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The Molecular and Crystal Structure of $B_{20}H_{16}(NCCH_3)_2 \cdot CH_3CN$

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Addition of acetonitrile to $B_{20}H_{16}$ yields crystals of $B_{20}H_{16} \cdot 3CH_3CN$ in which there is one CH_3CN of crystallization per $B_{20}H_{16}(NCCH_3)_2$. The B_{20} unit has rearranged to yield a B_{12} unit which shares a triangular face with a B_{11} icosahedral fragment. A mechanism similar to that for the o-$B_{10}C_2H_{12}$ to m-$B_{10}C_2H_{12}$ transformation is proposed for this rearrangement. The space group is $P2_1/c$, and there are four $B_{20}H_{16}(NCCH_3)_2$ and four CH_3CN of crystallization in a unit cell having parameters $a = 12.55$, $b = 10.70$, $c = 16.12$ A, and $\beta = 99°\ 40'$. The structure was solved by direct methods and refined by least squares to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.07$ for the 1495 observed reflections.

The boron hydride $B_{20}H_{16}$[1,2] is known to react with ligands without loss of hydrogen[1,2] and usually yields adducts containing two molecules of electron-pair donor. It has been presumed[2b] that the B_{20} arrangement of the parent $B_{20}H_{16}$ is retained in these adducts and that the ligands are probably *trans*.

Both $B_{20}H_{16} \cdot 2(CH_3)_2S$ and $B_{20}H_{16} \cdot 3CH_3CN$ were prepared here, and we chose $B_{20}H_{16} \cdot 3CH_3CN$ for this study, primarily because location of hydrogen atoms is easier when only first-row elements are present; but the results to be described were delayed owing to the difficulty of solution of the crystal structure. We shall show that $B_{20}H_{16} \cdot 3CH_3CN$ has a covalently bonded unit of $B_{20}H_{16}(NCCH_3)_2$ and a molecule of CH_3CN of crystallization. The B_{20} unit of the parent $B_{20}H_{16}$ is not retained, nor are the ligands *trans*. Instead, a most interesting rearrangement has occurred[3] which is closely related to a general theory[4] of rearrangements in polyhedral molecules and fragments.

Experimental Section

Preparation and Characterization.—Icosaborane-16, which had been prepared by both electric discharge[1b] and pyrolysis[2] methods, was sublimed before use. Eastman Spectro Grade acetonitrile was used without further purification. Infrared spectra were recorded with a Perkin-Elmer Model 21 spectrometer, and ^{11}B nuclear magnetic resonance spectra were obtained with a modified Varian instrument operating at 15.1 Mc sec^{-1}. All manipulations of $B_{20}H_{16}$ were carried out on a vacuum line or in a water-free air-filled glove box.

The $B_{20}H_{16}$ dissolved in CH_3CN without evolution of H_2, and yielded a pale yellow solution after 24 hr. Evaporation of excess CH_3CN yielded a yellow solid material, which became white upon washing with small amounts of CH_3CN. This derivative is stable to atmospheric oxygen and water vapor. It does not melt at 250° but discolors around 200°. The infrared spectrum in a KBr pellet shows maxima at 2900 (w), 2500 (s), 2330 (w), 1390 (m), 1100 (m), 980 (s), 950 (w), 920 (m), 825 (m), 800 (w), and 740 (m) cm^{-1}. An acetonitrile solution shows an ^{11}B nmr spectrum, grossly similar to that of $B_{20}H_{16}$, consisting of three poorly resolved peaks.

Single crystals, obtained by slow evaporation of acetonitrile solutions, were found by flotation in mixed solvents to have a density of 1.11 g cm^{-3}. Weissenberg and precession photographs of single crystals showed reciprocal lattice symmetry C_{2h}, and absences of $h0l$ for l odd and of $0k0$ for k odd are consistent with the space group $P2_1/c$. Calibration with Al powder diffraction lines then yielded unit cell parameters $a = 12.55$, $b = 10.70$, $c = 16.12$ A, all ± 0.02 A, and $\beta = 99°\ 40' \pm 10'$. The only reasonable number of molecules per unit cell is four, and hence the X-ray molecular weight is 357 ± 3 g $mole^{-1}$, which is consistent with the formula $B_{20}H_{16} \cdot 3CH_3CN$ (mol wt calcd = 356).

Data Collection.—A crystal $0.2 \times 0.4 \times 1.0$ mm was placed along the long axis (c) in a thin-walled glass capillary, which was sealed and then mounted on a Buerger automated X-ray diffractometer. Weissenberg geometry, an ω scan, and Ni-filtered Cu Kα radiation were employed. The proportional counter terminals were set at 1640 v throughout data collection. The base line of the pulse height analyzer and the window voltage were also held constant. In the measurement of each reflection the counter was positioned to the proper vertical Weissenberg coordinate Υ, the crystal was rotated about the horizontal coordinate angle ϕ to $\phi_r - \delta$, where ϕ_r refers to the reflection and δ is proportional to the Lorentz factor L, the background was read for a time t which is proportional to L, the angle ϕ was increased for a time $6t$ at 2°/min until it became $\phi_r + \delta$, the background was counted again for a time t, and finally LPF_o^2 was computed as the scan minus three times the sum of background counts (P is the polarization factor). As the levels hkL for $0 \leqslant L \leqslant 14$ were collected, the intensities of seven $hk0$ monitor reflections were measured after each level. After correction for one of the reflections which exceeded the 10^6 counts capacity of the instrument, all check reflections showed standard deviations less than 5%. In addition to these $hk0$ reflections, a check reflection was measured periodically during data collection of each level.

Because of the difficulty of finding suitable crystals for mounting on another axis, we chose to take correlation data on the same needlelike crystal mounted on a precession goniometer and photographed with Cu Kα radiation. Levels $0kl$, $1kl$, $2kl$, $h0l$, $h1l$, and $h2l$ were taken on timed films, and visual estimates of intensities served to place levels hkL for $L \leqslant 10$ on a common scale. This same scale was at first assumed for levels $hk11$ through $hk14$, but later five separate scale factors were refined by least-squares procedures which yielded final scale factors within 5% of one another. Because of this procedure, scale factors and temperature factors were never refined simultaneously. The final list of structure factors is shown in Table I.

