–H(25)	0.99	1.14	0.11
C(10)–H(26)	1.05	1.05	0.07
C(10)–H(27)	0.85	0.88	0.06
C(10)–H(28)	0.98	0.99	0.06

Shortest Intermolecular Distances

Bond type	Dist	σ
B–B	3.958	0.009
B–C	3.999	0.009
C–C	4.339	0.010
B–H	3.07	0.04
C–H	3.28	0.04
H–H	2.59	0.06

[a] The second atom is assumed to be riding on the first atom: W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964. [b] The errors listed were obtained from the full variance–covariance matrix calculated during the final least-squares refinement of all atom positions and heavy atom anisotropic and scale parameters and from the errors in determining the unit cell dimensions.

Results and Discussion

The final parameters (Table IV) are based upon refinements of the 1146 largest reflections and yield the bond distances and bond angles shown in Tables V and VI, respectively. Standard deviations in these tables include the final full variance–covariance matrix interactions of scale factors, all atomic positional parameters, and anisotropic thermal parameters of boron and carbon atoms (as well as errors in the unit cell parameters), but, owing to a program limitation, the isotropic thermal parameters of hydrogen atoms were not included. These scale factors and β_{33} values, though almost linearly dependent, changed insignificantly upon simultaneous refinement, but heavy reliance on their physical significance is to be avoided.[9] The molecule and numbering scheme is shown in Figure 1, and the crystal structure is presented in Figure 2 from which

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(8) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(9) E. C. Lingafelter and J. Donohue, *Acta Cryst.*, **20**, 321 (1966).

TABLE VI

BOND ANGLES AND STANDARD DEVIATIONS IN DEGREES

Atoms	Angle	σ[a]
B(7)-B(2)-B(6)	62.1	0.2
B(7)-B(2)-B(8)	61.7	0.2
B(6)-B(2)-B(1)	59.3	0.2
B(8)-B(2)-B(3)	59.5	0.2
B(1)-B(2)-B(3)	57.5	0.2
B(2)-B(7)-B(6)	61.6	0.2
B(2)-B(7)-B(9)	62.0	0.2
B(7)-B(6)-B(2)	56.3	0.2
B(7)-B(8)-B(2)	56.3	0.2
B(2)-B(6)-B(1)	59.3	0.2
B(2)-B(8)-B(3)	58.9	0.2
B(6)-B(1)-B(2)	61.4	0.2
B(8)-B(3)-B(2)	61.6	0.2
B(2)-B(1)-B(3)	61.2	0.2
B(2)-B(3)-B(1)	61.3	0.2
B(1)-B(3)-B(4)	60.2	0.2
B(3)-B(1)-B(4)	60.6	0.2
B(3)-B(4)-B(1)	59.2	0.2
B(6)-C(5)-B(1)	63.3	0.2
B(8)-C(9)-B(3)	63.9	0.2
B(4)-C(5)-B(1)	61.8	0.2
B(4)-C(9)-B(3)	61.6	0.2
B(4)-C(5)-B(6)	111.8	0.2
B(4)-C(9)-B(8)	111.9	0.2
B(6)-B(1)-C(5)	59.5	0.2
B(8)-B(3)-C(9)	58.9	0.2
B(4)-B(1)-C(5)	59.7	0.2
B(4)-B(3)-C(9)	60.3	0.2
C(11)-C(5)-B(1)	115.3	0.3
C(10)-C(9)-B(3)	115.9	0.3
C(11)-C(5)-B(4)	119.3	0.3
C(10)-C(9)-B(4)	119.8	0.2
C(11)-C(5)-B(6)	119.0	0.2
C(10)-C(9)-B(8)	118.8	0.2
B(7)-H(12)-B(6)	90	2
B(7)-H(13)-B(8)	93	3
H(12)-B(7)-B(6)	48	2
H(13)-B(7)-B(8)	47	2
H(12)-B(6)-B(7)	42	1
H(13)-B(8)-B(7)	40	1
B(6)-C(5)-H(18)	98	1
B(8)-C(9)-H(22)	96	2
B(4)-C(5)-H(18)	91	2
B(4)-C(9)-H(22)	94	2
B(1)-C(5)-H(18)	132	2
B(3)-C(9)-H(22)	134	2
C(11)-C(5)-H(18)	112	2
C(10)-C(9)-H(22)	110	2
C(5)-C(11)-H(23)	114	5
C(5)-C(11)-H(24)	105	5
C(5)-C(11)-H(25)	112	6
C(9)-C(10)-H(26)	107	3
C(9)-C(10)-H(27)	109	4
C(9)-C(10)-H(28)	112	3
B(7)-B(6)-H(19)	119	2
B(7)-B(8)-H(21)	119	2
B(6)-B(1)-H(14)	117	2
B(8)-B(3)-H(16)	116	2
B(4)-B(1)-H(14)	125	2
B(4)-B(3)-H(16)	126	2
B(3)-B(4)-H(17)	122	2
B(1)-B(4)-H(17)	122	2
B(7)-B(2)-H(15)	121	2
B(6)-B(2)-H(15)	122	2
B(8)-B(2)-H(15)	130	2
B(3)-B(2)-H(15)	120	2
B(1)-B(2)-H(15)	116	2
C(5)-B(6)-H(19)	118	2
C(9)-B(8)-H(21)	119	2
C(5)-B(1)-H(14)	119	2
C(9)-B(3)-H(16)	119	2
C(5)-B(4)-H(17)	121	2
C(9)-B(4)-H(17)	122	2
H(26)-C(10)-H(27)	121	6
H(27)-C(10)-H(28)	98	6
H(26)-C(10)-H(28)	110	5
H(23)-C(11)-H(24)	85	7
H(24)-C(11)-H(25)	95	8
H(23)-C(11)-H(25)	132	8

