Volume 3
Number 12
December 1, 1964

Inorganic Chemistry

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

Octaborane(12)

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Received August 3, 1964

The boron hydride B_8H_{12} has been synthesized in an electric discharge of pentaborane-9, diborane-6, and hydrogen, and purified samples have been prepared by careful fractionation procedures. The compound is thermally unstable above the melting point of very roughly $-20°$. Both the formula and structure are established by a three-dimensional single-crystal X-ray diffraction study. The symmetry of the isolated molecule is C_s, and there are eight terminal H, two symmetrical bridge H, and two unsymmetrical bridge H atoms attached to an icosahedral fragment of eight B atoms. The space group is Pbca, and there are eight molecules in a unit cell having dimensions $a = 13.613$, $b = 10.410$, and $c = 10.410$ Å. The value of $R = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o| = 0.11$ for the 1571 observed reflections.

The existence and structure of a B_8 hydride are of interest for several reasons. Probable structures for both a B_8H_{12} and a B_8H_{14} have been predicted[1,2] on the basis of structural principles derived from known boron hydrides and valence theory. Intramolecular H···H contracts in B_8H_{14} render this molecule a bit overcrowded although it may yet be found to exist with C_2 symmetry, and hence the more important prediction[1,2] has been B_8H_{12} having symmetry C_{2v}, C_s, or C_2 (Fig. 1). All three of these structures have the most compact possible icosahedral fragment for the boron arrangement, and they differ only in displacements of two H atoms by 0.25 Å. as the symmetry of the C_{2v} structure is lowered to C_s or C_2. Of these three closely related structures we shall see that the C_s structure is the correct one and that an extended Hückel theory confirms this result.

The previous experimental evidence is not conclusive as to the formula, but is indicative of the probable existence of a B_8 hydride. The B_9H_{15} composition[3] has now been assigned[4] to the earliest report of a B_8H_x compound.[5] Vapor pressure anomalies in the first B_9H_{15} preparation[6,7] were indicative of another hydride. The previous mass spectrographic evidence[7-9] has been ambiguous as to the formula, inasmuch as B_9H_{15}, B_5H_{11}, and B_4H_{10} show mass spectrum cut-offs at two mass units less than the maximum permitted.[9] Hence, both B_8H_{12}[8] and B_8H_{14}[10] have been assigned as possible formulas of the B_8 hydride. Improvements in the sensitivity of the method may soon yield reliable determinations of maximum mass numbers, but even the most recent mass spectroscopic study[11] was withheld until it was confirmed by the X-ray diffraction method. The isolation of a sample of B_8H_{12} appears not to have been accomplished previously in the earlier studies,[10] but a sample of a hydride[12] showing similar properties decomposed before it could be studied by X-ray diffraction methods. We report below the preparation, isolation, formula, and molecular structure of B_8H_{12}.

Experimental

Preparation and Isolation.—Octaborane(12) was prepared in extremely small yields in an electric discharge of a mixture of diborane-6, pentaborane-9, and hydrogen (Fig. 2). The hydrogen was freed of oxygen by passage through a Fisher Deoxo hydrogen purifier and was then introduced at 6 p.s.i.g. into the high vacuum system where the pressure was reduced to 12 mm. with the use of a needle valve. The hydrogen was then passed through a drying tube, through a $-196°$ trap packed with glass wool, and then into a short mixing tube D where the B_2H_6 and B_5H_9 were introduced into the stream. The B_2H_6, maintained as a liquid at $-126°$ in a reservoir F, was introduced into

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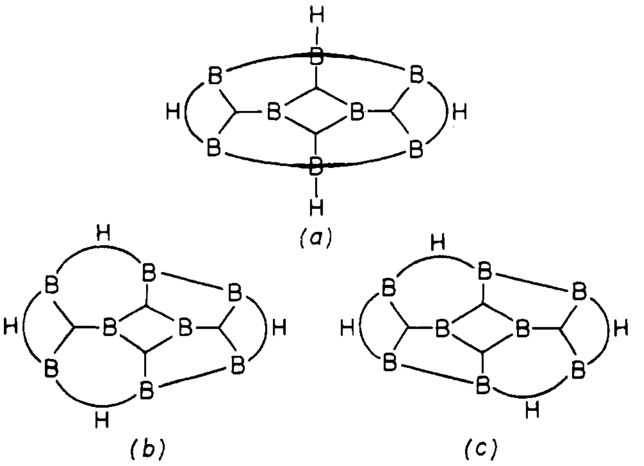

Fig. 1.—Structure proposals for B_8H_{12} of (a) symmetry C_{2v}, (b) symmetry C_s, and (c) symmetry C_2. One terminal H atom has been omitted from each B atom. Structure (b) is correct.

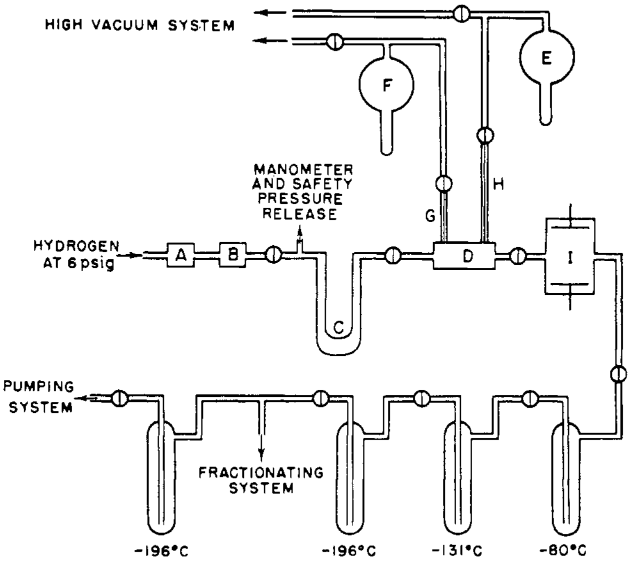

Fig. 2.—Schematic diagram of vacuum line: 1, stopcocks; A, Fisher Deoxo purifier; B, needle valve, set for 12 mm. pressure; C, glass wool packing; D, mixing tube; E, B_5H_9 reservoir, maintained at 0°; F, B_2H_6 reservoir, maintained at $-126°$; G, 0.25-mm. capillary 150 mm. long; H, 0.25-mm. capillary 330 mm. long; I, discharge tube, copper electrodes 90 mm. in diameter, 80 mm. apart.

the stream through a 0.25-mm. capillary 150 mm. in length. The B_5H_9, maintained at 0° in a reservoir E, was introduced into the mixing tube through a 0.5-mm. capillary 330 mm. in length. The resulting B_2H_6:B_5H_9 ratio was about 2:1. These gases mixed with H_2 were then passed into the discharge tube I, which contained two parallel circular electrodes 90 cm. in diameter and 80 mm. apart. The inlet and outlet geometry is shown in Fig. 2. An estimated 2700 volts was maintained between the electrodes by a 15,000-volt neon tube transformer which had a 20-volt input from a Variac. Runs in excess of 24 hr. were required in order to obtain adequate samples.