No corrections for extinction or absorption ($\mu = 3.64$ cm^{-1} for Cu Kα radiation) were made. Standard errors for the measurements of individual reflections were initially chosen as $\sigma = 0.05F_o^2$, but after preliminary refinement an examination of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ as a function of F_o^2 led to the choice

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(2) (a) N. E. Miller and E. L. Meutterties, *J. Am. Chem. Soc.*, **85**, 3506 (1963); (b) N. E. Miller, H. C. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1690 (1964).

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(4) W. N. Lipscomb, *Science*, **153**, 3734 (1966).

TABLE I

LIST OF 10|F_o| FOR $B_{20}H_{16}(NCCH_3)_2 \cdot CH_3CN^a$

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 L=0 (K)(H)(0)(0,15)8738,170,1345,841,557,346,441,288,328,
172,57+,27+,92,22+,28+,*,(1)(1,15)893,219,23+,314,213,
42+,27+,31+,215,*,82,29+,39+,29+,36+,(2)(0,14)675,79,838,
211,106,304,237,43+,54+,81,62+,71,84,44+,*,(3)(1,14)344,
361,422,231,186,85,79,75,138,46+,45+,64+,108,87,
(4)(0,14)497,243,224,246,120,170,163,160,285,95,*,65+,
44+,57+,82,(5)(1,13)237,403,161,141,196,82,254,23+,90,
50+,79,*,32+,(6)(0,13)55+,152,526,137,197,71+,84,181,152,
52+,26+,26+,104,30+,(7)(1,12)84,68+,108,69+,36+,63+,65+,
67+,54+,42+,64+,72,(8)(0,11)325,34+,39+,136,229,67+,46+,
136,99,19+,*,90,(9)(1,10)169,35+,29+,98,37+,52+,59+,*,75,
104,(10)(0,9)102,51+,123,38+,85,40+,67+,18+,62+,105,
(11)(1,8)173,56+,57+,47+,23+,38+,41+,*,(12)(0,6)170,44+,
32+,54+,28+,33+,64+,(13)(1,1)36+
 L=1 (K)(H)(1)(-15,14)*,30+,6+,56+,97,23+,*,59+,29+,119,
37+,54+,799,287,631,258,997,768,904,*,93,102,294,49+,296,
31+,42+,98,*,*,(2)(-15,14)23+,*,23+,17+,*,73,315,34+,319,
242,21+,332,66+,758,582,911,686,230,21+,221,*,322,114,210,
110,76,104,77,23+,32+,(3)(-14,14)*,20+,17+,16+,76,*,122,
119,251,*,283,109,70+,373,722,66+,636,483,173,23+,70+,84,
14+,*,28+,70+,72,14+,*,(4)(-14,14)59+,*,*,91+,38+,125,95,
61+,167,202,72,28+,516,185,203,182,57+,86,66+,110,*,*,135,
84,18+,29+,15+,*,25+,(5)(-14,13)43+,22+,44+,70+,16+,23+,
71,31+,77,27+,65+,152,414,26+,151,260,184,130,283,483,242,
131,66+,31+,23+,19+,82,61+,(6)(-13,13)35+,28+,*,67+,39+,
55+,85,*,15+,44+,57+,230,104,252,204,232,79,88,49+,*,*,
138,11+,42+,*,21+,6+,(7)(-12,12)*,72,*,31+,90,70+,278,124,
39+,349,115,94,124,22+,204,140,*,213,156,108,110,*,22+,
123,73,(8)(-12,11)17+,*,*,*,64+,88,15+,267,101,195,239,
116,78,64+,173,57+,177,28+,102,114,54+,49+,21+,41+,
(9)(-11,10)*,27+,50+,6+,44+,60+,20+,40+,24+,55+,125,71,
111,*,24+,60+,33+,*,72,19+,33+,53+,(10)(-9,9)16+,30+,27+,
29+,59+,126,65+,43+,*,62+,37+,31+,34+,*,33+,18+,31+,*,
21+,(11)(-8,7)24+,59+,52+,23+,12+,*,75,88,45+,152,98,21+,
112,18+,45+,*,(12)(-5,5)87,32+,30+,*,*,24+,93,36+,76,17+,
26+,(13)(-1,0)64+,74
 L=2 (K)(H)(0)(-15,14)15+,11+,*,*,141,45+,178,118,438,379,
674,588,428,61+,U,1147,1378,1864,55+,195,508,195,345,259,
547,195,59+,64+,80,83,(1)(-15,14)38+,38+,28+,32+,17+,62+,
137,45+,32+,259,580,337,132,546,114,220,796,131,516,381,
62+,153,85,173,187,86,40+,18+,95,16+,(2)(-15,14)*,40+,
53+,8+,37+,177,130,206,*,400,23+,84,109,114,758,994,207,
193,596,427,113,118,76,46+,213,*,28+,23+,15+,17+,
(3)(-14,14)*,31+,29+,69+,53+,45+,209,211,47+,228,201,447,
36+,139,319,109,632,318,179,190,255,115,141,90,*,33+,*,
39+,48+,(4)(-14,13)42+,50+,107,29+,*,28+,26+,163,174,85,
362,133,33+,375,112,93,223,242,310,141,*,305,*,107,48+,
17+,80,41+,(5)(-14,13)30+,87,*,*,53+,*,37+,22+,*,99,215,
120,58+,115,355,315,67+,115,288,111,72,150,57+,119,59+,
84,34+,44+,(6)(-13,12)41+,69+,28+,20+,39+,17+,107,148,215,
56+,155,205,*,*,160,208,119,31+,115,354,254,14+,74,38+,
47+,57+,(7)(-12,12)62+,59+,34+,*,43+,73,45+,40+,362,117,
44+,7+,27+,137,76,109,119,124,9+,118,38+,*,34+,65+,*,
(8)(-12,11)27+,*,88,36+,85,*,10+,68+,144,71,225,288,*,557,
*,112,*,110,*,75,31+,*,*,53+,(9)(-11,10)43+,*,70+,74,38+,*,
69+,33+,*,28+,153,162,76,75,35+,28+,67+,*,39+,*,37+,90+,
(10)(-9,9)*,38+,38+,24+,48+,146,26+,86,52+,38+,122,122,
79,92,99,33+,72,50+,38+,(11)(-8,7)53+,37+,29+,82,*,55+,
97,39+,142,28+,152,27+,39+,30+,51+,16+,(12)(-5,5)11+,*,
47+,85,137,*,94,*,22+,31+,7+
 L=3 (K)(H)(1)(-15,14)*,*,16+,*,37+,26+,30+,68+,*,459,143,
47+,176,243,165,433,190,239,300,196,308,300,27+,64+,31+,
23+,49+,171,*,37+,(2)(-15,14)*,49+,*,26+,76,100,182,60+,
251,39+,46+,247,203,392,295,1259,143,290,301,505,82,88,