[a] See footnote *b*, Table V.

hydrogen atoms have been omitted. No unusual features are present in the intermolecular contacts and packing.

The molecular structure tentatively suggested for $B_7C_2H_{11}(CH_3)_2$ by Tebbe, Garrett, and Hawthorne has been confirmed by these X-ray diffraction results. An important possibility that the chemical lability of the CH hydrogen is due to its tendency to form a CHB bridge can now be ruled out in view of the results that C(5)–H(18) = 0.93 and C(9)–H(22) = 0.98 in contrast with B(6)–H(18) = 2.05 and B(8)–H(22) = 2.04 A. The hydrogen bridges which are present are indeed unsymmetrical in that H(12) and H(13) are 0.15 A closer to B(7) than they are to B(6) and B(8), respectively. The molecule has a mirror plane, not required by the space group of the crystal, within twice σ for all distances involving B and C atoms. Indeed, the only bond angle problems, those involving two hydrogens of the CH_3 groups, are surely associated with some rotational or orientational disorder of these groups, already suggested by their lack of full resolution in the difference maps. The carborane framework is a slightly distorted icosahedral fragment, in which the outer six-membered ring, B(4), C(5), B(6), B(7), B(8), and C(9), resembles a cyclohexane ring in the chair conformation. The CH_3 groups are bound equatorially, while the CH hydrogen atoms are in a polar conformation relative to this ring. The intramolecular contact of 2.04 ± 0.04 between these CH hydrogen atoms is considerably shorter than the usual van der Waals contact of 2.4 A, but close to the value suggested[10,11] as a minimum in other borane structures.

Molecular orbital studies of $B_7C_2H_{13}$, idealized[11] to B–H terminal and C–H bond lengths of 1.196 and 1.100 A, respectively, were then carried out in an attempt to provide further understanding of the lability of the polar CH hydrogen atoms (unlike those in cyclohexane). A molecular mirror plane was assumed (Table VII), and parameters were taken from the recent nonempirical molecular orbital method.[2,3] Because of some uncertainty[12] in the value of the zero overlap

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(10) W. N. Lipscomb, *Inorg. Chem.*, **3**, 1683 (1964).

