H_{10}, so that no adjustments of the remainder of the molecule have been made. The energy gaps between the lowest filled and highest unfilled molecular orbitals are also given in Table IX. The C_2 structure seems to be distinctly less stable than the C_{2v} structure, which is only slightly less stable than the observed structure of C_s symmetry. We are not sure, without a considerably extended investigation of variations of many parameters, that this result is of significance, but we would surely have been disturbed if the method had yielded greater stability for either the C_{2v} or C_2 structures.

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Molecular and Crystal Structures of $B_4H_6C_2H_2$ and $B_4H_6C_2(CH_3)_2$

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Single crystal three-dimensional X-ray diffraction studies at −100° have established the structures of $B_4H_6C_2H_2$ (monoclinic, $P2_1/n$, four molecules in a unit cell having $a = 8.97$, $b = 10.60$, $c = 5.83$ Å., and $\beta = 95° 47'$) and of $B_4H_6C_2(CH_3)_2$ (orthorhombic, $P2_1nm$, two molecules in a unit cell having $a = 5.709$, $b = 6.046$, and $c = 10.556$ Å.). The structure is an icosahedral cap of B_4C_2 with one B as apex and a five-membered B_3C_2 ring having C atoms adjacent and two BHB bonds. These molecules have C_s symmetry and strongly resemble B_6H_{10} in geometrical and valence structures.

The dihydrocarborane $B_4H_6C_2H_2$, more precisely known as 2,3-dicarbahexaborane(8), was first discovered and synthesized by Weiss[1] in very small yields in a reaction of B_5H_9 with C_2H_2 at elevated temperatures and pressures. The syntheses of this compound and, for the first time, of its alkyl analogs[2] $B_4H_6C_2RR'$ (in particular $B_4H_6C_2(CH_3)_2$) in excellent yields from B_5H_9 and $RCCR'$ with the use of 2,6-dimethylpyridine as a catalyst represent a significant advance in the availability of these interesting molecules for further study.

The structure for $B_4H_6C_2H_2$ implied by the original name,[1] ethenyltetraborane(8), was shown to be inconsistent with the ^{11}B nuclear magnetic resonance spectrum[2] obtained by Williams, who first assigned[2,3] the structure confirmed below by X-ray diffraction methods and subsequently reported in a preliminary communication[4,5] on $B_4H_6C_2(CH_3)_2$. Further interest, which led to the elucidation of both structures described herein, was generated by the suggestion of a possible internal rearrangement,[6] perhaps leading to a more stable isomer in which the C atoms are nonadjacent. However, this rearrangement has not occurred, and it is shown below that the C atoms of the framework are adjacent to one another in both $B_4H_6C_2H_2$ and $B_4H_6C_2(CH_3)_2$.

Experimental

The samples, both stable liquids at room temperature, were distilled and sealed into capillaries on a vacuum line. During slow growth of the crystal, near −50° for both compounds, the capillary which was mounted on a Weissenberg or precession goniometer was maintained at low temperature by a cold gas stream obtained by evaporation of liquid N_2.[7] Supercooling of $B_4H_6C_2(CH_3)_2$ by as much as 20° caused some difficulty in obtaining single crystals, which were finally obtained from a suitable seed remaining after a polycrystalline sample was carefully melted.

Crystals of $B_4H_6C_2H_2$ were easily grown at about −50° as needles elongated along c, and were cooled to −100° for diffraction study. The reciprocal lattice symmetry of C_{2h} and the space group of $P2_1/n$ from extinctions of $h0l$ for $h + l$ odd and of $0k0$ when k is odd were established. Calibration of an $hk0$ Weissenberg level and a c axis oscillation pattern with an Al powder pattern yielded unit cell dimensions of $a = 8.97 \pm 0.03$, $b = 10.60 \pm 0.03$, and $c = 5.83 \pm 0.02$ Å., in conjunction with a precession $h0l$ level which established the monoclinic angle β as $95° 47' \pm 4'$. The assumption of four molecules per unit cell leads to the very reasonable calculated density of 0.903 g. cm.$^{-3}$. The levels hkL for $0 \leqslant L \leqslant 4$ were taken on a Weissenberg goniometer, and levels Hkl for $0 \leqslant H \leqslant 3$ and hKl for $0 \leqslant K \leqslant 1$ were photographed on a precession goniometer. Of the 1006 independent reciprocal lattice points only 93 were too weak to produce a measurable intensity. These photographs covered 75% of the Cu Kα sphere of reflection.

The $B_4H_6C_2(CH_3)_2$ crystals gave 470 out of a possible 491 unique reflections in the Cu Kα sphere. Levels Hkl for $0 \leqslant H \leqslant$

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TABLE I

THE OBSERVED STRUCTURE FACTORS[a] FOR $B_4H_6C_2H_2$ (A) AND $B_4H_6C_2(CH_3)_2$ (B)