46+,54+,75,13+,84,83,40+,12+,(3)(-14,14)47+,*,*,28+,73,*,
286,54+,112,47+,245,213,49+,154,105,95,480,284,218,468,
319,184,65+,*,44+,137,68+,89,46+,(4)(-14,13)27+,18+,16+,
44+,30+,118,*,134,132,88,271,88,303,230,270,109,163,411,
62+,88,145,89,9+,46+,*,76+,9+,50+,(5)(-14,13)14+,91+,7+,
6+,*,37+,112,19+,96,137,211,184,*,95,426,379,98,49+,292,
171,262,81,125,44+,94,52+,22+,67+,(6)(-13,12)16+,26+,47+,
25+,44+,106,26+,129,140,96,108,99,205,86,199,56+,132,77,
162,43+,*,*,13+,*,*,*,(7)(-12,12)36+,34+,76,21+,*,38+,*,
194,229,59+,19+,129,212,79,132,299,125,36+,277,60+,*,93,
43+,121,33+,(8)(-12,11)*,*,*,79,11+,16+,54+,167,134,248,
175,129,34+,42+,172,62+,68+,120,30+,*,51+,22+,71+,*,
(9)(-11,10)*,13+,51+,23+,34+,57+,36+,94,44+,36+,103,123,
16+,72,6+,139,*,*,30+,92,*,19+,(10)(-9,8)31+,42+,31+,21+,
26+,41+,42+,*,*,26+,65+,*,39+,42+,39+,21+,*,9+,
(11)(-8,7)56+,13+,50+,19+,*,52+,*,4+,35+,88,*,80,89,39+,
48+,46+,(12)(-5,4)107,34+,25+,36+,38+,36+,70+,182,79,107
 L=4 (K)(H)(0)(-15,14)41+,*,26+,28+,162,105,79,362,172,
159,438,43+,248,230,891,82,738,442,1037,136,287,404,354,
113,301,*,47+,146,26+,102,(1)(-15,14)20+,18+,27+,*,49+,
120,55+,269,127,360,272,323,172,9+,66+,490,46+,618,972,
103,163,413,55+,185,39+,48+,46+,27+,13+,35+,(2)(-15,13)
51+,*,*,32+,*,26+,130,126,253,145,60+,195,277,*,329,173,
487,68+,360,275,76,179,250,97,45+,36+,29+,149,76,
(3)(-14,13)31+,58+,*,41+,16+,*,*,202,25+,159,305,144,296,
306,74,555,45+,324,301,17+,153,116,62+,94,84,23+,165,10+,
(4)(-14,13)12+,59+,44+,71,215,54+,105,*,107,88,128,161,
643,167,151,466,105,34+,157,38+,120,206,130,57+,*,72,64+,
63+,(5)(-14,12)9+,48+,22+,62+,41+,11+,55+,94,293,128,318,
28+,103,128,220,194,363,25+,143,125,121,21+,69+,*,*,30+,*,
(6)(-13,12)*,48+,*,48+,*,32+,276,183,278,160,39+,185,586,*,
132,135,12+,114,366,33+,180,99,41+,83,12+,39+,(7)(-12,-5)
25+,26+,24+,105,84,*,*,182
 L=5 (K)(H)(1)(-15,13)*,8+,13+,15+,39+,83,69+,124,200,
15+,116,361,102,277,116,637,208,67+,253,98,82,299,276,88,
87,153,33+,169,62+,(2)(-14,13)*,49+,90,96,62+,402,93,270,
19+,98,547,403,500,127,199,303,404,387,96,346,366,28+,
44+,45+,74,129,16+,57+,(3)(-14,13)64+,102,82,21+,15+,108,
224,263,159,94,82,188,148,119,537,300,79,162,50+,61+,133,
105,193,53+,45+,26+,67+,79,(4)(-14,13)*,25+,*,113,133,
52+,208,170,246,345,180,18+,*,162,302,159,116,427,162,105,
58+,150,112,20+,30+,22+,34+,43+,(5)(-13,12)44+,21+,33+,
71+,105,93,237,125,92,50+,52+,264,209,65+,68+,264,212,138,
129,125,40+,20+,53+,*,25+,81,(6)(-13,12)*,58+,7+,*,86,93,
41+,225,195,42+,90,65+,58+,20+,284,14+,171,*,*,37+,97,145,
*,*,45+,8+,(7)(-12,11)28+,68+,20+,*,120,24+,107,90,*,67+,
100,168,204,313,112,105,160,106,82,131,113,142,13+,61+,
(8)(-11,10)45+,79,44+,89,69+,52+,43+,*,144,*,290,143,170,
133,36+,122,80,26+,66+,94,*,82,(9)(-10,9)*,79,29+,123,127,
*,19+,39+,74,*,68+,61+,125,17+,51+,28+,65+,78,30+,64+,
(10)(-9,8)4+,58+,43+,72,27+,25+,38+,50+,18+,42+,82,38+,*,
57+,11+,26+,15+,24+,(11)(-7,6)133,17+,40+,38+,26+,*,91,*,
97,30+,30+,*,70+,11+,(12)(-4,3)112,109,41+,70+,57+,116,
166,15+
 L=6 (K)(H)(0)(-15,13)*,40+,68+,82,89,90,332,55+,327,77,
151,219,72,59+,458,297,203,80,944,337,249,203,299,190,163,
71+,145,168,19,(1)(-14,13)63+,6+,20+,26+,22+,38+,93,142,
67+,58+,384,383,165,308,243,76,254,197,*,559,210,90,286,
63+,*,33+,60+,34+,(2)(-14,13)22+,56+,45+,122,64+,54+,283,
86,19+,48+,181,225,385,353,126,185,55+,371,219,389,457,
48+,308,47+,*,21+,130,*,(3)(-14,13)23+,*,28+,*,21+,168,*,
65+,217,17+,32+,29+,358,15+,237,103,27+,300,183,96,*,249,
65+,66+,35+,9+,19+,11+,(4)(-14,12)*,30+,15+,76,105,*,58+,
128,210,199,55+,59+,148,288,358,69+,25+,360,104,81,24+,
86,88,87,*,75,*,(5)(-13,12)21+,26+,59+,86,120,9+,159,377,
50+,154,224,85,90,183,193,234,90,338,149,56+,112,130,48+,*,
50+,37+,(6)(-13,11)*,20+,41+,23+,39+,84,114,115,258,41+,*,
333,82,53+,316,59+,316,35+,36+,90,33+,*,93,92,74,
(7)(-12,10)*,*,64+,23+,44+,*,59+,9+,192,182,203,20+,62+,
43+,32+,57+,163,184,50+,34+,62+,90,54+,(8)(-11,10)*,46+,
31+,110,108,63+,37+,95,74,96,176,57+,61+,101,36+,116,*,*,
46+,56+,53+,90,(9)(-10,8)44+,73,33+,98,23+,13+,28+,18+,
80,77,*,37+,79,143,55+,164,69+,141,108,(10)(-9,7)*,152,*,
109,117,112,122,32+,*,62+,31+,42+,95,63+,64+,172,25+,
(11)(-7,5)*,47+,64+,*,61+,33+,70+,153,24+,66+,81,25+,50+,
(12)(-4,2)*,*,19+,24+,*,74,16+
 L=7 (K)(H)(1)(-14,13)20+,40+,12+,78,45+,78,173,150,61+,
183,187,259,77,531,185,360,45+,227,107,155,43+,92,40+,