The development of the complex separation procedure was carefully monitored by mass spectrographic studies. The gaseous mixture passed from the discharge tube into four successive traps, at -80, -131, -196, and $-196°$. The two $-196°$ traps contained mainly B_2H_6, while the -80 and $-131°$ traps contained mainly B_5H_9. Of course, the octaborane was in the $-80°$ trap, along with small amounts of B_4H_{10}, B_5H_{11}, B_6H_{10}, B_9H_{15}, $B_{10}H_{14}$, and $B_{10}H_{16}$, all of which were identified. Interestingly, very small amounts of other materials were present, but were neither separated nor identified. Most of the B_5H_9 in this $-80°$ trap was then allowed to pass through two $-57°$ traps over a period of several days. The remaining mixture was then fractionated rapidly through a $-45°$ trap, which retained nearly all material except for B_6H_{10} and small amounts of B_5H_9 and octaborane. This process was repeated until the material which passed through showed the presence of no B_5H_9 or B_6H_{10}. The final fractionation which passed through this $-45°$ trap then was pure octaborane, provided the fractionation was carried out sufficiently rapidly that B_9H_{15} and $B_{10}H_{16}$ were retained. The octaborane was then sealed into thin-walled Pyrex capillaries having an inside diameter of about 0.5 mm.

X-Ray Diffraction Study.—The growth of single crystals proved to be very difficult. All but two of more than twenty samples had to be discarded either because the material decomposed so rapidly near the melting point of very roughly $-20°$ or because the liquid became very viscous and finally glassy before a crystal of significant size was grown as the temperature was lowered. Indeed, seed crystals had to be grown deftly and quickly, at a rate which was fast compared with the rate at which decomposition lowered the melting point. The purer samples seemed to be more stable, a phenomenon usually observed in boron hydride chemistry, and hence we are very unsure of either the intrinsic stability or the melting point of *pure* B_8H_{12}.

The usual low temperature techniques were employed. A cold stream of N_2 was blown at the crystal through an insulated tube leading from a 25-l. dewar containing a heating coil for adjusting the rate of the stream. The capillary containing the sample was mounted on a Weissenberg goniometer and observed through a polarizing short-focus telescope between crossed polaroids during growth. During X-ray diffraction photography the whole goniometer was encased in polyethylene sheet in order to keep the sample free of frost.

In all, four different crystals were used for data as follows: crystal 1, hkL, $L = 0, 1, 8, 9$; crystal 2, hkL, $L = 2, 3, 4$; crystal 3, Hkl, $H = 0$ through 10; crystal 4, hkL, $L = 5, 6, 7$. The first three were from the same capillary, and the last from a second capillary. The first sample was never above the melting point for 4 months of experimentation. Crystal 1 was grown from a single seed at about $-20°$, but growth stopped owing to high viscosity when less than half of the material was crystalline. The temperature was then lowered slowly to $-30°$ and quickly to $-100°$. Unfortunately, the 25° tilt of the c axis from the axis resulted in diffraction photographs which showed a few variations of intensity of symmetry related reflections by 30% due to varying path lengths of X-rays through the glass. Nevertheless, we recorded levels $hk0$ through $hk9$, and also levels 0 through 10 about the $[0\bar{1}1]$ axis; of these levels we later used only $hk0$, $hk1$, $hk8$, and $hk9$. Crystal 2 was very favorably oriented with the c axis along the capillary axis, and hence no absorption problems were present. Crystal 3 was regrown along the a axis and yielded a complete set of data. Crystal 4 was grown on a completely different apparatus, which yielded three levels before the cork blew.

The crystal data establish the reciprocal lattice symmetry of D_{2h}, the systematic absences of $0kl$ when k is odd, of $h0l$ when l is odd, and of $hk0$ when h is odd and therefore the space group of Pbca. A single film on which were exposed a powder pattern of Al, a $0kl$ Weissenberg level, and an a axis oscillation pattern yielded the unit cell dimensions of $a = 13.613 \pm 0.013$, $b = 10.410 \pm 0.007$, and $c = 10.410 \pm 0.007$ Å. In spite of the equality of b and c (within experimental error) the crystal symmetry is orthorhombic. The assumption of eight molecules in the unit cell of volume 1472 Å.^{3} gives a calculated density of 0.896 g. cm.$^{-3}$, but, of course, there is no measured density for comparison. However, the molecular volume in the crystal fits exactly on the linear plot[3] of $V/(nB)$ vs. n_H/n_B if one assumes that the formula is B_8H_{12}, but this evidence is not sufficient to fix the number of H atoms (n_H) with certainty. If, as we found later, the molecule lies in a general position in the space group, no molecular symmetry is required by the space group. Of the 1679 possible unique reflections, plus 274 systematic absences, in the Cu Kα

TABLE I

OBSERVED F VALUES AND STANDARD DEVIATIONS[a]