A

```
H= 0(K)(L) ( 0)( 1,7),571/26,,372/18,,U,, ( 1)( 0,5),2213/299,219/16,411/17,
399/20,314/29, ( 2)( 0,7)2076/162,655/28,711/35,504/20,242/12,U,U,264/27,
 ( 3)( 0,4),75/5,62/4,131/7,66/5, ( 4)( 0,5)226/11,892/41,439/18,169/10,484/
21,250/26, ( 5)( 0,5),271/15,757/32,750/29,145/8,262/27, ( 6)( 0,4)692/27,965/
40,70/5,305/16,471/21, ( 7)( 0,4),78/7,589/25,219/10,167/9, ( 8)( 0,4)386/20,
83/7,683/30,139/9,187/11, ( 9)( 0,4),30*,268/14,218/11,112/6, (10)( 0,4)250/
15,346/19,167/10,32*,239/13, (11)( 0,4),50/6,141/8,80/7,160/9, (12)( 0,3)195/
10,24*,144/8,70/6, (13)( 0,2),223/16,81/7
H= 1(K)(L) ( 0)(-3,7)526/26,,1478/163,,1581/128,,341/14,,560/32,,374/30,
 ( 1)(-6,4)421/39,U,313/15,670/34,925/45,1674/198,812/54,707/71,241/14,133/
7,478/26, ( 2)(-5,5)536/47,403/20,187/10,784/43,1344/87,2237/200,336/17,697/
37,266/13,202/11,601/52, ( 3)(-6,6)471/57,U,439/20,1114/58,361/18,473/21,467/
21,627/31,485/24,839/35,262/13,279/34,412/50, ( 4)(-5,5)412/50,374/19,226/12,
636/29,92/7,648/31,140/10,1032/56,361/18,499/23,281/34, ( 5)(-4,4)172/10,125/
7,209/11,687/31,370/18,527/26,63/4,429/21,228/11, ( 6)(-4,4)31*,315/17,187/
12,500/25,818/39,795/36,83/6,354/15,31*, ( 7)(-5,4)270/33,354/18,316/17,898/
41,430/22,387/19,99/8,195/14,33*,137/8, ( 8)(-4,4)103/8,155/10,199/15,855/39,
469/26,717/34,190/11,283/15,204/11, ( 9)(-4,5)392/19,329/18,654/32,326/18,224/
11,434/25,96/9,300/16,29*,331/40, (10)(-4,4)80/7,300/16,300/15,101/9,164/9,
299/20,291/16,288/15,154/9, (11)(-4,4)140/8,148/9,216/16,44/5,101/7,70/7,153/
9,70/6,113/6, (12)(-3,3)155/8,22*,87/7,64/5,71/6,98/7,178/11, (13)(-2,2)71/
6,189/14,22*,62/5,85/8
H= 2(K)(L) ( 0)(-6,7)315/27,,669/31,,59/8,,2698/242,,715/33,,386/18,,163/38,,
 ( 1)(-5,7)287/36,663/38,1034/53,496/26,3092/365,994/51,329/18,281/16,590/25,
306/15,U,334/41,321/40, ( 2)(-5,7)488/74,20*,415/16,319/14,981/62,1703/112,
172/11,443/22,330/17,273/14,U,U,365/55, ( 3)(-5,6)306/46,333/17,177/11,36/3,
1036/65,314/18,403/21,407/21,290/13,419/21,U,356/54, ( 4)(-6,4)295/45,268/41,
505/24,73/5,279/17,183/13,661/32,622/29,149/11,164/9,692/43, ( 5)(-7,5)347/
52,U,U,78/6,386/20,833/41,419/20,391/20,111/8,327/20,592/24,45/4,295/45,
 ( 6)(-7,4)283/43,U,U,233/12,799/36,26*,695/34,253/14,93/8,142/8,225/13,490/
25, ( 7)(-5,5)383/58,132/7,382/17,888/43,292/19,89/6,226/15,121/8,322/18,296/
15,311/47, ( 8)(-4,4)32*,189/12,183/11,200/13,35*,29*,185/11,141/9,84/7,
 ( 9)(-5,4)305/46,130/7,413/21,339/18,242/19,37*,303/46,55/5,249/15,70/6,
 (10)(-5,4)295/45,26*,144/9,148/9,120/9,89/8,49/6,44/4,142/9,193/10,
 (11)(-4,4)204/11,85/8,61/6,27*,188/11,125/9,105/7,108/7,36/4, (12)(-3,3)97/
6,121/7,149/11,64/5,98/8,279/16,45/4, (13)(-1,1)62/5,21*,244/16
H= 3(K)(L) ( 0)(-7,7)361/31,,250/42,,295/13,,198/12,,673/30,,740/28,,248/27,,
206/34, ( 1)(-6,6)316/38,289/63,226/11,689/29,859/55,248/15,112/6,505/26,694/
44,70/6,837/43,U,249/54, ( 2)(-4,5)727/43,526/20,132/10,1182/74,369/21,768/
45,357/24,206/11,521/25,291/42, ( 3)(-7,5)303/43,392/56,U,217/12,391/19,955/
74,267/17,330/19,159/12,949/64,481/24,82/7,262/38, ( 4)(-5,5)372/53,76/6,47/
4,165/11,242/18,115/6,596/36,656/32,634/28,398/20,388/56, ( 5)(-4,4)168/9,30*,
277/15,23*,948/50,602/30,83/6,533/26,31*, ( 6)(-6,4)321/46,U,59/5,204/10,157/
9,159/10,220/14,466/23,767/39,225/11,241/12, ( 7)(-4,4)166/9,46/4,815/40,344/
23,238/16,309/20,260/14,187/12,32*, ( 8)(-5,4)338/48,60/5,523/26,172/9,277/
18,323/18,185/13,201/12,34*,159/9, ( 9)(-4,4)280/15,34*,441/27,313/20,222/12,
115/10,179/10,212/11,175/10, (10)(-4,4)24*,96/9,114/8,218/16,293/16,209/19,
142/8,29*,315/16, (11)(-4,3)128/6,110/7,79/6,233/17,360/19,26*,136/8,23*,
 (12)(-3,2)88/6,126/7,60/5,129/7,84/7,100/7, (13)(-1,0)95/10,65/8
H= 4(K)(L) ( 0)(-4,6)952/49,,339/19,,24*,,1005/55,,88/7,,260/43, ( 1)(-4,4)
164/9,431/22,601/30,953/58,273/15,285/17,564/28,472/24,381/18, ( 2)(-4,4)150/
8,399/22,910/71,201/15,552/38,291/19,301/20,900/46,243/13, ( 3)(-4,4)283/15,
102/6,516/30,1542/97,884/50,604/36,93/6,502/28,238/13, ( 4)(-4,4)30*,461/25,
482/25,120/9,166/9,469/26,294/17,32*,575/31, ( 5)(-4,4)249/14,326/20,406/28,
520/31,164/9,583/35,224/16,678/32,32*, ( 6)(-4,4)143/8,493/27,80/6,497/27,60/
5,447/29,298/17,227/14,174/10, ( 7)(-4,4)188/11,35*,399/27,43/5,536/37,182/
13,69/7,380/20,44/4, ( 8)(-4,4)83/7,155/10,90/6,153/11,82/7,131/9,538/36,89/
8,326/18, ( 9)(-4,4)121/7,135/8,60/6,94/8,218/12,30*,79/5,119/7,163/9,
 (10)(-4,4)129/7,96/9,108/7,28*,211/12,113/9,26*,197/11,41/3, (11)(-3,3)183/
10,183/13,73/9,31*,339/22,255/14,109/7, (12)(-2,2)95/7,154/10,69/5,132/10,168/
9
H= 5(K)(L) ( 0)(-7,6)428/46,,U,,83/7,,600/27,,663/30,,903/37,,U,, ( 1)(-6,4)
280/61,220/48,94/8,264/15,348/21,680/35,743/38,160/11,95/7,289/17,465/24,
 ( 2)(-4,4)185/10,330/15,420/24,240/17,34/3,894/52,26*,72/9,264/14,
 ( 3)(-4,4)96/8,200/12,717/42,107/8,169/9,369/24,837/49,412/23,139/8,
 ( 4)(-4,4)139/8,903/47,437/30,468/26,52/4,249/18,327/18,263/16,81/7,
 ( 5)(-4,4)238/13,108/8,511/35,242/18,877/50,613/37,429/29,252/15,233/13,
 ( 6)(-4,4)258/14,574/32,176/10,300/22,448/31,29*,696/41,53/7,30*, ( 7)(-4,4)
31*,162/10,226/17,30*,37*,630/38,101/7,143/9,28*, ( 8)(-4,4)96/8,80/7,44/4,
71/8,111/7,249/18,129/9,31*,134/8, ( 9)(-4,4)92/6,152/10,29*,197/14,84/7,256/
19,42/4,198/12,19*, (10)(-4,3)157/9,82/7,286/16,238/17,33*,26*,107/7,90/6,
 (11)(-3,2)65/6,20*,355/23,356/25,137/10,134/8, (12)(-1,0)255/17,95/6
H= 6(K)(L) ( 0)(-5,5),291/15,,228/12,,261/13,,148/9,,148/8,, ( 1)(-6,4)282/
61,223/48,146/8,107/7,27*,102/9,287/16,88/7,383/24,222/11,184/10, ( 2)(-4,4)
212/11,695/33,785/46,602/40,33*,144/10,495/34,348/21,160/9, ( 3)(-4,4)517/28,
385/18,402/27,613/37,475/28,28*,277/16,447/25,102/8, ( 4)(-4,4)433/19,590/32,
860/50,28*,486/28,29*,350/20,110/10,101/8, ( 5)(-4,4)158/9,118/7,263/15,63/
7,108/7,346/25,30*,209/13,29*, ( 6)(-4,4)193/11,182/11,51/5,440/29,302/17,100/
9,341/19,156/10,173/10, ( 7)(-4,4)71/6,33*,105/7,72/8,378/22,320/23,127/9,189/