42+,99,30+,60+,23+,(2)(-14,12)24+,70+,59+,21+,77,80,*,103,
122,257,285,12+,609,160,252,172,32+,*,84,191,32+,211,133,
84,90,78,19+,(3)(-14,12)12+,42+,26+,17+,71,69+,24+,180,
265,6+,280,25+,138,22+,58+,247,40+,350,69+,151,336,58+,
35+,9+,14+,29+,46+,(4)(-14,12)*,13+,*,91,*,30+,234,62+,
186,19+,228,357,91,436,37+,63+,48+,282,*,166,164,89,30+,
89,*,76,52+,(5)(-13,11)32+,41+,41+,50+,67+,78,*,101,73,
22+,58+,253,106,167,193,168,184,196,46+,37+,36+,*,49+,
26+,43+,(6)(-13,11)*,31+,43+,86,11+,105,105,201,33+,11+,
134,50+,136,39+,143,76,429,199,44+,37+,42+,91,38+,*,*,
(7)(-12,10)20+,*,28+,12+,41+,54+,125,*,87,198,353,118,131,
150,39+,34+,64+,54+,40+,21+,52+,29+,17+,(8)(-11,9)27+,
24+,70+,17+,38+,33+,*,26+,184,*,180,135,105,112,*,37+,93,
24+,93,154,28+,(9)(-10,8)25+,53+,20+,131,130,33+,21+,*,
47+,*,41+,19+,52+,18+,*,54+,123,120,43+,(10)(-8,7)46+,
31+,26+,15+,70+,45+,30+,54+,24+,88,88,36+,66+,*,*,*,
(11)(-6,4)37+,24+,40+,30+,82,21+,*,116,48+,*,97,
(12)(-2,1)54+,30+,86,141
 L=8 (K)(H)(0)(-14,12)33+,*,39+,100,85,306,171,201,125,
316,190,254,370,*,231,224,61+,304,47+,326,209,43+,54+,126,
*,71,88,(1)(-14,12)*,*,*,51+,118,34+,44+,66+,406,157,22+,
116,103,237,103,168,268,*,89,80,166,95,19+,*,74,*,*,
(2)(-14,12)42+,11+,*,36+,19+,87,62+,174,*,22+,192,*,12+,
283,112,51+,136,137,122,236,49+,285,45+,64+,46+,*,*,
(3)(-14,12)41+,26+,45+,31+,39+,40+,33+,364,116,*,248,32+,
133,41+,231,256,249,105,169,150,7+,88,98,49+,14+,59+,*,
(4)(-13,11)*,35+,33+,76,*,77,224,211,285,106,102,365,272,
71,101,209,279,188,68+,104,57+,*,*,48+,59+,(5)(-13,11)*,
16+,*,*,41+,12+,145,184,133,230,153,106,69+,90,92,187,
52+,259,133,55+,23+,46+,53+,*,*,(6)(-12,10)33+,22+,30+,*,
43+,127,40+,112,*,185,117,463,37+,90,131,33+,110,157,49+,*,
*,34+,13+,(7)(-12,9)*,18+,*,27+,34+,*,*,62+,*,149,161,86,
146,88,138,29+,64+,31+,88,66+,29+,16+,(8)(-11,8)*,28+,
59+,18+,61+,14+,117,*,*,118,79,97,162,33+,33+,173,31+,81,
41+,*,(9)(-9,7)*,56+,24+,54+,52+,*,14+,52+,54+,29+,44+,
31+,*,50+,37+,81,33+,(10)(-8,6)62+,102,47+,50+,34+,44+,*,
46+,*,24+,67+,45+,54+,97,56+,(11)(-5,3)27+,*,67+,40+,19+,
88,*,50+,34+
 L=9 (K)(H)(1)(-14,12)*,27+,*,36+,88,*,150,253,235,50+,
121,231,232,22+,117,*,123,31+,274,103,52+,198,58+,*,27+,
50+,18+,(2)(-14,11)21+,8+,*,*,*,142,128,79,387,145,303,
43+,156,107,226,96,223,185,111,209,87,182,*,52+,*,17+,
(3)(-13,11)34+,30+,*,47+,110,32+,224,32+,236,61+,53+,72,
215,105,*,252,91,*,298,131,*,134,92,43+,29+,(4)(-13,11)
39+,17+,32+,86,34+,96,192,237,140,163,273,174,220,82,294,
113,174,164,152,141,50+,*,16+,*,13+,(5)(-13,10)*,35+,31+,
38+,8+,*,129,*,184,112,122,245,*,168,97,253,98,190,27+,
58+,23+,27+,*,81,(6)(-12,10)37+,*,44+,20+,101+,*,36+,214,
127,107,6+,158,47+,154,25+,193,9+,*,*,*,46+,*,19+,
(7)(11,9)*,*,47+,58+,25+,62+,14+,42+,12+,219,*,141,*,54+,
63+,24+,53+,119,64+,72,19+,(8)(-10,8)*,23+,37+,*,*,26+,
23+,31+,24+,47+,*,34+,31+,101,86,7+,51+,69+,27+,
(9)(-9,6)12+,34+,14+,64+,*,25+,*,47+,*,51+,63+,33+,93,
54+,49+,6+,(10)(-7,5)*,*,11+,41+,46+,37+,67+,43+,60+,62+,
25+,24+,*,(11)(-4,2)58+,*,63+,59+,20+,39+,*
 L=10 (K)(H)(0)(-14,11)26+,*,*,23+,87,24+,72,89,189,48+,
258,91,375,15+,102,37+,93,153,147,117,8+,*,83,94,97,*,
(1)(-14,11)14+,*,*,51+,40+,122,77,248,201,154,19+,50+,215,
25+,17+,163,*,427,157,43+,50+,*,*,*,45+,41+,(2)(-13,11)*,*,
6+,*,71,*,156,155,97,145,264,238,155,339,110,203,*,*,63+,
199,74,82,*,44+,43+,(3)(-13,10)*,39+,*,40+,19+,28+,41+,
357,14+,186,162,275,37+,350,31+,448,31+,155,*,22+,*,111,
44+,(4)(-13,10)10+,*,7+,*,43+,*,114,326,77,36+,245,93,402,
*,78,345,*,169,55+,19+,29+,40+,12+,141,(5)(-12,10)*,18+,
29+,62+,*,43+,*,202,96,196,250,105,174,112,43+,242,43+,
108,47+,17+,23+,36+,21+,(6)(-12,9)*,23+,39+,11+,42+,34+,
53+,105,*,136,56+,159,261,21+,82,42+,76,29+,43+,12+,28+,
(7)(-11,8)*,5+,*,35+,*,12+,*,113,66+,48+,*,*,43+,*,31+,
93,49+,46+,50+,30+,(8)(-10,7)15+,25+,22+,*,24+,27+,*,80,
21+,102,24+,63+,*,56+,10+,95,*,(9)(-8,6)7+,30+,34+,70+,
72,*,4+,148,69+,29+,*,*,45+,57+,33+,(10)(-6,4)24+,53+,*,
122,63+,40+,108,66+,95,30+,48+,(11)(-2,-1)19+,48+
 L=11 (K)(H)(1)(-13,10)12+,*,28+,*,29+,39+,130,220,*,49+,
255,66+,329,106,4+,122,111,99,142,*,10+,*,26+,*,
(2)(-13,10)*,20+,27+,12+,38+,117,100,285,109,51+,32+,110,
119,58+,146,138,165,125,172,85,45+,38+,*,36+,(3)(-13,10)*,
31+,47+,*,73,50+,49+,123,135,327,60+,30+,307,22+,219,21+,
223,133,121,18+,36+,20+,16+,36+,(4)(-12,9)15+,39+,34+,
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TABLE I (*Continued*)