(11) W. N. Lipscomb, "Boron Hydrides," The W. A. Benjamin Co., New York, N. Y., 1963, Chapter I.

(12) J. A. Potenza and M. D. Newton, unpublished results.

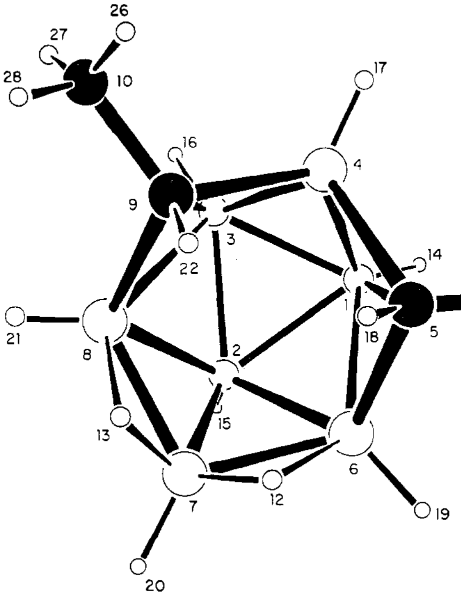

Figure 1.—The molecular structure and numbering scheme for $B_7C_2H_{11}(CH_3)_2$. Boron atoms are represented by large unfilled circles, hydrogen atoms by small unfilled circles, and carbon atoms by filled circles.

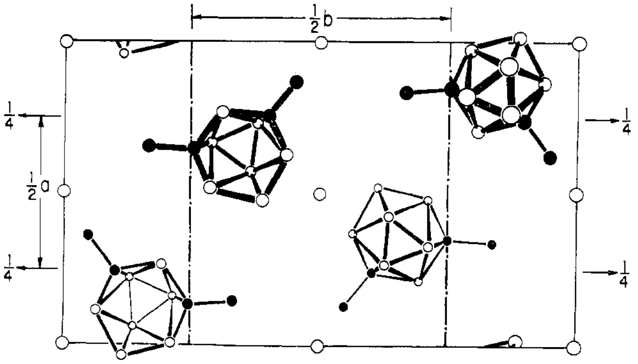

Figure 2.—The molecular packing of $B_7C_2H_{11}(CH_3)_2$ as seen in projection along the c axis. The hydrogen atoms have been omitted for the sake of clarity.

Table VII

Atomic Coordinates Used for MO Calculations of $B_7C_2H_{13}$ in Angstroms[a] (in Orthogonal Coordinates)

Atom[b]	x	y	z
B(1)	−0.855	−1.144	2.544
B(2)	0.000	−1.394	1.006
B(3)	0.855	−1.144	2.544
B(4)	0.000	0.000	3.523
C(5)	1.402	0.433	2.658
B(6)	−1.430	−0.270	1.099
B(7)	0.000	0.000	0.000
B(8)	1.430	−0.270	1.099
C(9)	−1.402	0.433	2.658
H(10)	2.351	0.570	3.197
H(11)	−2.351	0.570	3.197
H(12)	−0.892	0.719	0.359
H(13)	0.892	0.719	0.359
H(14)	−1.555	−2.026	2.950
H(15)	0.000	−2.489	0.531
H(16)	1.555	−2.026	2.950
H(17)	0.000	−0.065	4.716
H(18)	−0.971	1.398	2.357
H(19)	−2.489	−0.546	0.617
H(20)	0.000	−0.112	−1.190
H(21)	2.489	−0.546	0.617
H(22)	0.971	1.398	2.357

[a] The bond distances were calculated by averaging the $B_7C_2H_{11}(CH_3)_2$ atom coordinates (Table IV) about the molecular mirror plane. All B–H terminal and C–H bond distances were restricted to 1.196 and 1.100 A, respectively. [b] The numbering scheme used is that found in Figure 1 with C(10) and C(11) changed to H(10) and H(11), respectively.