9,24*, ( 8)(-4,4)158/9,147/9,115/8,178/13,154/9,217/18,394/27,51/5,91/5,
 ( 9)(-4,3)198/11,52/5,198/14,154/11,132/10,139/8,22*, (10)(-3,2)271/16,34/
3,99/7,233/13,124/9,19*, (11)(-2,1)84/6,18*,22*,229/17
H= 7(K)(L) ( 0)(-7,4)355/38,,U,,83/7,,688/31,,541/24,,272/15,, ( 1)(-6,4)296/
64,235/51,70/6,267/15,323/18,197/14,627/34,272/19,83/6,52/6,237/12,
 ( 2)(-4,4)139/8,147/9,403/27,29*,36*,470/31,351/20,206/13,157/9, ( 3)(-4,4)
257/14,35*,86/6,78/7,183/10,120/10,89/6,94/8,140/8, ( 4)(-4,4)86/7,772/40,304/
17,321/23,99/6,422/28,126/9,141/9,115/6, ( 5)(-4,4)558/30,324/19,198/11,88/
8,37*,224/14,73/7,200/10,121/7, ( 6)(-4,4)98/6,469/26,286/16,163/12,313/18,
216/17,322/18,73/7,190/10, ( 7)(-4,3)38/3,126/8,68/6,116/10,36*,243/18,110/
8,340/17, ( 8)(-4,3)57/5,163/9,26*,114/10,33*,112/9,89/6,40/5, ( 9)(-3,2)22*,
106/7,24*,29*,124/9,115/7, (10)(-2,1)186/11,125/9,128/7,118/9
H= 8(K)(L) ( 0)(-5,5),U,,84/6,,435/22,,166/10,,137/8,, ( 1)(-6,4)250/54,U,118/
7,84/8,238/17,135/10,187/10,111/9,155/9,303/18,205/11, ( 2)(-4,4)167/9,214/
11,243/18,237/17,135/9,149/11,309/17,140/9,100/6, ( 3)(-4,4)416/23,290/17,128/
9,30*,37*,299/22,37/3,54/5,217/12, ( 4)(-4,4)154/9,433/24,250/18,132/10,57/
5,180/13,143/8,163/10,140/8, ( 5)(-4,4)65/5,188/10,175/10,229/21,99/6,196/14,
306/17,293/15,101/6, ( 6)(-4,3)47/4,112/7,35/5,28*,111/7,226/16,158/10,59/5,
 ( 7)(-4,3)87/5,68/6,25*,127/13,32*,173/11,263/15,79/5, ( 8)(-3,2)87/5,58/6,
103/8,44/4,207/15,265/18, ( 9)(-2,1)127/7,72/6,182/10,51/6
H= 9(K)(L) ( 0)(-4,4),171/28,,253/17,,615/29,,181/9,, ( 1)(-5,3)257/56,U,U,
46/4,51/6,534/29,181/13,81/6,152/8,(2)(-3,3)36/5,153/9,48/8,332/16,932/10,
116/8,108/7, ( 3)(-4,3)133/10,86/8,75/5,57/7,150/10,222/16,250/14,204/10,
 ( 4)(-4,3)23*,180/9,86/6,192/18,99/6,83/13,52/5,103/6, ( 5)(-4,3)231/13,132/
7,115/8,104/9,254/15,54/9,74/5,119/7, ( 6)(-3,2)140/8,84/6,41/5,151/8,144/10,
281/19, ( 7)(-3,1)85/8,195/11,65/6,71/6,19*, ( 8)(-1,0)255/17,45/4
H=10(K)(L) ( 0)(-3,3),U,,328/17,,264/14,, ( 1)(-3,3)280/61,U,329/71,181/10,
68/7,66/5,71/6, ( 2)(-1,2)66/11,110/7,254/16,47/4, ( 3)(-1,2)85/7,29*,87/7,
86/6, ( 4)(-2,2)107/7,102/9,233/13,191/14,130/8, ( 5)(-2,1)83/6,34/5,203/15,
163/12, ( 6)(-1,1)122/9,78/5,247/34
H=11(K)(L) ( 0)(-2,1),U,,206/14, ( 1)(-3,1)288/62,U,U,314/17,55/5, ( 2)( 0,1)
150/8,14*, ( 3)( 0,0)19*
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B

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H=0(K)(L),(0)(1,12),,1085/9,,693/7,,181/3,,485/7,,140/3,,21*,(1)(0,13),279/
16,1654/184,856/21,587/16,907/25,629/18,241/7,186/6,336/10,143/5,334/9,173/
5,38/2,100/4,(2)(0,13),979/49,481/17,202/6,207/8,66/3,122/4,667/20,145/4,598/
20,231/8,121/5,46/3,23*,121/4,(3)(0,12),606/27,329/13,648/29,872/35,575/20,
185/6,131/4,525/17,229/7,181/5,114/3,226/6,168/5,(4)(0,11),75/7,236/8,377/11,
333/16,435/13,168/5,51/4,427/11,168/5,95/4,100/3,70/3,(5)(0,10),361/23,156/
8,201/10,187/9,217/9,67/3,300/13,108/4,131/5,24*,67/3,(6)(0,8),290/15,423/21,
116/11,188/12,274/14,261/14,140/9,23*,144/8,(7)(0,5),328/16,84/8,47/4,159/10,
203/13,37/3
H=1(K)(L),(0)(0,13),,1640/13,,663/9,,261/4,,151/2,,192/3,,134/2,,170/3,
(1)(0,13),1448/38,1253/33,547/11,828/23,318/6,340/7,321/9,479/10,133/4,302/
6,141/4,191/5,83/3,58/2,(2)(0,12),943/30,229/6,415/9,400/10,676/19,411/9,220/
5,543/12,366/9,272/6,223/6,101/3,157/5,(3)(0,12),337/8,477/11,285/7,438/12,
168/4,98/2,414/9,235/6,386/10,100/2,40/1,115/3,126/3,(4)(0,11),534/15,150/4,
435/10,309/8,461/10,172/4,206/5,177/4,177/4,89/3,173/4,124/3,(5)(0,10),396/
13,368/11,155/4,232/8,111/3,265/7,235/7,270/6,216/5,119/3,36/1,(6)(0,8),323/
10,29*,132/6,201/7,272/7,52/3,189/6,111/4,136/5,(7)(0,5),230/7,226/7,163/6,
76/3,144/4,90/4
H=2(K)(L),(0)(0,12),325/5,,482/6,,238/4,,492/5,,442/7,,58/2,,180/3,
(1)(0,12),896/25,691/18,551/13,518/11,646/14,157/4,205/5,304/6,298/6,162/4,
215/5,98/4,171/4,(2)(0,12),829/24,372/11,306/6,529/12,278/7,345/8,263/6,446/
9,177/4,171/4,136/4,216/5,44/2,(3)(0,11),455/13,251/7,285/8,363/9,94/2,390/
9,152/4,184/4,139/4,209/5,80/2,144/3,(4)(0,11),336/8,630/16,114/3,393/9,165/
4,133/3,95/3,177/4,195/4,53/2,37/2,129/3,(5)(0,9),423/11,242/7,119/4,300/7,
230/7,190/6,206/6,203/6,242/6,114/3,(6)(0,7),219/8,97/4,100/4,58/3,55/3,184/
6,75/3,294/8,(7)(0,4),144/6,225/7,177/6,161/7,121/5
H=3(K)(L),(0)(0,11),,214/3,,976/10,,362/5,,604/7,,204/3,,305/4,(1)(0,12),294/
7,199/5,430/10,425/10,238/4,324/6,316/ 6,246/5,369/7,130/3,38/2,136/2,126/2,
(2)(0,11),270/5,493/11,145/3,337/7,170/3,304/5,243/5,154/4,128/3,188/4,25*,
181/4,(3)(0,11),632/15,494/9,96/2,112/2,463/9,156/3,96/2,155/3,142/3,116/2,
188/4,68/1,(4)(0,10),519/10,327/6,241/5,74/3,69/2,88/3,40/2,177/3,83/2,78/2,
109/2,(5)(0,8),51/2,153/4,135/3,61/2,159/4,71/2,39/2,211/5,18*,(6)(0,6),89/
3,193/5,73/3,117/4,105/3,53/3,193/6,(7)(0,2),171/6,70/3,75/3
H=4(K)(L),(0)(0,10),138/3,,562/5,,549/6,,143/3,,286/4,,194/4,(1)(0,11),465/
7,131/3,146/4,255/6,289/8,74/4,332/7,338/7,230/6,191/4,86/2,68/2,(2)(0,10),
287/5,416/8,182/4,166/4,347/6,146/4,239/6,189/4,187/4,54/2,196/5,(3)(0,10),
479/9,414/7,256/6,199/5,72/2,137/3,98/2,109/3,70/3,68/2,46/1,(4)(0,9),316/7,
225/5,119/3,115/3,142/4,107/3,77/3,221/5,73/2,125/3,(5)(0,7),101/3,57/2,118/
3,157/4,133/4,107/3,147/4,58/3,(6)(0,4),139/6,116/5,20*,129/5,86/4
H=5(K)(L),(0)(0,9),,295/6,,114/3,,105/3,,136/2,,163/3,(1)(0,9),271/10,259/
10,168/5,279/10,33*,153/6,148/6,195/8,186/7,71/3,(2)(0,9),512/17,122/5,101/
4,98/4,196/7,109/4,149/5,192/8,189/8,111/5,(3)(0,8),241/9,194/5,215/8,83/3,
83/3,73/3,117/4,96/3,132/5,(4)(0,7),317/9,124/4,171/5,124/4,63/3,120/4,212/
8,41/2,(5)(0,4),77/3,102/5,126/6,187/12,202/13
H=6(K)(L),(0)(0,7),420/11,,67/3,,299/5,,161/3,,(1)(0,7),270/9,269/9,117/5,
64/4,45/3,98/6,116/4,110/5,(2)(0,6),170/6,145/5,201/8,59/4,134/5,46/3,99/5,
(3)(0,5),36/1,183/7,84/3,111/5,104/4,53/2,(4)(0,3),80/3,156/5,61/3,147/5
H=7(K)(L),(0)(0,3),,256/6,,126/3,(1)(0,3),225/7,110/5,96/4,180/8,(2)(0,1),
50/4,169/8
```