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H= 0(K)(L) ( 0)( 1,13),2725/232,,1427/60,,1119/42,,719/25,,279/14,,221/11,,
 ( 1)( 0,13),,,,,,,,,,,,,,, ( 2)( 0,13)1866/95,2865/205,161/5,52/7,588/16,626/
21,173/5,518/17,39/7,479/21,38*,35*,172/7,94/5, ( 3)( 0,12),,,,,,,,,,,,,,
 ( 4)( 0,12)2027/97,1009/34,552/13,404/12,543/15,485/15,563/15,457/17,195/7,
186/8,175/8,32*,240/8, ( 5)( 0,12),,,,,,,,,,,,,, ( 6)( 0,11)215/10,1133/37,306/
7,32*,159/6,1068/37,262/9,658/25,92/5,197/8,56/4,276/10, ( 7)( 0,11),,,,,,,,,,,
,, ( 8)( 0,10)112/6,469/17,195/6,139/5,92/4,39*,445/15,129/6,63/9,263/9,150/
6, ( 9)(0,9),,,,,,,,,,, (10)(0,8)106/5,38*,247/7,38*,323/9,302/10,86/5,139/5,,
150/5, (11)(0,7),,,,,,,,, (12)(0,4)209/10,100/5,164/4,134/4,71/3, (13)(0,2),,
 H= 1(K)(L) ( 0)( 0,13),,685/25,,151/7,,183/11,,436/16,,39*,,103/7,,
 ( 1)( 0,13),335/16,13*,13*,394/9,65/3,442/10,164/13,387/14,126/8,39*,52/7,
200/10,21*, ( 2)( 0,13),206/7,501/14,244/7,462/11,176/7,453/10,508/13,163/8,
277/12,183/11,213/9,29*,85/5, ( 3)( 0,12),111/4,105/4,221/6,58/3,453/11,404/
11,413/13,442/15,157/8,108/10,166/10,248/8, ( 4)( 0,12),642/21,25*,73/5,99/
5,269/8,126/6,66/6,189/8,164/9,97/9,288/10,137/6, ( 5)( 0,12),374/9,351/8,259/
6,26*,239/8,103/7,275/10,162/8,18*,95/8,221/10,60/5, ( 6)( 0,11),30*,758/16,
121/5,256/10,150/6,77/10,242/9,103/7,121/7,279/9,46/6, ( 7)( 0,11),480/12,83/
4,579/13,96/5,219/7,39*,39*,29*,100/7,45/6,55/5, ( 8)(0,9),402/13,472/12,496/
12,179/7,217/7,39*,37*,106/7,92/7, ( 9)(0,9),219/7,258/7,228/7,73/6,122/6,37*,
212/7,81/5,105/6, (10)(0,8),144/7,269/8,65/6,411/12,220/8,272/9,64/6,20*,
 (11)(0,7),76/7,133/5,138/6,306/8,138/6,176/8,74/6, (12)(0,5),129/7,29*,334/
9,134/5,237/8, (13)(0,2),21*,152/4
 H= 2(K)(L) ( 0)( 0,13)1094/100,,135/7,,187/8,,71/4,,122/7,,44*,,202/9,,
 ( 1)( 0,13)1430/131,2353/252,417/11,355/14,51/2,498/21,96/5,157/6,188/8,213/
8,173/7,40*,96/5,22*, ( 2)( 0,13)1213/111,1490/160,841/31,265/8,95/4,461/19,
397/12,261/10,278/11,151/6,134/6,186/7,104/4,128/5, ( 3)( 0,12)48/12,68/3,611/
18,337/11,174/5,202/7,277/9,30*,23*,84/5,154/6,38*,86/5, ( 4)( 0,12)745/35,26*,
374/10,482/17,225/8,128/4,462/14,193/6,267/10,136/5,67/4,175/6,174/8,
 ( 5)( 0,12)549/21,127/4,532/14,352/11,237/8,148/5,585/18,153/5,54/10,113/5,
281/12,159/6,23*, ( 6)( 0,11)261/9,254/8,368/11,156/5,70/3,185/6,242/8,83/8,
115/5,122/7,36*,155/6, ( 7)( 0,11)355/14,285/9,153/5,122/4,247/9,183/6,307/
10,111/6,48/7,251/10,87/5,69/3, ( 8)( 0,10)83/5,360/12,41*,226/7,172/6,164/
6,275/11,268/9,54/5,130/5,152/5, ( 9)(0,9)448/19,44*,234/6,261/9,189/6,94/5,
146/5,77/4,241/9,14*, (10)(0,8)79/5,144/5,42*,167/6,33*,88/5,36*,159/5,88/3,
 (11)(0,7)88/5,40*,182/5,157/5,29*,204/7,159/6,22*, (12)(0,5)68/4,33*,120/4,
72/4,68/3,23*, (13)(0,2)52/3,74/4,20*
 H= 3(K)(L) ( 0)( 0,13),,129/4,,121/6,,62/6,,51/10,,45*,,U,, ( 1)( 0,13),496/
24,68/2,301/8,137/5,245/9,301/7,319/9,430/14,236/8,80/6,170/8,89/7,21*,
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10,230/8,104/8,77/6,70/5, ( 4)( 0,12),148/5,150/4,250/7,291/7,185/6,453/12,
425/13,296/11,237/8,117/9,56/4,210/9, ( 5)( 0,11),162/5,371/9,733/22,118/5,
620/19,140/6,149/6,28*,19*,125/6,50/4, ( 6)( 0,10),119/5,272/8,112/4,243/8,42*,
170/7,61/4,101/6,70/14,37*, ( 7)( 0,10),518/15,327/7,330/9,362/10,156/6,202/
8,114/7,29*,75/5,32*, ( 8)( 0,10),95/6,481/12,226/6,341/10,172/6,177/7,40*,
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59/4
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113/10,39*,63/6, ( 2)( 0,12)377/14,482/20,167/5,537/19,290/9,209/8,48/5,423/
15,23*,108/8,43*,70/6,114/7, ( 3)( 0,12)76/4,417/16,823/32,672/24,459/12,33*,
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629/24,108/5,507/14,395/13,147/6,200/8,306/11,160/8,106/8,39*,137/9,
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8,27*, ( 8)(0,9),43*,352/11,246/8,35*,199/8,42*,94/6,155/7,118/6, ( 9)(0,8),
44*,98/5,95/6,49/4,41*,175/8,175/6,153/6, (10)(0,7),283/12,149/5,277/10,94/
5,36*,33*,27*, (11)(0,6),37*,189/5,32*,72/4,29*,23*, (12)(0,4),164/7,103/4,
183/6,44/3
 H= 6(K)(L) ( 0)( 0,12)649/47,,695/21,,197/7,,840/30,,305/13,,295/14,,121/5,
 ( 1)( 0,12)468/22,125/6,20*,203/7,379/11,271/10,223/9,35*,26*,295/13,192/9,
265/13,108/5, ( 2)( 0,12)580/25,144/6,769/23,343/11,173/6,257/10,441/13,429/
17,200/8,18*,38*,73/5,124/6, ( 3)( 0,12)449/18,485/21,80/4,28*,250/9,307/12,
222/7,240/8,28*,19*,151/7,101/5,81/4, ( 4)( 0,11)471/17,261/9,390/12,568/18,
29*,270/10,277/9,64/5,193/8,46/10,35*,235/11, ( 5)( 0,11)283/12,416/17,111/
5,78/4,243/9,298/18,251/8,212/8,42/8,72/5,163/8,104/5, ( 6)( 0,10)178/8,950/
42,287/9,198/8,179/6,333/12,193/7,369/14,50/7,243/11,70/5, ( 7)( 0,10)38*,213/
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207/7,122/6,51/4,87/5,101/6,95/5,209/9,13*, ( 9)(0,8)493/20,41*,303/9,66/4,
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7,54/3, (11)(0,5)174/8,245/10,91/4,30*,101/4,104/4, (12)(0,3)43/3,25*,76/3,
118/4
 H= 7(K)(L) ( 0)( 0,12),,686/23,,301/6,,277/7,,256/8,,133/5,,62/3, ( 1)( 0,12)
,17*,171/6,138/5,27*,34*,37*,201/6,28*,18*,86/4,212/7,21*, ( 2)( 0,11),650/
18,340/7,711/16,523/10,272/8,213/6,39*,127/6,114/5,37*,105/4, ( 3)( 0,11),81/
3,193/4,101/3,273/7,83/3,336/9,113/5,137/5,19*,126/5,84/4, ( 4)( 0,11),211/
6,539/10,124/4,305/8,384/8,40*,93/4,159/5,18*,124/5,49/2, ( 5)( 0,11),34*,199/