Table VIII

Net Mulliken Charges for $B_7C_2H_{13}$[a]

Atom	$K^{ZO}_{2s2p} = 0.354$	$K^{ZO}_{2s2p} = 0$
B(1)	0.37	0.06
B(2)	−0.00	−0.25
B(4)	0.09	−0.08
C(5)	−0.32	−0.45
B(6)	0.14	−0.04
B(7)	−0.08	−0.17
H(11)	0.10	0.18
H(12)	0.13	0.12
H(14)	−0.24	0.10
H(15)	−0.22	0.01
H(17)	−0.22	0.10
H(18)	0.30	0.33
H(19)	−0.20	0.10
H(20)	−0.15	0.05

[a] The assumed molecular symmetry is C_s. Equivalent atoms can be determined by referring to Table VII where the appropriate atomic coordinates are listed.

matrix element K^{ZO} between 2s and 2p orbitals on the same atom, we have used both the value K^{ZO} = 0.354 from self-consistent field results[13] on B_2H_6, probably as one extreme, and the value of $K^{ZO} = 0$ (Table VIII). It is of considerable interest that the axial H atoms are the most positive in the molecule, while all other H atoms are in ranges of Mulliken charge expected from earlier molecular orbital studies.[3] As has already been established previously,[3] the main effect of inclusion of zero overlap matrix elements is to transfer electron density from B and C atoms to terminal hydrogen atoms, including both hydrogens of the CH_2 groups. Overlap populations are but little changed: 0.621 to 0.622 for CH (axial) and 0.710 to 0.713 for CH (equatorial) for K^{ZO} = 0.354 and K^{ZO} = 0, respectively. It appears that the CH (axial) bond is significantly weaker than the CH (equatorial) bond. Both these charges and bond strengths in the ground state of $B_7C_2H_{13}$ may carry over their effect into the transition state for proton dissociation. Both of these overlap populations in CH_2 groups appear to be significantly lower than those[14,15] for CH in CH_4 (0.76), C_2H_6 (0.76), C_2H_4 (0.78), C_2H_2 (0.78), $C_2B_4H_8$ (0.81), $C_2B_5H_7$ (0.87), o-$C_2B_{10}H_{12}$ (0.82), m-$C_2B_{10}H_{12}$ (0.82), and p-$C_2B_{10}H_{12}$ (0.82).

The precursor of $B_7C_2H_{13}$ is $B_9C_2H_{11}$, for which the original suggestion[16] of an icosahedral fragment was modified to a closed polyhedron[17] of C_{2v} symmetry with

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[13] W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966).

[14] F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2367 (1966).

[15] F. P. Boer, Ph.D. Thesis, Harvard University, 1965, Chapter IV.

[16] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).

[17] T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Letters*, **12**, 715 (1965).

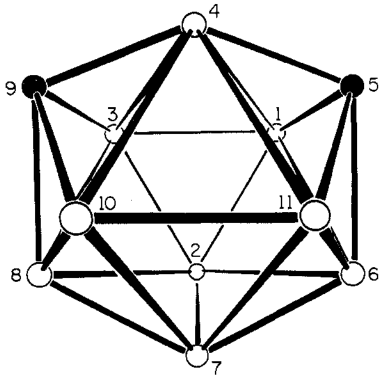

Figure 3.—Molecular structure of $B_9C_2H_{11}$. The hydrogen atoms have been omitted.

C atoms at positions 5 and 9 (Figure 3). However, the chemical and nuclear magnetic resonance evidence did not rule out the possibility[18] that the C atoms of $B_9C_2H_{11}$ are at positions 6 and 8. If the removal of B atoms from $B_9C_2H_{11}$ occurs without rearrangement of the boron framework, then the structure found here for $B_7C_2H_{11}(CH_3)_2$ and hence inferred for $B_7C_2H_{13}$ supports positions 5 and 9 for C atoms in $B_9C_2H_{11}$ (Figure 3). After completion of this study, we have received results of an X-ray diffraction study of $B_9C_2H_{11}$ itself by Tsai and Streib,[19] who have proved that the structure shown in Figure 3 for $B_9C_2H_{11}$ is correct.