[a] The range of l and the value of k are given in parentheses. For observed reflections, the value of $10|F_o|$, and its standard error, are listed and are separated by a slant line. The standard error of $|F_o|$ is obtained from the standard error of F_o^2 by the relation

$$\sigma(|F_o|) = \frac{[\sigma(F_o^2)/F_o^2]}{\sqrt{4 + [\sigma(F_o^2)/2F_o^2]^2}}$$

For absent reflections, which are indicated by an asterisk, the standard error is not given but is $1.4|F_o|$. Extinctions are indicated by an extra comma, experimentally unobserved reflections by U. No extinction or absorption corrections were made.

4 and hKl for $0 \leqslant K \leqslant 5$ were taken on a Weissenberg goniometer. The reciprocal lattice symmetry of D_{2h}, and extinctions of $h + l$ for $h + l$ odd in the $h0l$ zone restrict the space group to Pmnm, Pmn2_1, or P2_1nm. Unit cell dimensions, calibrated against an Al powder pattern, are $a = 5.709 \pm 0.008$, $b = 6.046 \pm 0.004$, and $c = 10.556 \pm 0.010$ Å. Only two molecules are present in this unit cell, if we assume that the density of the crystal is near 1 g. cm.$^{-3}$ (calculated value 0.942 g. cm.$^{-3}$). The ^{11}B nuclear magnetic resonance spectrum[2] is inconsistent with the high molecular symmetry required by the twofold positions of Pmnm, and the molecular packing was considerably less favorable in Pmn2_1 than in P2_1nm, which was tentatively chosen as the correct space group. Later analysis of the Patterson function showed that this choice is correct.

Structure Determinations

$B_4H_6C_2H_2$.—Sharpened coefficients of a three-dimensional Patterson function were computed after visual estimates of intensities had been corrected for Lorentz-polarization factors and correlated to a single scale. The line, $^1/_2$, $^1/_2 - 2y$, $^1/_2$, the plane, $^1/_2 - 2x$, $^1/_2$, $^1/_2 - 2z$, and the centrosymmetric interaction, $2x$, $2y$, $2z$, were searched for mutually consistent peaks. After several false choices were made, one of these regions yielded all six of the heavier atoms upon three-dimensional superposition. Two cycles of least-squares refinement of the 18 position parameters were carried out, and a three-dimensional electron density map was found to show six peaks at heights, in arbitrary units, of 6000, 4700, 4950, 5250, 4950, and 6000. The assignment at this stage of the two peaks at 6000 as C atoms was confirmed later by the reasonable background of difference maps and behavior of individual

Table II

Disagreement Factors Based on F

$B_4H_6C_2H_2$

$\sin\theta$	R
0.00–0.40	0.099
0.40–0.50	0.053
0.50–0.60	0.056
0.60–0.65	0.066
0.65–0.70	0.084
0.70–0.75	0.086
0.75–0.80	0.084
0.80–0.85	0.114
0.85–0.90	0.104
0.90–1.00	0.100

Classes of reflections	HKL	$0KL$	$H0L$	$HK0$	$H00$	$0K0$	$00L$
All orders	0.078	0.098	0.063	0.071	0.296	0.125	0.087
$H = 2N$	0.077		0.049	0.081	0.296		
$H = 2N + 1$	0.080		0.070	0.064			
$K = 2N$	0.079	0.051		0.068		0.125	
$K = 2N + 1$	0.078	0.145		0.074			
$L = 2N$	0.077	0.052	0.049				0.087
$L = 2N + 1$	0.079	0.130	0.070				
$K + L = 2N$	0.076	0.131					
$K + L = 2N + 1$	0.081	0.059					
$L + H = 2N$	0.082		0.063				
$L + H = 2N + 1$	0.075						
$H + K = 2N$	0.082			0.071			
$H + K = 2N + 1$	0.075			0.071			
$H + K + L = 2N$	0.075						
$H + K + L = 2N + 1$	0.082						

$$R_F = \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o| = 0.081$$

$$R_{F^2} = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2 = 0.187$$

$$R_{wF^2} = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w F_o^4]^{1/2} = 0.213$$