4,301/8,181/5,364/10,265/7,170/5,72/3,51/11,30*,20*, ( 6)( 0,10),60/3,139/4,
39*,353/9,84/4,42*,248/7,275/8,164/6,26*, ( 7)( 0,10),40*,41*,226/6,35*,280/
7,40*,56/3,52/7,97/3,61/3, ( 8)(0,9),42*,42*,181/6,108/4,71/4,270/7,206/5,327/
7,122/4, ( 9)(0,8),41*,189/5,139/4,70/3,92/4,33*,131/4,16*, (10)(0,7),94/4,37*,
34*,77/3,78/3,99/3,82/3, (11)(0,5),55/3,157/4,27*,46/2,51/2, (12)(0,1),80/4
 H= 8(K)(L) ( 0)( 0,11)497/38,,296/10,,359/12,,261/8,,328/13,,485/22,,
 ( 1)( 0,11)687/46,164/8,327/9,26*,30*,229/8,127/5,98/8,199/9,305/13,149/8,
100/5, ( 2)( 0,11)458/21,184/9,226/8,196/7,93/4,498/19,191/8,241/8,196/8,293/
13,71/6,265/10, ( 3)( 0,11)629/30,308/12,28*,203/7,285/10,168/6,106/6,219/9,
104/6,66/5,U,45/4, ( 4)( 0,11)645/31,85/6,379/11,118/5,244/9,57/4,414/14,40*,
87/6,47/3,173/7,59/5, ( 5)( 0,10)470/18,49/4,68/3,226/7,287/10,96/7,63/5,39*,
85/5,69/5,56/4, ( 6)( 0,10)331/13,280/11,98/5,115/7,124/6,173/7,91/5,38*,106/
5,98/7,21*, ( 7)(0,9)127/6,84/7,63/3,138/5,35*,207/8,54/4,180/8,45/3,119/6,
 ( 6)(0,8)405/14,630/25,150/5,196/8,162/6,177/8,99/6,269/11,19*, ( 9)(0,7)289/
12,238/8,79/4,95/6,44/4,211/7,69/4,156/6, (10)(0,6)391/15,305/11,288/9,44/4,
50/3,118/5,126/5, (11)(0,4)28*,151/6,117/4,24*,86/3
 H= 9(K)(L) ( 0)( 0,11),,500/18,,496/17,,40*,,277/12,,114/7,, ( 1)( 0,11),396/
20,555/16,275/11,521/16,37*,239/10,114/7,29*,18*,89/7,82/7, ( 2)( 0,11),75/
5,27*,330/12,110/5,334/13,196/8,41*,99/6,123/6,64/5,83/7, ( 3)( 0,11),310/13,
609/17,614/21,284/11,466/18,41*,41*,75/5,99/7,228/12,19*, ( 4)( 0,10),222/9,
325/11,318/12,333/12,93/5,107/7,134/6,141/7,97/7,125/7, ( 5)(0,9),436/20,104/
5,461/16,158/6,124/7,92/6,40*,243/11,169/8, ( 6)(0,9),235/9,40*,289/11,35*,42*,
40*,196/8,24*,127/6, ( 7)(0,9),157/7,175/6,64/5,137/6,112/6,80/6,423/20,139/
6,117/6, ( 8)(0,7),41*,41*,117/6,59/7,88/6,34*,29*, ( 9)(0,7),86/6,94/4,274/
10,28*,215/8,145/6,70/4, (10)(0,5),105/6,125/4,138/6,70/4,50/4, (11)(0,3),36/
4,99/3,45/4
 H=10(K)(L) ( 0)( 0,10)503/34,,241/9,,149/6,,44*,,344/17,,322/20, ( 1)( 0,10)
520/35,669/49,294/12,91/6,193/8,104/6,44*,265/12,285/14,363/20,287/18,
 ( 2)( 0,10)96/6,422/21,31*,53/3,70/4,115/7,133/8,145/8,108/7,193/11,155/9,
 ( 3)( 0,10)146/8,33*,94/5,204/9,35*,196/8,151/8,40*,159/8,191/11,149/10,
 ( 4)( 0,10)136/7,183/9,39*,228/8,35*,65/4,44*,114/7,85/6,15*,50/4,
 ( 5)(0,9)41*,41*,215/7,176/8,124/6,66/6,271/10,38*,148/7,78/6, ( 6)(0,9)108/
9,44*,168/6,206/9,56/3,78/5,256/9,118/8,40/5,95/5, ( 7)(0,8)268/15,369/18,159/
6,118/7,74/4,69/4,194/9,58/5,122/6, ( 8)(0,7)82/7,105/7,116/5,80/5,29*,93/6,
148/7,23*, ( 9)(0,6)491/26,68/5,214/7,157/7,69/4,30*,57/4, (10)(0,4)102/7,197/
9,100/5,28*,17*, (11)(0,1)U,76/12
 H=11(K)(L) ( 0)(0,9),,286/12,,138/8,,49*,,235/20,, ( 1)(0,9),322/21,221/8,
373/14,181/9,47*,70/7,170/11,26*,112/32, ( 2)(0,9),274/18,42*,194/12,222/14,
47*,144/9,151/10,26*,121/18, ( 3)(0,9),U,42*,122/9,185/16,123/10,168/16,38*,
72/14,14*, ( 4)(0,9),253/16,211/9,181/11,102/6,46*,47*,113/11,37/5,44/9,
 ( 5)(0,9),84/10,268/11,40*,253/15,224/13,70/7,249/13,163/12,141/24,
 ( 6)(0,9),78/9,301/12,112/10,161/10,143/8,143/9,191/13,69/6, ( 7)(0,7),50*,
185/8,56/5,51/4,37*,137/18,61/8, ( 8)(0,6),105/12,137/6,125/8,26*,93/7,123/
8, ( 9)(0,3),38*,29*,27*, (10)(0,2),U,73/4
 H=12(K)(L) ( 0)(0,8)551/38,,117/7,,74/6,,62/8,,161/12, ( 1)(0,8)163/19,90/
11,109/6,139/8,35*,165/9,111/11,50/6,50/7, ( 2)(0,8)54*,53*,207/9,41*,211/13,
268/14,46*,73/7,73/10, ( 3)(0,7)107/19,325/25,65/4,109/10,95/7,117/9,75/7,178/
12, ( 4)(0,7)153/17,362/28,109/6,274/14,98/6,208/12,146/9,253/14, ( 5)(0,7)
187/21,52*,41*,110/10,133/8,184/11,73/7,38/5, ( 6)(0,7)50*,187/15,183/8,36*,
129/8,37*,158/21,25*, ( 7)(0,5)117/21,45*,162/7,33*,151/7,32*, ( 8)(0,4)440/
34,40*,145/6,53/5,133/6, ( 9)(0,3)182/15,31*,97/4,40/4
 H=13(K)(L) ( 0)(0,7),,131/8,,163/10,,77/10,, ( 1)(0,7),141/12,110/7,62/6,33*,
114/9,43*,33*, ( 2)(0,7),91/11,160/7,350/18,33*,372/23,132/8,100/9,
 ( 3)(0,7),52*,111/7,105/10,68/5,109/9,40*,30*, ( 4)(0,7),51*,315/13,287/14,
408/19,334/20,252/13,67/6, ( 5)(0,7),79/9,38*,59/5,118/7,36*,52/5,22*,
 ( 6)(0,6),78/9,35*,153/9,209/13,185/9,175/9, ( 7)(0,4),53/6,31*,50/5,22*,
 ( 8)(0,3),33*,174/7,52/5, ( 9)(0,0)
 H=14(K)(L) ( 0)(0,7)77/14,,40*,,31*,,68/7,, ( 1)(0,7)161/18,199/16,123/7,223/
11,116/7,116/9,215/19,194/13, ( 2)(0,7)330/27,95/11,249/10,46/6,61/5,38*,136/
9,25*, ( 3)(0,7)354/32,132/11,294/12,111/8,56/4,171/10,279/14,23*, ( 4)(0,6)
47*,239/15,36*,146/9,88/6,73/6,30*, ( 5)(0,6)153/17,217/14,34*,131/8,58/5,84/
7,24*, ( 6)(0,4)179/20,222/14,153/5,124/8,21*, ( 7)(0,3)237/19,235/17,133/4,
68/6
 H=15(K)(L) ( 0)(0,6),,331/10,,219/13,,127/8, ( 1)(0,6),170/14,36*,58/5,27*,
89/7,29*, ( 2)(0,6),175/14,90/5,212/11,61/5,31*,27*, ( 3)(0,6),65/8,119/5,65/
6,286/13,29*,139/9, ( 4)(0,4),40*,202/7,105/6,158/10, ( 5)(0,4),36*,27*,183/
9,126/7, ( 6)(0,3),154/18,41/2,193/7
 H=16(K)(L) ( 0)(0,1)178/14,, ( 1)(0,5)203/16,63/7,87/7,U,U,54/6, ( 2)(0,3)38*,
195/13,66/4,66/6, ( 3)(0,3)58/10,132/11,71/4,49/6, ( 4)(0,3)76/13,31*,U,48/
4, ( 5)(0,0)68/17
 H=17(K)(L) ( 0)(0,1),, ( 1)(0,1),28*, ( 2)(0,1),142/9
```

[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 separated by a slant line. The standard error of $|F_o|$ is obtained from the standard error of $|F_o|^2$ by the relation

$$\sigma(|F_o|) = \frac{[\sigma(F_o^2)/F_o^2]}{\{4 + [\sigma(F_o)^2/2F_o^2]^2\}^{1/2}} F_o$$