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56+,93,62+,41+,254,161,186,89,175,147,124,109,99,114,*,
132,34+,31+,*,(5)(-12,9)20+,*,27+,*,14+,24+,74,*,164,116,
126,84,102,63+,42+,116,*,28+,100,28+,*,39+,(6)(-11,8)23+,*,
18+,23+,62+,52+,144,43+,203,102,18+,123,43+,56+,*,108,
25+,148,*,32+,(7)(-10,7)*,23+,*,*,38+,132,61+,32+,52+,
34+,33+,84,32+,*,96,*,74,15+,(8)(-9,6)31+,37+,22+,20+,*,
14+,106,36+,*,163,21+,*,24+,31+,80,*,(9)(-7,5)14+,21+,*,
93,40+,21+,128,26+,*,*,25+,87,92,(10)(-5,2)52+,46+,85,*,
43+,42+,82,67+
 L=12 (K)(H)(0)(-13,10)20+,*,15+,17+,33+,198,40+,*,90,185,
82,U,3+,197,124,115,56+,133,69+,52+,*,62+,25+,*,
(1)(-13,10)*,17+,*,5+,20+,*,170,153,122,161,293,27+,171,
44+,62+,55+,118,86,25+,33+,30+,56+,30+,*,(2)(-12,9)*,19+,
31+,16+,*,51+,83,19+,187,17+,39+,179,174,93,45+,94,28+,
72,*,27+,78,32+,(3)(-12,9)*,*,42+,*,124,23+,41+,87,*,152,
112,85,136,*,45+,61+,57+,37+,94,51+,89,35+,(4)(12,9)6+,*,
85,42+,60+,104,107,31+,50+,34+,110,237,209,37+,78,8+,*,
68+,139,75,62+,25+,(5)(-11,8)34+,*,67+,82+,52+,31+,53+,
71,89,74,66+,112,56+,112,75,68+,49+,35+,32+,33,
(6)(-10,7)49+,15+,*,39+,94,43+,135,*,30+,72,*,57+,78,*,
86,130,15+,33+,(7)(-9,6)*,24+,*,*,32+,*,38+,33+,176,50+,*,
70+,*,78,6+,39+,(8)(-8,5)9+,8+,22+,44+,48+,64+,87,31+,84,
15+,35+,7+,99,23+,(9)(-6,3)24+,*,69+,101,94,66+,42+,95,
88,47+,(10)(-3,-1)123,111,109
 L=13 (K)(H)(1)(-12,9)21+,24+,*,*,53+,92,34+,52+,82,28+,
67+,140,128,86,10+,94,15+,44+,19+,68+,47+,*,(2)(-12,9)*,
22+,36+,14+,62+,27+,45+,27+,134,52+,216,115,56+,*,*,11+,
28+,76,56+,40+,*,19+,(3)(-12,8)21+,27+,39+,56+,106+,11+,
76,19+,74,204,*,57+,111,90,26+,32+,*,124,19+,14+,40+,
(4)(-11,8)*,17+,11+,*,126,28+,58+,*,115,88,84,132,*,73,
66+,139,87,144,96,23+,(5)(-11,7)*,29+,*,*,70+,30+,40+,
8+,25+,37+,30+,38+,85,99,46+,67+,49+,130,13+,(6)(-10,6)
16+,21+,*,23+,86,129,80,85,*,49+,*,27+,94,44+,106,*,109,
(7)(-9,5)13+,*,27+,45+,*,*,*,*,87,106,89,9+,31+,110,10+,
(8)(-7,4)17+,*,*,63+,25+,124,23+,86,51+,25+,*,*,
(9)(-5,1)33+,29+,69+,102,19+,74,25+
 L=14 (K)(H)(0)(-11,8)*,*,25+,51+,42+,98,22+,161,57+,U,U,U,
56+,31+,46+,*,25+,51+,48+,32+,(1)(-11,8)36+,*,30+,21+,
61+,24+,57+,138,28+,75,138,49+,43+,12+,66+,49+,60+,53+,
21+,*,(2)(-11,8)8+,*,17+,18+,21+,13+,187,50+,136,158,122,
35+,64+,54+,35+,68+,53+,49+,*,17+,(3)(-11,7)14+,42+,*,
71+,78,57+,140,97,67+,39+,39+,46+,9+,49+,40+,70+,15+,127,*,
(4)(-10,7)31+,62+,8+,68+,59+,*,*,49+,*,28+,78,49+,118,
58+,97,212,34+,66+,(5)(-10,6)*,*,52+,*,18+,36+,47+,66+,*,
129,119,67+,104,115,33+,19+,44+,(6)(-9,5)19+,7+,*,24+,*,
8+,99,8+,84,*,132,*,67+,62+,29+,(7)(-7,4)32+,57+,*,*,48+,
13+,62+,*,124,72,89,*,(8)(-5,2)45+,*,132,24+,159,30+,77,44+
```

[a] The value of k and the range of h are given in parentheses. Unobserved reflections are indicated by an asterisk, reflections experimentally unobservable by a U, and reflections not used in refinement by a plus sign. F_{000} is on the arbitrary scale of the observed intensities and is summed over the entire unit cell. The scale factors are: 1.2003 for $0 \leq L \leq 10$; 1.1850 for $L = 11$; 1.1399 for $L = 12$; 1.1388 for $L = 13$; and 1.1791 for $L = 14$.

of $\sigma = 0.05F_o^2$ for $F_o^2 \geq 100$, with σ increasing linearly to $\sigma = 0.10F_o^2$ for $F_o^2 = 50$. Reflections for which $F_o^2 < 50$ were not included in the refinements.

Solution of the Structure

Two unsuccessful attempts were made to solve the structure from the c axis diffractometer data only. In the first attempt, the symmetry minimum function[5] was computed from the sharpened (average coefficients independent of sin θ) three-dimensional Patterson function. Several peaks separated by a B–B distance were found, but superposition on these trial atoms did not yield the structure after extensive investigation. In the second attempt the rotation–translation searching method[6,7] was used, but it was based upon the incorrect assumption from chemical studies[2] that the B_{20} arrangement was like that in $B_{20}H_{16}$. Intramolecular vectors computed from this B_{20} unit were used in a rotational search of the Patterson function, and the "best" rotational configurations were moved through the unit cell to find "best" translational positions. Two trial structures resulted, but electron density maps based on phases from these atoms failed to indicate the CH_3CN groups, and refinements were unsuccessful.