$B_4H_6C_2(CH_3)_2$

$\sin\theta$	R
0.00–0.40	0.101
0.40–0.50	0.095
0.50–0.60	0.071
0.60–0.65	0.053
0.65–0.70	0.050
0.70–0.75	0.046
0.75–0.80	0.079
0.80–0.85	0.068
0.85–0.90	0.057
0.90–1.00	0.093

Classes of reflections	HKL	$0KL$	$H0L$	$HK0$	$H00$	$0K0$	$00L$
All orders	0.068	0.122	0.063	0.045	0.013	0.243	0.059
$H = 2N$	0.067		0.033	0.044	0.013		
$H = 2N + 1$	0.068		0.080	0.047			
$K = 2N$	0.072	0.140		0.041		0.174	
$K = 2N + 1$	0.065	0.113		0.048		0.302	
$L = 2N$	0.068	0.118	0.033				0.059
$L = 2N + 1$	0.067	0.126	0.080				
$K + L = 2N$	0.064	0.133					
$K + L = 2N + 1$	0.071	0.111					
$L + H = 2N$	0.065		0.063				
$L + H = 2N + 1$	0.070						
$H + K = 2N$	0.072			0.054			
$H + K = 2N + 1$	0.063			0.037			
$H + K + L = 2N$	0.071						
$H + K + L = 2N + 1$	0.065						

Over-all R factor based on F = 0.078

R factor based on F^2 = 0.154

R factor based on wF^2 = 0.180

TABLE III: ATOMIC PARAMETERS[a]

Atomic parameters for $B_4H_6C_2H_2$

	B(1)	B(2)	B(3)	B(3′)	C(4)	C(4′)
X	0.2903	0.1694	0.0951	0.2930	0.1750	0.2759
Y	0.1231	0.1909	0.1218	0.0670	−0.0034	−0.0313
Z	0.3636	0.5373	0.2713	0.6490	0.2692	0.4657
$\beta(1,1)$	0.0090	0.0127	0.0094	0.0129	0.0110	0.0114
$\beta(2,2)$	0.0074	0.0076	0.0080	0.0114	0.0068	0.0073
$\beta(3,3)$	0.0148	0.0278	0.0253	0.0161	0.0224	0.0255
$\beta(1,2)$	−0.0016	−0.0021	−0.0003	−0.0019	−0.0012	−0.0004
$\beta(1,3)$	0.0021	0.0064	−0.0008	−0.0002	+0.0008	0.0019
$\beta(2,3)$	−0.0005	−0.0037	0.0003	0.0026	−0.0016	0.0023

	X	*Y*	*Z*	*T*
H(5)	0.1841	−0.0568	0.1243	2.647
H(5′)	0.3594	−0.1005	0.4518	5.839
H(6)	0.3786	0.1587	0.2470	1.623
H(7)	0.1631	0.2852	0.6078	2.928
H(8)	0.0331	0.1695	0.1129	2.480
H(8′)	0.3724	0.0787	0.7976	3.182
H(9)	0.0379	0.1469	0.4543	2.628
H(9′)	0.1695	0.1140	0.7111	2.174

Maximum values of σ for the atomic parameters

	Boron	Carbon	Terminal	Bridge
X	0.0002	0.0002	0.0039	0.0026
Y	0.0002	0.0002	0.0029	0.0022
Z	0.0004	0.0003	0.0053	0.0042
T			0.766	0.455
$\beta(1,1)$	0.0003	0.0002		
$\beta(2,2)$	0.0002	0.0002		
$\beta(3,3)$	0.0010	0.0008		
$\beta(1,2)$	0.0002	0.0001		
$\beta(1,3)$	0.0003	0.0003		
$\beta(2,3)$	0.0003	0.0002		

Atomic parameters for $B_4H_6C_2(CH_3)_2$

	B(1)	B(2)	B(3)	C(4)	C(5)
X	0.2847	0.0000	0.1047	0.2412	0.4128
Y	0.0338	−0.0513	0.1096	0.2970	0.4349
Z	0.0000	0.0000	0.1291	0.0678	0.1420
$\beta(1,2)$	0.0120	0.0149	0.0177	0.0145	0.0269
$\beta(2,2)$	0.0136	0.0175	0.0170	0.0109	0.0135
$\beta(3,3)$	0.0057	0.0071	0.0048	0.0043	0.0060
$\beta(1,2)$	−0.0014		0.0012	0.0026	−0.0020
$\beta(1,3)$			0.0019	−0.0003	−0.0013
$\beta(2,3)$			0.0002	−0.0012	−0.0016

	X	*Y*	*Z*	*T*
H(6)	0.4451	−0.0965	0.0	3.286
H(7)	−0.0980	−0.2312	0.0	1.699
H(8)	0.1326	0.0589	0.2603	3.491
H(9)	−0.1044	0.0902	0.0858	0.966
H(10)	0.4230	0.3949	0.2410	1.923
H(11)	0.3867	0.5616	0.1465	3.009
H(12)	0.5904	0.4322	0.1097	3.397

Maximum values of σ for the atomic parameters

	Boron	Carbon	Terminal H	Bridge H	Methyl H
X	0.0010	0.0010	0.0148	0.0064	0.0119
Y	0.0009	0.0006	0.0147	0.0072	0.0120
Z	0.0002	0.0002	0.0053	0.0033	0.0052
T			1.425	0.652	1.036
$\beta(1,1)$	0.0017	0.0014			
$\beta(2,2)$	0.0021	0.0010			
$\beta(3,3)$	0.0005	0.0003			
$\beta(1,2)$	0.0012	0.0009			
$\beta(1,3)$	0.0009	0.0005			
$\beta(2,3)$	0.0004	0.0004			

[a] The atomic parameters and the maximum value of the standard deviation for each type of atom are given. x, y, z are in units of the cell edges, the isotropic temperature factors (T) are in units of Å.^{2}, and the anisotropic temperature factors (β_{ij}) are dimensionless. The isotropic thermal parameters are in the form $\exp(-T \sin^2 \theta/\lambda^2)$ and the anisotropic thermal parameters are in the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}))$.

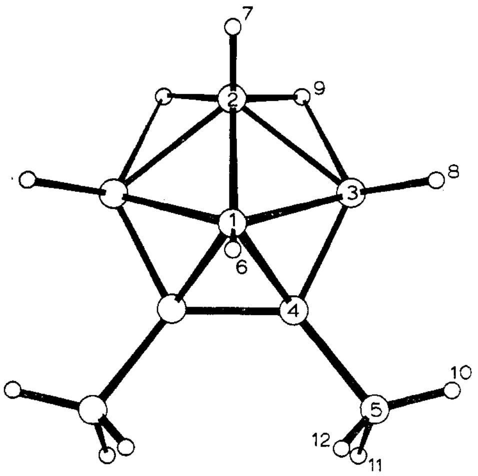

Fig. 1.—The structure and labeling convention for X-ray designation of atoms in $B_4H_6C_2(CH_3)_2$. In $B_4H_6C_2H_2$ atom 5 becomes a hydrogen atom.