For reflections too weak to be measured (indicated by an asterisk) the standard error is not given but is $1.4|F_o|$. Extinctions are indicated by an extra comma, and reflections which were not observed are labeled U.

sphere of reflection, we photographed regions of 1571 reflections but 280 of these were below the observational limit. These intensities were estimated visually with the use of a standard scale prepared from timed exposures of a representative reflection. The usual multiple film technique was used, and two independent measurements were made of each reflection on each film. Corrections for Lorentz and polarization factors, correlation of levels, averaging of reflections, and analyses of standard errors of each reflection were carried out with the aid of programs written for the IBM 7094.[13] The observed structure factors F_o and their standard errors are listed in Table I.

Method of Solution and Structure

A three-dimensional sharpened Patterson function was computed. A search for peaks was then made among the three Harker lines ($^1/_2 - 2x$, $^1/_2$, 0), (0, $^1/_2 - 2y$, $^1/_2$), and ($^1/_2$, 0, $^1/_2 - 2z$), the three planes ($^1/_2$, $^1/_2 - 2y$, $2z$), ($2x$, $^1/_2$, $^1/_2 - 2z$), and ($^1/_2 - 2x$, $2y$, $^1/_2$), and the centrosymmetric interaction ($2x$, $2y$, $2z$). Three consistent sets of interactions were obtained, which later were found to correspond to boron atoms 1, 2, and 6 (Fig. 3). Each one of these boron atoms and its symmetry related congeners formed the basis of a three-dimensional superposition function, computed as a minimum function on the IBM 7094. These three completely independent superposition functions gave, respectively, 10, 11, and 13 peaks of height greater than one-third of the maximum height of any peak. Comparison of

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(13) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 2339 (1963).

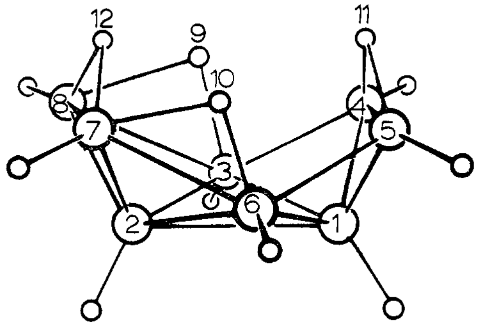


Fig. 3.—Molecular geometry of B_8H_{12}. Terminal hydrogens are numbered the same as their parent borons. The molecular mirror plane lies in the plane of the paper.

these superposition functions yielded eight peaks common to all three functions, and a preliminary model of the structure indicated an icosahedral fragment having reasonable B–B distances. Thus the boron arrangement was solved. The 500 strongest reflections gave $R_F = \Sigma\left||F_o| - |F_c|\right|/\Sigma|F_o| = 0.24$ and $R_{wF^2} = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma wF_o^4]^{1/2} = 0.64$.

After two cycles of three-dimensional least-squares refinement in which isotropic temperature factors and boron positions were refined with the use of all reflections, a three-dimensional electron density map was computed from which boron atoms had been subtracted (Table IIa). As was expected the incomplete refinement and anisotropic thermal motion yielded boron residuals, which were the strongest eight peaks. The next twelve peaks, however, were found in positions which were eminently reasonable for a boron hydride. The assignment of remaining peaks as false is based on both their chemically unreasonable positions and their substantially lower heights. At this stage the structure and formula were established, but we chose not to accept all of the details of the structure without further study.

Table IIa

Difference Fourier I[a,b]

Peak height	x	y	z	Assignment
272	0.250	0.150	0.167	Residual of boron 5
152	0.167	0.083	0.417	Residual of boron 3
125	0.067	0.083	0.300	Residual of boron 2
116	0.433	0.467	0.183	Residual of boron 7
114	0.117	0.133	0.150	Residual of boron 6
111	0.183	0.200	0.300	Residual of boron 1
110	0.283	0.100	0.333	Residual of boron 4
88	0.383	0.433	0.367	Residual of boron 8
76	0.450	0.383	0.167	Hydrogen 8
75	0.483	0.433	0.133	Hydrogen 7
65	0.167	0.417	0.017	Hydrogen 3
64	0.300	0.050	0.233	Hydrogen 11
62	0.350	0.117	0.367	Hydrogen 4
62	0.483	0.133	0.167	Hydrogen 2
56	0.300	0.183	0.083	Hydrogen 5
55	0.175	0.317	0.317	Hydrogen 1
54	0.083	0.183	0.067	Hydrogen 6
54	0.317	0.467	0.367	Hydrogen 9
51	0.367	0.383	0.250	Hydrogen 12
46	0.150	0.017	0.117	Hydrogen 10
35	0.133	0.183	0.067	False peak
32	0.217	0.500	0.233	False peak
32	0.233	0.000	0.400	False peak

[a] Electron density of borons 1–8 is removed. Boron positions and isotropic temperature factors have been refined. [b] Peaks ≤30 not listed.

Every known boron hydride which is based upon a single icosahedral fragment has one terminal H atom on each B atom with the B–H pointed away from the polyhedral center. Hence we accepted eight of the twelve H atoms as a basis for further refinement, omitting the remaining four H atoms. After two cycles of least-squares refinement of anisotropic thermal parameters and distance parameters of B atoms only, the values of $R_F = 0.14$ and $R_{wF^2} = 0.34$ were obtained. A three-dimensional difference map then yielded the remaining four H atoms as the highest peaks (Table IIb). Although some residuals of other atoms remained, the highest false peak was reduced to about half of the H atom peak heights. At this stage we introduced bridge H atoms 11 and 12, which were expected in all of the predicted models and had already appeared in both difference maps. Another round of refinement and difference synthesis yielded H atoms 9 and 10, now for the third time (Table IIc). We felt at this stage that there was no doubt about the formula, B_8H_{12}.