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[18] Refer to footnote 3 of ref 12.

[19] C-c. Tsai and W. E. Streib, private communication, Aug 1966; see also *J. Am. Chem. Soc.*, **88**, 4513 (1966).

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The Crystal Structure of Twinned Low-Temperature Lithium Phosphate

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It is shown that lithium phosphate (Li_3PO_4) prepared by precipitation from an aqueous solution differs from the form that has been described in the literature. When heated it transforms irreversibly at 502 ± 5° to the familiar form. The low-temperature form crystallizes in space group Pmn2$_1$ with $a_0 = 6.1150 \pm 0.0010$ A, $b_0 = 5.2394 \pm 0.0011$ A, and $c_0 = 4.8554 \pm 0.0010$ A; $Z = 2$. It exhibits merohedral twinning with the twin plane normal to the *z* axis. The multiplicity of the predominant image is 0.75. All atoms are tetrahedrally coordinated. The final reliability index is 0.054.

Introduction

The assumption of Zambonini and Laves[2] that lithium phosphate (Li_3PO_4) crystallizes with a structure similar to that of olivine (Mg_2SiO_4) was generally accepted prior to 1960. In that year, Zemann[3] determined the structure for a single crystal obtained by recrystallization of a precipitate of lithium phosphate from molten lithium chloride. He showed conclusively that the lithium atoms are in tetrahedral coordination, thus ruling out the olivine-type structure.

In 1963 Swanson, *et al.*,[4,5] reported the existence of a second form of lithium phosphate prepared by precipitation from an aqueous solution. From the powder diffraction data it appeared to have the same space group and nearly the same lattice parameters as the phase described by Zemann. Speculation arose as to the relationship of the two forms and an investigation of the crystal structure was undertaken.

Experimental Section

Sample Preparation.—Samples of low-temperature lithium phosphate (Li_3PO_4) were prepared by neutralizing a slurry of lithium carbonate by slowly adding phosphoric acid. The mixture was boiled for a few minutes and the precipitate was washed with water and centrifuged. Spectrographic analysis indicated no impurities greater than 0.01%. A few crystals, large enough for X-ray studies, were grown by slow evaporation over a period of 2 months from a 1-l. water solution of the very slightly soluble lithium phosphate. The one selected for intensity measurements was tabular with nicely formed prism faces, probably {110}. The over-all dimensions were 0.07, 0.16, and 0.05 mm in the *a*, *b*, and *c* directions, respectively.

A study by the differential thermal analysis technique using 12°/min and 1°/min heating rates showed that the new form of lithium phosphate transforms at 502 ± 5° to the form described by Zemann (see Figure 1). The transformation does not appear to be reversible. There is no weight change associated with it, so both phases are assumed to have the same composition. A second transition was observed at 1183 ± 5° by differential thermal anaysis and confirmed by high-temperature powder diffraction. It has not been shown that the phase that occurs above 1183° has the Li_3PO_4 composition, and it will not be considered here. The discussion will be limited to the low-temperature form as prepared by Swanson, *et al.*, by precipita-

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[2] F. Zambonini and F. Laves, *Z. Krist.*, **83**, 26 (1932).

[3] J. Zemann, *Acta Cryst.*, **13**, 863 (1960).

[4] H. E. Swanson, M. C. Morris, E. H. Evans, and L. Ulmer, "Standard X-ray Diffraction Powder Patterns," National Bureau of Standards Monograph 25, Section 3, U. S. Government Printing Office, Washington, D. C., 1964, p 38.

[5] H. E. Swanson, M. C. Morris, and E. H. Evans, "Standard X-ray Diffraction Powder Patterns," National Bureau of Standards, Monograph 25, Section 4, U. S. Government Printing Office, Washington, D. C., 1966, p 21.