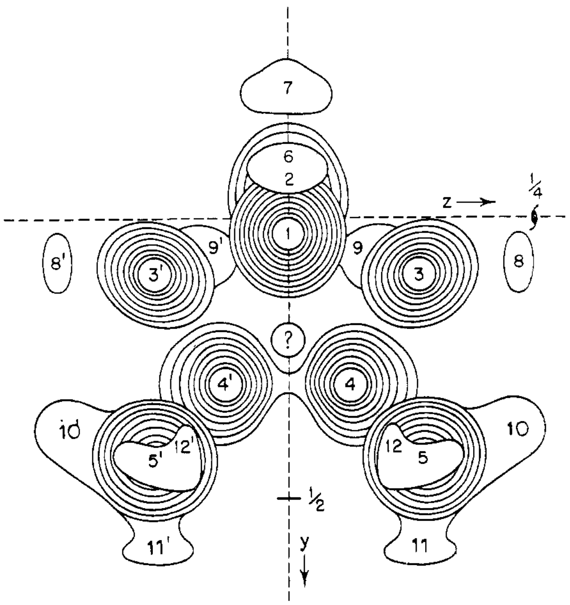

Fig. 2.—Electron density sections through atoms of the $B_4H_6C_2(CH_3)_2$ structure. The false peak is indicated by a question mark.

atomic thermal parameters. After two cycles of refinement of B and C with isotropic thermal parameters, a difference electron density map showed all eight H atoms uniquely at an average height of 390 ± 60 units, whereas the highest peak which could not be accounted for was 150 units in height. We then carried out a refinement of B and C atoms with anisotropic thermal parameters, another difference electron density map which showed only random noise, two cycles of refinement of H atom positions and isotropic thermal parameters, and a final cycle of refinement of all atomic positions with anisotropic thermal parameters on B and C. The final value of $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.081 for all reflections (Tables I and II).

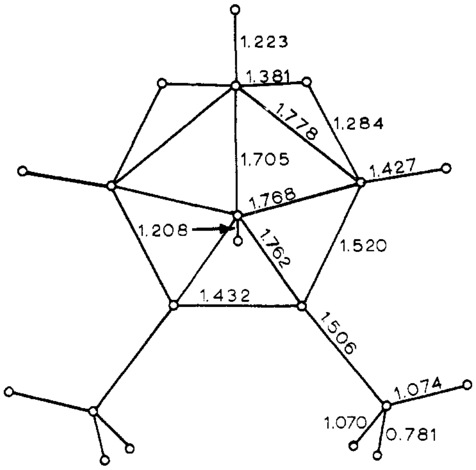

Fig. 3.—Bond distance in $B_4H_6C_2(CH_3)_2$.

$B_4H_6C_2(CH_3)_2$.—A brief attempt to solve this structure in two-dimensional projections failed, but it was readily solved from the three-dimensional Patterson function without the use of superposition techniques. Both B and C atoms were located and identified, and the arbitrary origin along x was chosen by setting the x coordinate of atom 2 at zero (Fig. 1). The structure determination was completed by (a) least-squares refinements of B and C positional parameters (atoms 1–5) with the use of the 190 largest reflections, (b) refinement of B and C atoms with isotropic thermal parameters with the use of all reflections, (c) a difference electron density map which located all nonmethyl H atoms (atoms 6–9), (d) isotropic refinement of atoms 1–9, (e) refinement of B and C atoms with anisotropic thermal parameters, (f) another difference electron density map which confirmed H atoms 6–9 and showed the locations of H atoms 10–12, (g) refinement of all H atoms with isotropic thermal parameters, and (h) final least-squares refinements of all position parameters in the complete structure. The final R value is 0.078 for all reflections (Tables I and II). A final electron density map of the molecule is shown in Fig. 2. The interesting occurrence of a peak nearly the height and area of an H atom on the symmetry plane and near the molecular center was shown to be due to lack of convergence of the Fourier series: a least-squares refinement of H atom 6 and of a new H atom placed at the question mark (Fig. 2) was subject to seven cycles of least-squares refinement during which the thermal parameter B in the temperature factor exp $(-B \sin^2 \theta/\lambda^2)$ behaved normally for H_6, but rose from 2.0 to 53,710 Å.^{2} for this new "H atom." Thus the presence of a peak at this new position is clearly inconsistent with the observed X-ray data. Finally, we made an additional attempt to distinguish between B and C atoms by noting that if all B and C atoms are assumed to be equal in weight (to C atoms) the values of R_F, R_{F^2}, and R_{wF^2}, for observed reflections only, refined no lower than 0.10, 0.20, and 0.29, considerably higher than the values 0.08, 0.15, and 0.18, respectively, obtained for the correct structure.

Results and Discussion

Final atomic coordinates are given in Table III. In Table IV we give the polar angles ϕ, in the x, y plane, and ρ, from the z axis, in a form[5] so that a molecu-

TABLE IV[a]

(A) $B_4H_6C_2H_2$

Center atom	Coordinating atom	ϕ^b	ρ^b	Distance, Å.	Corrected distance,[c] Å.
B_1	B_2	90.0		1.741	1.724
	B_3	0.	61.3	1.779	1.786
	$B_{3'}$	236.7	62.2	1.765	1.777
	C_4	322.5	96.8	1.748	1.754
	$C_{4'}$	274.3	96.8	1.751	1.757
	H_6	116.5	133.6	1.061	1.045
B_2	B_1	90.0	0.	1.714	1.704
	B_3	0.1	61.1	1.783	1.780
	$B_{3'}$	123.3	60.3	1.798	1.801
	H_7	236.8	132.1	1.084	1.072
	H_9	15.6	103.4	1.315	1.304
	$H_{9'}$	108.7	104.3	1.300	1.289
B_3	B_1	90.0	0.	1.779	1.772
	B_2	0.	57.5	1.783	1.785
	C_4	231.5	63.6	1.509	1.507
	H_8	116.4	128.5	1.146	1.135
	H_9	343.8	102.4	1.258	1.253
B_3'	B_1	90.0	0.	1.765	1.753
	B_2	0.	57.5	1.798	1.795
	$C_{4'}$	127.9	64.4	1.489	1.491
	$H_{8'}$	252.9	131.9	1.072	1.057
	$H_{9'}$	14.4	101.7	1.299	1.289
C_4	B_1	90.0	0.1	1.748	1.743
	B_3	0.	65.7	1.509	1.511
	$C_{4'}$	223.2	66.2	1.418	1.419
	H_5	116.3	126.0	1.027	1.017
C_4'	B_1	90.0	0.	1.751	1.745
	$B_{3'}$	0.	65.4	1.489	1.488
	C_4	137.7	66.0	1.418	1.417
	$H_{5'}$	247.6	123.1	1.057	1.085
H_5	C_4	. . .	. . .	1.027	1.036
H_5'	$C_{4'}$	. . .	. . .	1.057	1.028
H_6	B_1	. . .	. . .	1.061	1.745
H_7	B_2	. . .	. . .	1.084	1.099
H_8	B_3	. . .	. . .	1.146	1.158
H_8'	$B_{3'}$	. . .	. . .	1.072	1.086
H_9	B_2	90.0	0.	1.315	1.324
	B_3	0.	87.7	1.258	1.264
H_9'	B_2	90.0	0.	1.300	1.312
	$B_{3'}$	0.	87.5	1.299	1.310