The correlation of these c-axis diffractometer data with the precession data then showed that there were three reflections which were in error because they had exceeded the counting capacity. No additional erroneous reflections were found after photographically recording all Weissenberg levels hkL for $0 \leq L \leq 12$. Probably the three overflow reflections played little or no role in the failure of the methods described above, because the new Patterson function computed from corrected and rescaled data was virtually identical with the earlier function.

The structure was solved by Sayre's direct method[8] for centrosymmetric space groups. The data were prepared by computation of normalized[9] structure factors

$$E_H^2 = F_H^2/(\epsilon \sum_{j=1}^{N} f_{jH}^2)$$

for all reflections for which $\rho = \sin^2 \theta/\lambda^2 \leq 0.30$, where F_H^2 has been corrected for thermal motion, N is the number of atoms per unit cell, $\epsilon = 2$ for $h0l$ and $0k0$ reflections, and $\epsilon = 1$ for all other reflections. The distribution of E's is shown in Table II.

TABLE II

DISTRIBUTION OF E's[a,b]

	Obsd	Theory
$\langle \lvert E \rvert \rangle$	0.777	0.798
$\langle E^2 \rangle$	1.000	1.000
$\langle \lvert E^2 - 1 \rvert \rangle$	0.998	0.968
$\lvert E \rvert \geqslant 3.0$	0.39%	0.3%
$\lvert E \rvert \geqslant 2.0$	4.7%	5.0%
$\lvert E \rvert \geqslant 1.0$	30.3%	32.0%

[a] $E_H^2 = F_H^2/\epsilon \sum_{j=1}^{N} f_{jH}^2$, where F_H^2 has been corrected for thermal motion, N is the number of atoms in the unit cell, $\epsilon = 2$ for $0k0$ and $h0l$ reflections, and $\epsilon = 1$ for all other reflections. [b] $\langle E^2 \rangle$ normalized to 1.000 by adjustment of the scale factor.

Sayre's equation was implemented by the multiple solution computer program of Long.[10] The signs of three reflections are chosen to fix the origin,[8b] and n additional signs are assumed in order to initiate phasing. Each of the 2^n solutions is iterated to self-consistency; *i.e.*, the phasing is continued until no new signs are determined and no signs change after a pass through the data. Long defines the consistency index

$$C = \frac{\langle \lvert E_H \sum_K E_K E_{H-K} \rvert \rangle}{\langle \lvert E_H \rvert \sum_K \lvert E_K \rvert \lvert E_{H-K} \rvert \rangle}$$

where the average is taken over all H. The correct solution is usually the one which has the largest C and

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(5) P. G. Simpson, R. D. Dobrott, and W. N. Lipscomb, *Acta Cryst.*, **18**, 169 (1965).

(6) C. E. Nordman and K. Nakatsu, *J. Am. Chem. Soc.*, **85**, 353 (1963).

(7) R. Lewin, Ph.D. Thesis, Harvard University, 1964.

(8) (a) D. Sayre, *Acta Cryst.*, **5**, 60 (1952); (b) M. M. Woolfson, "Direct Methods in Crystallography," Oxford University Press, London, 1961.

(9) I. L. Karle, K. Britts, and S. Brenner, *Acta Cryst.*, **17**, 1506 (1964).

(10) R. E. Long, Ph.D. Thesis, part III, UCLA, 1965.

requires the smallest number of cycles to reach self-consistency.

For the $B_{20}H_{16} \cdot 3CH_3CN$ data three origin-determining reflections and four assumed reflections were chosen internally by the program on the basis of large values of $|E_H| \sum_K |E_K||E_{H-K}|$. Then the 16 independent solutions were calculated from those 364 reflections for which $|E| \geq 1.5$. The highest consistency index, $C = 0.61$, was also a solution which required the smallest number (9) of cycles for phasing of all 364 reflections. All other solutions had C values less than 0.50, and only one of these required as few as nine cycles.