Table IIb

Difference Fourier II[a,b]

Peak height	x	y	z	Assignment
54	0.283	0.050	0.233	Hydrogen 11
51	0.383	0.400	0.233	Hydrogen 12
43	0.317	0.450	0.367	Hydrogen 9
42	0.150	0.017	0.117	Hydrogen 10
37	0.167	0.200	0.267	Residual of boron 1
35	0.150	0.417	0.000	Residual of hydrogen 3
35	0.283	0.117	0.333	Residual of boron 4
32	0.150	0.067	0.417	Residual of boron 3
32	0.450	0.467	0.183	Residual of boron 7
29	0.283	0.167	0.150	Residual of boron 5
27	0.383	0.450	0.350	Residual of boron 8
26	0.000	0.450	0.417	Residual of hydrogen 7
26	0.317	0.117	0.417	Residual of hydrogen 4
26	0.150	0.283	0.350	Residual of hydrogen 1
25	0.117	0.133	0.433	Residual of boron 6
25	0.000	0.167	0.333	Residual of hydrogen 2
24	0.300	0.300	0.333	False peak
23	0.050	0.167	0.117	Residual of hydrogen 6
21	0.483	0.383	0.383	Residual of hydrogen 8
21	0.267	0.233	0.100	Residual of hydrogen 5
21	0.083	0.417	0.125	False peak
21	0.083	0.400	0.417	False peak

[a] Electron density of borons 1–8 and terminal hydrogens 1–8 is removed. Borons have been refined with anisotropic thermal parameters. Hydrogens are unrefined. [b] Peaks ≤20 not listed.

In the final refinement all atomic positions, boron anisotropic thermal parameters and hydrogen isotropic thermal parameters were varied. Final values of $R_F = 0.112$, $R_{F^2} = \Sigma\left|F_o^2 - F_c^2\right|/\Sigma F_o^2 = 0.212$, and $R_{wF^2} = 0.253$ were obtained for all reflections. For observed reflections only a value of $R_F = 0.099$ was found. A summary of disagreement factors is given in Table III.

TABLE IIc

DIFFERENCE FOURIER III[a,b]

Peak height	x	y	z	Assignment
38	0.317	0.441	0.367	Hydrogen 9
34	0.167	0.033	0.133	Hydrogen 10
28	0.283	0.117	0.333	Residual of boron 4
27	0.017	0.417	0.333	Residual of hydrogen 7
26	0.450	0.333	0.417	Residual of hydrogen 8
25	0.150	0.100	0.483	Residual of boron 4 and hydrogen 4
25	0.283	0.200	0.067	Residual of hydrogen 5
25	0.400	0.433	0.383	Residual of boron 8
25	0.433	0.450	0.417	Residual of boron 7
25	0.067	0.500	0.433	False peak
24	0.450	0.417	0.450	Residual of hydrogen 8
24	0.225	0.000	0.358	False peak
24	0.183	0.408	0.208	False peak
23	0.133	0.133	0.200	Residual of boron 6
22	0.400	0.017	0.467	False peak
22	0.083	0.333	0.150	False peak
22	0.367	0.000	0.417	False peak
21	0.000	0.167	0.267	Residual of hydrogen 2

[a] Electron density of borons 1–8, terminal hydrogens 1–8, and bridge hydrogens 11 and 12 are removed. All positions and thermal parameters have been refined. [b] Peaks ⩽20 not tested.

TABLE III

FINAL VALUES OF $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

	R
All (h, k, or $l \neq 0$)	0.114
h even	0.117
h odd	0.113
k even	0.112
k odd	0.116
l even	0.109
l odd	0.119
$k + l$ even	0.112
$k + l$ odd	0.117
$h + l$ even	0.115
$h + l$ odd	0.114
$h + k$ even	0.114
$h + k$ odd	0.115
$h + k + l$ even	0.121
$h + k + l$ odd	0.108
over-all	0.112
Range of sin θ	
0.00 to 0.40	0.105
0.40 to 0.50	0.085
0.50 to 0.60	0.084
0.60 to 0.65	0.097
0.65 to 0.70	0.097
0.70 to 0.75	0.129
0.75 to 0.80	0.155
0.80 to 0.85	0.151
0.85 to 0.90	0.128
0.90 to 1.00	0.134

One further, and final, test was made of the structure. An objective resolution of the C_{2v}, C_s, or C_2 ambiguity was made by placement of H atoms 9 and 10 in the intermediate C_{2v} model and then allowing their parameters to refine. After two cycles of three-dimensional least-squares refinement these atoms had moved three-quarters of the way toward the final positions of the C_s structure of Fig. 3. This same type of test was similarly successful in B_9H_{15} where the same kind of choice between a terminal and bridge position had arisen.[3]

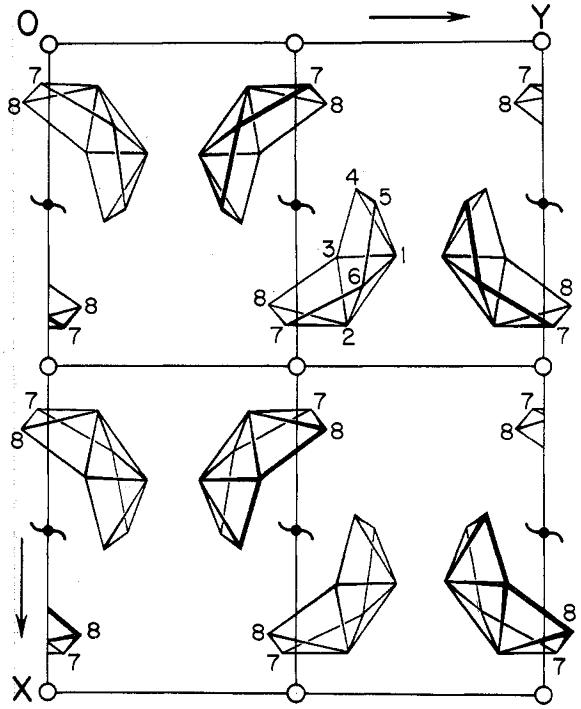


Fig. 4.—Unit cell of the crystal structure of B_8H_{12}. The origin at upper left is chosen at a center of symmetry. Only B atoms are shown.

TABLE IV

FINAL STRUCTURE PARAMETERS

Boron positions

Boron no.	x	y	z
1	0.3275	0.6969	0.2934
2	0.4384	0.5980	0.3032
3	0.3355	0.5712	0.4108
4	0.2223	0.6142	0.3286
5	0.2481	0.6492	0.1753
6	0.3802	0.6299	0.1509
7	0.4360	0.4780	0.1899
8	0.4104	0.4424	0.3460

Boron anisotropic temperature factors

Boron no.	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
1	38	50	62	2	2	−2
2	32	66	71	5	2	0
3	42	65	56	8	1	−1
4	36	81	91	2	−3	−10
5	41	77	79	−3	13	−2
6	44	69	61	−3	2	3
7	49	73	86	12	10	−2
8	47	64	81	8	−9	10

Hydrogen positions and isotropic temperature factors

Hydrogen no.	X	Y	Z	B
1	0.3397	0.8013	0.3216	3.0
2	0.5074	0.6439	0.3344	1.8
3	0.3410	0.5780	0.5186	1.3
4	0.1543	0.6284	0.3894	2.8
5	0.2045	0.6949	0.1010	1.5
6	0.4133	0.6836	0.0690	1.8
7	0.4911	0.4351	0.1275	1.2
8	0.4482	0.3758	0.4033	2.4
9	0.3026	0.4600	0.3735	3.4
10	0.3486	0.5202	0.1157	3.5
11	0.2056	0.5446	0.2251	1.6
12	0.3825	0.3895	0.2432	1.5

TABLE V

BOND LENGTHS[a] AND SPHERICAL COORDINATES[b] FOR B_8H_{12}

Center atom	Coordinating atom	ϕ	ρ	Bond length, Å.	Corrected bond length,[c] Å.
1 B_1	2 B_2	90.	0	1.830	1.832
	3 B_3	0	60.1	1.794	1.795
	4 B_4	34.1	113.3	1.710	1.718
	5 B_5	98.5	113.4	1.711	1.718
	6 B_6	132.6	59.7	1.789	1.793
	9 H_1	246.9	113.8	1.138	1.142
1 B_2	1 B_1	90.0	0	1.830	1.828
	3 B_3	0	58.9	1.814	1.814
	6 B_6	227.4	59.0	1.804	1.807
	7 B_7	261.8	110.8	1.718	1.725