(B) $B_4H_6C_2(CH_3)_2$

Center atom	Coordinating atom	ϕ^b	ρ^b	Distance, Å.	Corrected distance,[c] Å.
B_1	B_2	90.0	0.	1.705	1.709
	B_3	0.	61.6	1.767	1.772
	$B_{3'}$	237.5	61.6	1.767	1.772
	C_4	322.9	98.0	1.762	1.763
	$C_{4'}$	274.5	98.0	1.762	1.763
	H_6	118.7	121.7	1.208	1.221
B_2	B_1	90.0	0.	1.705	1.701
	B_3	0.	60.9	1.778	1.776
	$B_{3'}$	122.5	60.9	1.778	1.776
	H_7	241.3	134.8	1.223	1.214
	H_9	19.0	103.0	1.381	1.367
	$H_{9'}$	103.6	103.0	1.381	1.367
B_3	B_1	90.0	0.	1.767	1.763
	B_2	0.	57.5	1.778	1.780
	C_4	230.2	64.3	1.521	1.514
	H_8	119.8	128.9	1.428	1.438
	H_9	339.4	104.0	1.284	1.272
B_3'	B_1	90.0	0.	1.767	1.763
	B_2	0.	57.5	1.778	1.780
	$C_{4'}$	129.8	64.3	1.521	1.514
	$H_{8'}$	240.2	128.3	1.428	1.438
	$H_{9'}$	20.6	104.0	1.284	1.272
C_4	B_1	90.0	0.	1.762	1.762
	B_3	0.	64.6	1.521	1.526
	$C_{4'}$	223.4	66.0	1.431	1.431
	C_5	111.5	128.3	1.507	1.516
C_4'	B_1	90.0	0.	1.762	1.762
	$B_{3'}$	0.	64.6	1.521	1.526
	C_4	136.6	66.0	1.431	1.431
	$C_{5'}$	248.5	128.3	1.507	1.516
C_5	C_4	. . .	. . .	1.507	1.496
C_5'	$C_{4'}$	. . .	. . .	1.507	1.496
H_6	B_1	. . .	. . .	1.208	1.195
H_7	B_2	. . .	. . .	1.223	1.234
H_8	B_3	. . .	. . .	1.428	1.417
H_8'	$B_{3'}$	. . .	. . .	1.428	1.417
H_9	B_2	90.0	0.	1.381	1.395
	B_3	0.	83.6	1.284	1.295
H_9'	B_2	90.	0.	1.381	1.395
	$B_{3'}$	0.	83.6	1.284	1.295

[a] Maximum standard deviations obtained from the full variance–covariance matrix are ±0.006 Å. for BB and BC and ±0.03 Å. for BH and CH distances. [b] Spherical coordinates for construction of boron hydride models, W. N. Lipscomb, "Boron Hydrides," The W. A. Benjamin Co., New York, N. Y., 1963, p. 227. [c] Distances corrected for thermal motion on the assumption that the first atom rides on the second. These corrections are made with the use of the standard Busing–Levy program and are very much larger than the corresponding corrections based on the assumption that the molecule moves as a rigid body.

lar model can readily be made. Bond distances are also shown in Table IV, both uncorrected and then corrected for molecular oscillation on the assumption that each second atom rides on each first atom. Bond distances and angles for $B_4H_6C_2(CH_3)_2$ are also shown in Fig. 3 and 4. No unusual features are present in the intermolecular contacts (Table V), or in the molecular packing of the crystal structures (Fig. 5 and 6). In $B_4H_6C_2H_2$ the five-membered B_3C_2 ring lies roughly parallel to the $(11\bar{1})$ plane, while in $B_4H_6C_2(CH_3)_2$ the ring lies almost parallel to the (110) plane and, for the other molecule in the unit cell, the $(\bar{1}10)$ plane. The shortest intermolecular contact is H···H at 2.5 Å., in excellent agreement with similar distances in the boron hydrides, and close to the expected van der Waals contact of 2.4 Å.

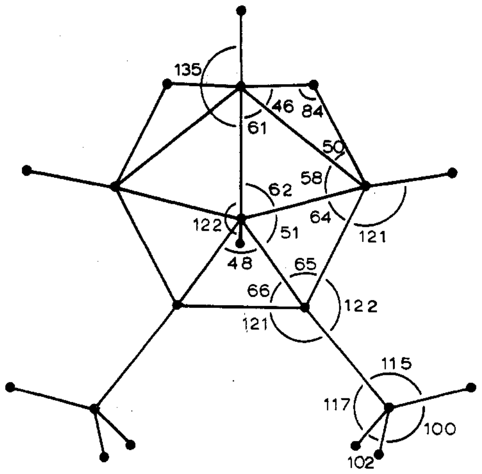

Fig. 4.—Bond angles in $B_4H_6C_2(CH_3)_2$.

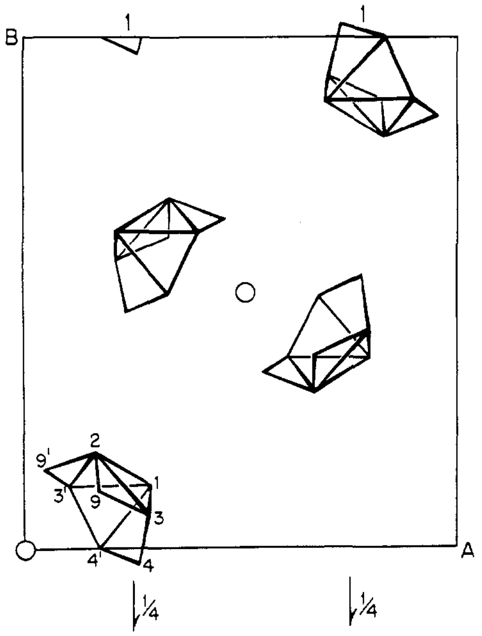

Fig. 5.—Projection of the $B_4H_6C_2H_2$ structure along the monoclinic *c* axis. Atoms 1, 2, 3, and 3′ are B, atoms 4 and 4′ are C, and atoms 9 and 9′ are bridge H.

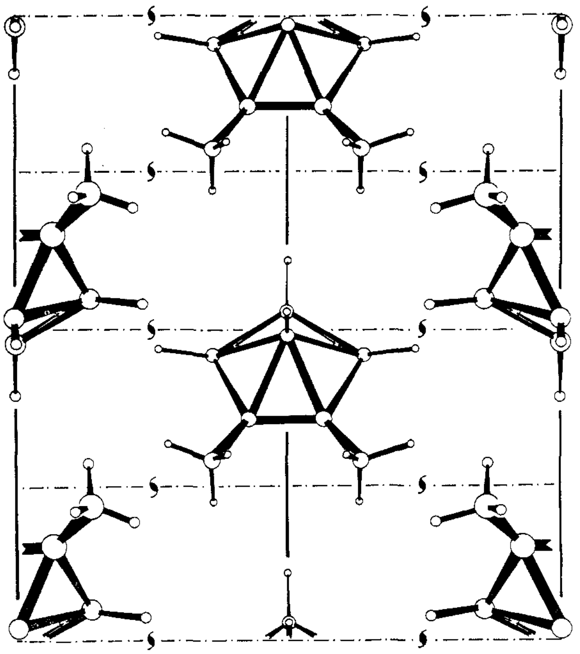

Fig. 6.—Projection of the $B_4H_6C_2(CH_3)_2$ structure along the *x* axis.