The E map computed from these 364 signs showed 29 peaks, ranging from 401 to 906 in arbitrary units, and showed all other regions in the range from 340 down to -432. A model of this structure showed that one CH_3CN of crystallization was present per molecule of $B_{20}H_{16}(NCCH_3)_2$. Careful examination of the E map suggested that one side of the B_{20} cage had a vacancy and that there were distortions from the B_{20} unit of $B_{20}H_{16}$ itself. An electron density map based upon 26 of the 29 atoms, omitting three questionable B atoms directly opposite this vacancy region, yielded all 29 peaks again, but somewhat more clearly because all 1081 reflections having $F_o^2 \geq 100$ were included. Further study of the model then showed clearly that a closed B_{12} icosahedron was sharing a triangular face with a B_{11} icosahedral fragment and that one CH_3CN ligand was covalently attached to each half of this fused-cage system.

All atoms of the CH_3CN of crystallization were given scattering factors of C, and a structure factor calculation based on 29 B, C, and N atoms gave $R = 0.196$ for the 1081 largest reflections. Two cycles of least-squares refinement of the atomic positions and one cycle of refinement of scale factors yielded $R = 0.153$. The bond distances of 1.26 and 0.99 A for the unbound CH_3CN indicated that the peak closest to the screw axis was the N atom. This atom also had the largest positive residual of the three in the difference electron density map calculated after the above refinement. This difference map contained 32 peaks ranging from 0.33 to 0.54 e A^{-3}, all of which were assigned to H atoms or heavy-atom residuals. Of the 15 terminal H atoms, 14 were found. In addition, a peak of 0.30 e A^{-3} occurred above the open pentagonal face of the B_{11} icosahedral fragment. Two cycles of isotropic refinement of all 29 B, C, and N atoms, with the parameters of the 14 H atoms fixed, gave $R = 0.102$. Another difference map from which all 43 B, C, N, and H atoms were subtracted yielded six peaks in the range 0.26–0.52 e A^{-3}. One peak was the remaining terminal hydrogen and a peak of 0.30 e A^{-3} again appeared above the open pentagonal face. All other peaks were residuals of atoms already assigned, so that we concluded that the peak over the open face was indeed an H atom, perhaps partially bridging, thus completing the molecule.

Further refinement was made anisotropically on C and N for two cycles of least squares after fixing the 20 B and 16 H atoms. Then all data with $F_o^2 \geq 50$ were included, and anisotropic refinement of all B, C, and N atoms was carried out in two sections, because of limitations of the program. First the closed icosahedron B_{12} unit and C_3, C_4, C_5, C_6, N_2, and N_3 were refined anisotropically, and then the open icosahedral fragment and C_1, C_2, C_5, C_6, N_1, and N_3 were refined anisotropically; in each case all other atoms were fixed. Then after one cycle of scale factor refinement the above sequence was repeated for a total of four anisotropic cycles, in which B_2, B_3, B_7, C_5, C_6, and N_3 were refined in all cycles. Next, H atoms were refined isotropically for two cycles. Finally, atomic coordinates of all atoms and the five scale factors were refined in one cycle, and the variance–covariance matrix for these parameters was obtained. The final value of R is 0.070 for the 1495 observed reflections (Table III). A final difference electron density map from which all B, C, N, and the 16 H atoms were subtracted showed no peak greater than 0.17 e A^{-3}, and only very diffuse regions around the CH_3 groups and the methyl H atoms could not be located. The value of R is 0.145 for all 3587 reflections of Table I, including those below the standard deviations of observation. No significant discrepancies occur, and these final results confirm that all 364 E values were indeed phased correctly.