	8 B_8	326.0	111.2	1.723	1.730
	10 H_2	113.2	118.3	1.104	1.089
3 B_3	1 B_1	90.0	0.	1.794	1.792
	2 B_2	0	61.0	1.814	1.814
	4 B_4	144.5	56.5	1.819	1.824
	8 B_8	31.6	108.8	1.812	1.816
	11 H_3	248.7	129.5	1.127	1.108
	17 H_9	90.8	115.1	1.300	1.308
4 B_4	1 B_1	90.	0.	1.710	1.702
	3 B_3	0.	61.0	1.819	1.814
	5 B_5	137.4	60.7	1.674	1.673
	12 H_4	259.8	137.7	1.132	1.123
	19 H_{11}	109.0	104.2	1.318	1.305
5 B_5	1 B_1	90.	0.	1.711	1.703
	4 B_4	0.	60.7	1.674	1.675
	6 B_6	136.8	60.7	1.826	1.823
	13 H_5	239.4	137.0	1.085	1.062
	19 H_{11}	27.8	103.4	1.337	1.328
6 B_6	1 B_1	90.	0.	1.789	1.785
	2 B_2	0.	61.3	1.804	1.801
	5 B_5	215.3	56.4	1.826	1.829
6 B_6	7 B_7	327.8	109.0	1.800	1.803
	14 H_6	115.2	126.8	1.115	1.102
	18 H_{10}	268.6	116.9	1.274	1.288
7 B_7	2 B_2	90.	0.	1.718	1.711
	6 B_6	0.	61.6	1.800	1.797
	8 B_8	136.4	60.4	1.707	1.708
	15 H_7	252.9	134.	1.087	1.066
	18 H_{10}	24.6	99.1	1.486	1.493
	20 H_{12}	115.8	103.5	1.299	1.289
8 B_8	2 B_2	70.	0.	1.723	1.716
	3 B_3	0.	61.7	1.812	1.808
	7 B_7	224.6	60.1	1.707	1.706
	16 H_8	111.6	131.4	1.047	1.038
	17 H_9	333.4	98.6	1.506	1.511
	20 H_{12}	246.0	104.7	1.266	1.256
9 H_1	1 B_1	...	...	1.138	1.135
10 H_2	2 B_2	...	...	1.104	1.119
11 H_3	3 B_3	...	...	1.127	1.146
12 H_4	4 B_4	...	...	1.132	1.141
13 H_5	5 B_5	...	...	1.085	1.108
14 H_6	6 B_6	...	...	1.115	1.128
15 H_7	7 B_7	...	...	1.087	1.109
16 H_8	8 B_8	...	...	1.047	1.056
17 H_9	3 B_3	90.	0.	1.300	1.292
	8 B_8	0	80.1	1.506	1.501
18 H_{10}	6 B_6	90.	0.	1.274	1.260
	7 B_7	0.	81.1	1.486	1.479
19 H_{11}	4 B_4	90.	0.	1.318	1.331
	5 B_5	0.	78.2	1.337	1.346
20 H_{12}	7 B_7	90.	0.	1.299	1.309
	8 B_8	0.	83.4	1.266	1.276

[a] Standard deviations were obtained from the full variance–covariance matrix calculated during the final least-squares refinement of the position parameters. These ranged from 0.003 to 0.004 Å. for boron-to-boron, from 0.02 to 0.03 Å. for boron-to-terminal hydrogen, and from 0.03 to 0.04 Å. for boron-to-bridge hydrogen distances. [b] Spherical coordinates of bonds at each atom are given for construction of precise models of boron hydrides. [c] Corrected for torsional oscillation assuming second atom rides on first. 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.

The final structural parameters (Table IV) refer to a complete molecule and can be related to the peaks in Table II by the symmetry operations of Pbca. The final difference electron density map from which all atoms were subtracted showed the highest false peak at 23 units on the scale reported in Table II. Bond distances and standard deviations (Table V) were computed from the full variance–covariance matrix. Within these standard deviations the molecule has a plane of symmetry. In Table V a set of bond distances is listed after correction for torsional oscillation of the molecule on the assumption that each atom "rides" on its neighboring atoms. Because the method of correction for this effect is not unique we have used the uncorrected values of bond distances throughout the discussion.

A three-dimensional model of the structure indicated reasonable intermolecular packing. Computation of all close H· · ·H contacts yielded none closer than the expected minimum value of about 2.5 Å. In Fig. 4 a schematic projection of this three-dimensional structure is shown.

Discussion

The geometrical structure is very closely related to that[3] of B_9H_{15}. If the doubly-bridged BH_2 group of B_9H_{15} is simply replaced by a bridge H one obtains B_8H_{12}. A close relation to the B_8 residue of $C_2H_5NH_2B_8H_{11}NHC_2H_5$[14] is also to be found. The lowering of symmetry from C_{2v} to C_s, discussed below in the valence theory, suggests that B_8H_{12} is not overcrowded with H· · ·H contacts in the open face region of bridge H atoms. Probably therefore $B_8H_{13}^-$ can reasonably be expected,[2] and possibly even B_8H_{14} might be found in C_2 symmetry.[2]

Bond distances involving H_9 and H_{10} indicate that these atoms are very unsymmetrically bridged. The distances $B_7 \cdots H_{10}$ = 1.49 Å. and $B_8 \cdots H_9$ = 1.51 Å. are long for H bridges, but the distances $B_6 \cdots H_{10}$ = 1.27 Å. and $B_3 \cdots H_9$ = 1.30 Å. are short for H bridges. Evidence that the close contacts $H_9 \cdots H_{12}$ = 1.89 Å. and $H_{10} \cdots H_{12}$ = 1.96 Å. are crowding H_{12} is found in the dihedral angle of 153° between the planes (H_{12}, B_8,

(14) R. Lewin, P. G. Simpson, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 478 (1963); *J. Chem. Phys.*, **39**, 1532 (1963).

TABLE VI

POSSIBLE VALENCE STRUCTURES OF B_8H_{12}

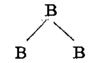
	Generating symmetry	No. of resonance structures	B–B	
1	. .	1	3–4, 5–6	
2	σ_v	2	3–4, 2–8	
3	σ_v	2	3–4, 2–6	
4	σ_v	2	3–4, 1–6	5–6–2
5	σ_v	2	3–4, 1–5	4–1–6, 5–6–2
6	σ_v	2	3–4, 2–7	6–2–8

TABLE VII

ESTIMATED CHARGE DISTRIBUTION OF B_8H_{12}

Atom	LCAO	Valence structures	Most symmetric valence structure
1	−0.094	−0.182	0.000
2	−0.176	−0.182	0.000
3, 6	−0.074	−0.106	−0.167
4, 5	+0.032	0.000	−0.167
7, 8	+0.177	+0.288	+0.333

TABLE VIII

BOND ORDERS IN B_8H_{12}

	Bond length, Å. (av.)	LCAO overlap population	3-center bond order of resonance hybrid	3-center bond order of most sym. structure	Order of increasing bond length	Order of decreasing overlap population	Order of decreasing resonance bond order