The molecular structure has some nice geometrical features. The five-membered rings are nearly planar. Atom 2 of $B_4H_6C_2H_2$ lies 0.026 Å. above the plane defined by 3 and 3′ and the midpoint of 4 and 4′, while atoms 4 and 4′ lie 0.022 Å. off this plane in opposite directions from one another. Atoms designated by primes are related to corresponding unprimed atoms by the molecular symmetry plane, exact for the $B_4H_6C_2(CH_3)_2$ structure, in which atom 2 lies 0.032 Å. above the plane defined by atoms 3, 3′, 4, and 4′. Some of these deviations may be statistically significant in view of the calculated standard deviations of 0.006 Å. for bond distances involving B and C atoms (Table IV).

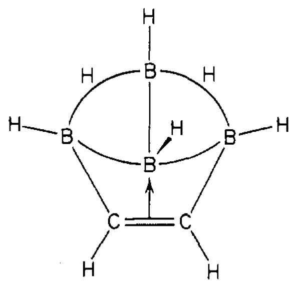

Fig. 7.—The π-donation model for bonding in $B_4H_6C_2H_2$. Bond angles about C atoms are consistent with sp^2 hybridization in both compounds.

Table V

Shortest Intermolecular Contacts

Atom (basic molecule)	Atom (symmetry related molecule)	Type of symmetry transformations[a]	Distance, Å.
		$B_4H_6C_2H_2$	
8	5	I	2.57
7	5	2_1	2.62
8	5′	2_1	2.66
6	8	2_1, I	2.93
7	6	2_1, I, −TZ	2.88
6	8′	−TX	2.90
8	9′	−TZ	2.81
		$B_4H_6C_2(CH_3)_2$	
6	11	−TY	2.60
7	10	2_1	2.91
8	9	2_1	2.39
9	8	-2_1	2.39
10	12	2_1, TY	2.68
11	6	TY	2.60
12	10	-2_1, TY	2.68

[a] 2_1, twofold screw rotation at $X = {}^1/_4$, $Z = {}^1/_4$ for $B_4H_6C_2H_2$, at $Y = 0$, $Z = {}^1/_4$ for $B_4H_6C_2(CH_3)_2$; I, center of inversion; TX, cell translation in the *X* direction; TY, cell translation in the *Y* direction; TZ, cell translation in the *Z* direction.

The valence structure is most interesting because of the very short C–C distances of 1.419 ± 0.006 Å. in $B_4H_6C_2H_2$ and 1.431 ± 0.006 Å. in $B_4H_6C_2(CH_3)_2$, and because the C atoms of the B_3C_2 ring show bond angles, most accurately known in $B_4H_6C_2(CH_3)_2$, near 120° (Fig. 4). Because this distance and angle resemble those in graphite we have suggested[4] a structure which has some multiple bonding between these C atoms, but weakened by a localized π donation to the apex B atom (Fig. 7). Thus, we start with sp^2 hybridized C atoms which are only slightly modified by the participation of the sp^2 bonds in the direction of the relatively long distance of 1.762 Å. over which some π donation has been shown to occur in a molecular orbital analysis.[4] This π donation results in a charge transfer which has been shown to be partially compensated by some stabilizing back donation of electron density from the boron framework into the antibonding π-orbitals associated with the C atoms. This bonding description seems to be at least consistent[3] with the highly resolved ^{11}B nuclear magnetic resonance spectrum obtained[3] at 32 Mc.

These structures are closely related to the structure of B_6H_{10} by the substitution of CC in these molecules for H_bBBH_b in B_6H_{10}. On the surface, it is the same near invariance in bonding which occurs when the bridge H atoms (H_b) of B_2H_6 are moved into the B nuclei in order to convert them conceptually to C atoms. It is not yet known how general these orbital invariances are, but it must be noted that the corresponding B–B bond[5] of 1.596 ± 0.012 Å. in B_6H_{10} is by far the shortest known B–B distance in the boron hydrides, and our study of these dihydrocarboranes may well indicate that this B–B distance in B_6H_{10} involves some multiple bonding. Chemical studies which explore this idea may be worth the effort.

Finally, we strongly emphasize that short C–C bonds are not general in the carboranes.[8]

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Molecular Structure of Carboranes. A 1,2-Dicarbaclovododecaborane Derivative, $B_{10}Cl_8H_2C_2H_2$

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The near-icosahedral geometry of the $B_{10}C_2$ unit exists in $B_{10}Cl_8H_2C_2H_2$. The C–C bond distance of 1.67 ± 0.02 Å. can be predicted from proportional distribution of the thirteen electron pairs among the thirty icosahedral edges. Chlorine substitution has occurred at all B atoms except those two which are most positive and which are bonded to both C atoms. There are eight molecules in the unit cell which has dimensions a = 17.11, b = 13.47, and c = 13.65 Å.; the space group is Pbna.

o-Carborane[1,2] (1,2-dicarbaclovododecaborane, $B_{10}H_{10}C_2H_2$) is most frequently assumed[3,4] to have nearly regular icosahedral symmetry, differing from the $B_{12}H_{12}^{-2}$ ion[5] by the slight shortening of C–C and B–C bonds in accord with the decrease in covalent radius from 0.83 Å. for B to 0.77 Å. for C. This assumption has been based, in part, on the extraordinary thermal stability of *o*-$B_{10}H_{10}C_2H_2$, which transforms to neocarborane[6,7] (*m*-$B_{10}H_{10}C_2H_2$) without decomposition at 470°.

However, a model with a short C–C distance of 1.54 Å. has been suggested[7] for *o*-carborane, which is conjectured to transform to *m*-carborane by expansion of this short distance to one of about 1.77 Å. in the transition state, but the valence theory here is not clear, especially as to the nature of the barrier between these suggested structures. In even stronger disagreement with the usually accepted structure is the recent report of an X-ray diffraction study[8] which indicates an ethylenedecaborane type of structure for the $B_{10}C_2$ unit. We show below that both the proposal of the short C–C bond and the ethylenedecaborane unit are not correct for the $B_{10}C_2$ unit in $B_{10}Cl_8H_2C_2H_2$ and, furthermore, that the near-icosahedral structure is indeed correct. Thus the two bonded C atoms share in the electron deficiency of the boron polyhedral environment to an extent not hitherto proven.

The possibility[3] that polyhedral boranes form a superaromatic system raises questions of position and mechanism of electrophilic and nucleophilic substitution. The ground-state charge distribution should be reasonably indicative of the position of substitution under the conditions that the charge distribution in the transition state resembles that in the ground state, and that steric or neighbor effects are not dominant. Successive substitution changes the charge distribution for predictions of yet further substitution. Nevertheless, the very strongly positive character found[3] for the two B atoms bonded to *both* C atoms might be preserved in successive Cl substitution such that eight Cl atoms would appear on all B atoms except these two. We show that this result is indeed correct and, hence, that probably electrophilic substitution has taken place.

Structure Determination

A needle-like crystal, 0.8 mm. in length with a square base 0.11 mm. on edge, was mounted along the needle axis (b). The reciprocal lattice symmetry is D_{2h}, and unit cell dimensions are (λ 1.5418 Å.) a = 17.11 ± 0.02, b = 13.47 ± 0.02, and c = 13.65 ± 0.02 Å. Extinctions of $0kl$ when k is odd, of $hk0$ when h is odd,

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