1–2	1.831	0.40	0.73	1.33	9	8	6
1–3, 1–6	1.792	0.45	0.70	0.67	5	6	8
1–4, 1–5	1.711	0.51	0.88	0.67	3	2	3
2–3, 2–6	1.809	0.45	0.71	0.67	7	5	7
2–7, 2–8	1.721	0.51	0.73	0.67	4	3	5
3–4, 6–5	1.823	0.46	0.86	1.00	8	4	4
4–H–5	1.674	0.56	1.05	1.17	1	1	1
6–H–7, 3–H–8	1.807	0.35	0.56	0.50	6	9	9
7–H–8	1.707	0.44	0.92	1.17	2	7	2

B_7) and (B_2, B_8, B_7). The corresponding dihedral angle for H_{11} is 144°. This crowding, strain, and associated valence interactions may be associated with the 0.033 Å. greater length of $B_7 \cdots B_8$ as compared with that of $B_4 \cdots B_5$. This lowering of symmetry from C_{2v} to C_s, and that illustrated by comparison of the $H_9 \cdots B_4$ = 2.00 Å. and $H_{10} \cdots B_5$ = 2.02 Å. with the $H_9 \cdots B_8$ = 1.51 Å. and $H_{10} \cdots B_7$ = 1.49 Å. pairs of distances are well outside the standard deviations of the corresponding values in this study. Shifts of both H_9 and H_{10} by 0.25 Å. are required to obtain the C_{2v} structure, and a shift of one of these two atoms by 0.5 Å. is required to obtain the C_2 structure.

The valence structures of the boron hydrides have previously[2,15] been discussed from both the three-center resonance and the molecular orbital points of view. If for B_8H_{12} we assume four bridge H atoms, there are[2] four three-center bonds and two two-center bonds in the boron framework. A two-center bond between B_3 and B_4 (or B_5 and B_6) and a three-center bond among B_1, B_2, and B_3 (or B_1, B_2, and B_6) must be common to all valence structures of which there are only eleven (Table VI). For want of a better criterion all valence structures are weighted equally[15] in the computation of charge distribution (Table VII) and bond orders (Table VIII) for B_8H_{12}. Bond orders, defined as $2c_ic_j$, are also given for the one most symmetrical valence structure and for the extended Hückel LCAO results in Table VIII. Parameters for the Hückel treatment are Coulomb integrals of −15.20 for 2s of B and −8.50 for 2p of B, resonance integrals of $\beta = {}^1/_2K(\alpha_i + \alpha_j)S_{ij}$ where $K = 1.75$, α_i is a Coulomb integral, and S_{ij} is an overlap integral having the usual Slater exponent.[15] The average charge of a bridge H of 0.03 and that of a terminal H of −0.16 are probably anomalous as usual,[15] and hence in order to facilitate comparisons of the two theories in Table VII all H atoms were required to be electrically neutral. Thus the net charge of B is the sum of its net charge plus that of its terminal H plus half of the net charge of each adjacent bridge H.

Boron atoms 7 and 8, each bonded to two bridge H atoms, are most positive in both methods, whereas B_1 and B_2, and to a lesser extent B_3 and B_6 toward the center of the molecule, carry an excess of negative charge. The Mulliken overlap populations[16] were also computed from the extended Hückel treatment (Table VIII). The bridge B_4–H_{11}–B_5 is the shortest hydrogen bridge yet found in the boron hydrides and does have a large bond order in the three-center resonance treatment, which is independent of the experimental value of the distance. Weak bonding across B_6–H_{10}–B_7 is also confirmed by the valence theory, where the situation is much like that of the B_5–H–B_6 bridge[15] in B_9H_{15}. The agreement is disappointing only in the B_7–H_{12}–B_8 bridge, where the LCAO theory gives a lower result than the resonance theory predicts, but the crowding of bridges B_6–H_{10}–B_7, B_7–H_{12}–B_8, and B_8–H_9–B_3 referred to above may prevent full participation of bonding in the actual molecule as compared with an idealized sterically free situation.

TABLE IX

TOTAL ENERGIES OF THE THREE ISOMERS OF B_8H_{12}

Isomer symmetry	C_s	C_{2v}	C_2
Energy, kcal.	−12,529.05	−12,528.77	−12,525.52
Gap, e.v.	3.34	3.48	3.20

Most interesting is a comparison of the total energies of the C_s, C_{2v}, and C_2 structures by the extended Hückel method (Table IX). The C_{2v} and C_2 structures differ from the C_s structure only in the positions of H_9 and

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[15] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962).

[16] R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962).

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.

Acknowledgments.—We wish to thank R. D. Dobrott and J. A. Potenza for help in maintaining the single crystals over 4 months, and W. E. Streib for a considerable amount of aid in obtaining the early photographs. We also acknowledge use of computer programs written by Busing, Martin, and Levy, by Van der Hende, and by Sly and Shoemaker. Support of this research by the Office of Naval Research, the National Science Foundation, the U. S. Army Research Office (Durham), and the Advanced Research Projects Agency is gratefully acknowledged.

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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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Received August 3, 1964

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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(1) H. G. Weiss, to be published. Also H. G. Weiss and I. Shapiro, U. S. Patent 3,086,996 (April 23, 1963, filed June 13, 1956).

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