TABLE III

VARIATION OF R WITH SIN θ[a]

Range of sin θ	R
0.00–0.40	0.082
0.40–0.50	0.055
0.50–0.60	0.056
0.60–0.65	0.060
0.65–0.70	0.070
0.70–0.75	0.082
0.80–0.85	0.083
0.85–0.90	0.110
0.90–1.00	0.087

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

Results and Discussion

The numbering scheme is shown in Figure 1. Also shown for comparison are $B_{20}H_{16}$ (Figure 2) and a proposed intermediate (Figure 3). The full molecule is shown in Figure 4, and the crystal structure is projected along b in Figure 5. Atomic coordinates in Tables IV and V yield the bond distances of Table VI and bond angles of Tables VII and VIII. Unfortunately, the individual deviations could not be computed from the full variance–covariance matrix, because of a limitation in total parameters, so that these individual deviations include only effects of coordinates and scale factors. For this reason, we call attention to the somewhat larger standard deviations for average bond distances and urge that they be used in any discussions of distances and angles.

The possible atypical nature of $B_{20}H_{16} \cdot 3CH_3CN$ as a triligand derivative of $B_{20}H_{16}$ has been clearly resolved

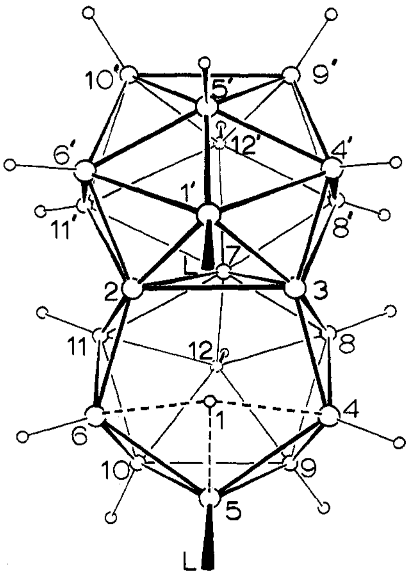

Figure 1.—The structure of $B_{20}H_{16}(NCCH_3)_2$. L is CH_3CN. Molecular symmetry is very nearly C_s with the C and N atoms of the CH_3CN groups lying in the mirror plane. See Figure 6 regarding the position of H_1.

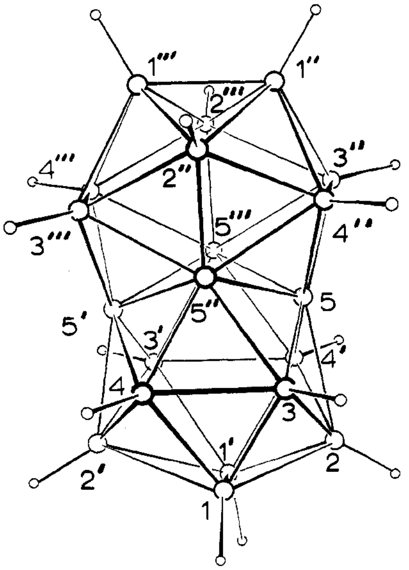

Figure 2.—Structure of $B_{20}H_{16}$.

into the diligand derivative $B_{20}H_{16}(NCCH_3)_2$ and an acetonitrile of crystallization. However, much more interesting is the rearrangement of the B_{20} cage of $B_{20}H_{16}$ (Figure 2) into a B_{12} icosahedron sharing a triangular face with a B_{11} icosahedral fragment (Figures 1, 4). This is the first example in boron hydride chemistry of two icosahedra (or fragments) sharing a face.

No molecular symmetry is required by the space group, but the isolated molecule shows distances (Table VI) very nearly indicating C_s symmetry, with the two CH_3CN units lying in the mirror plane. Moreover, if $B_{1'}$ is removed, the remaining B_{19} unit has nearly C_{2v} symmetry. Nevertheless, both cages show significant distortions from regular icosahedral symmetry. In particular, B_7–B_8, B_7–$B_{8'}$, B_7–B_{11}, and B_7–$B_{11'}$

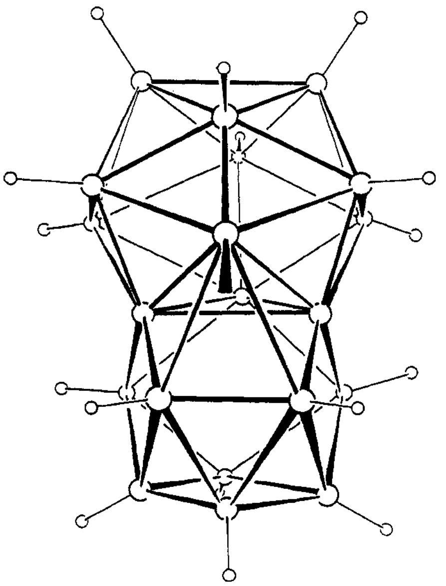

Figure 3.—Proposed cuboctahedron intermediate for the rearrangement of $B_{20}H_{16}$. Solid terminal line is CH_3CN.

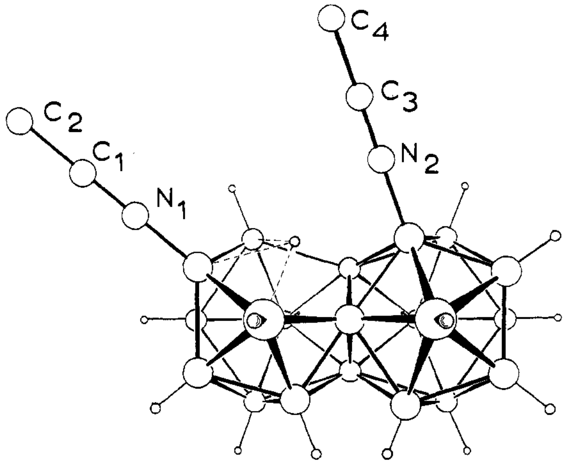

Figure 4.—The structure of $B_{20}H_{16}(NCCH_3)_2$ showing the CH_3CN groups. See Figure 6 regarding the position of H_1.

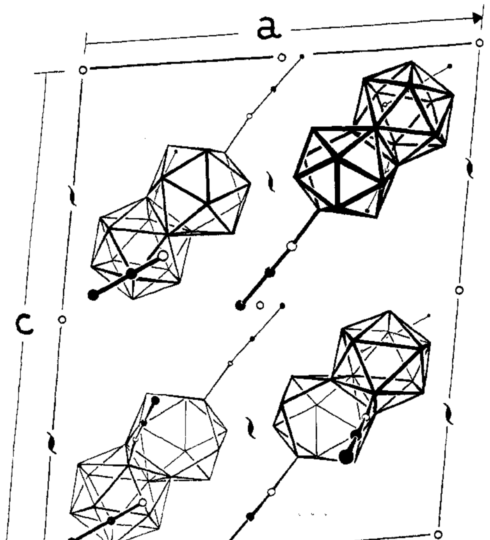

Figure 5.—Projection of the crystal structure along *b*. Solid circles are C; open circles are N.

TABLE IV

FINAL ATOMIC PARAMETERS FOR B, C, AND N ATOMS[a,b]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
$B_{1'}$	0.1969 (5)	0.2534 (5)	0.3073 (3)	79 (5)	64 (7)	33 (3)	−1 (5)	0 (4)	−2 (4)
B_2	0.1867 (4)	0.4040 (5)	0.2628 (3)	59 (5)	69 (5)	32 (3)	5 (4)	1 (3)	−4 (3)
B_3	0.3083 (5)	0.3538 (5)	0.3388 (3)	68 (5)	65 (5)	31 (3)	−3 (5)	0 (3)	−1 (3)
B_4	0.4265 (5)	0.3554 (5)	0.2908 (3)	70 (5)	72 (6)	33 (3)	4 (5)	0 (3)	1 (3)
$B_{4'}$	0.2594 (5)	0.2585 (5)	0.4143 (4)	77 (6)	81 (8)	29 (4)	4 (5)	−1 (4)	5 (4)
B_5	0.3750 (5)	0.3958 (6)	0.1838 (4)	76 (5)	94 (6)	27 (3)	0 (5)	11 (3)	−2 (3)
$B_{5'}$	0.1157 (6)	0.2472 (6)	0.3875 (4)	90 (6)	76 (8)	42 (4)	−8 (6)	5 (4)	7 (4)
B_6	0.2294 (5)	0.4335 (5)	0.1625 (4)	57 (5)	77 (6)	41 (3)	−4 (4)	1 (3)	12 (4)
$B_{6'}$	0.0712 (5)	0.3381 (5)	0.2958 (4)	65 (5)	75 (8)	46 (3)	−2 (5)	7 (3)	6 (4)
B_7	0.2520 (5)	0.5093 (5)	0.3422 (3)	64 (5)	72 (6)	35 (3)	6 (5)	1 (3)	0 (3)
B_8	0.4096 (5)	0.4859 (5)	0.3508 (4)	70 (5)	64 (6)	44 (3)	−5 (4)	3 (3)	−3 (3)
$B_{8'}$	0.2898 (5)	0.4144 (5)	0.4423 (4)	77 (5)	76 (7)	33 (3)	13 (5)	7 (3)	2 (4)
B_9	0.4438 (5)	0.5082 (5)	0.2529 (4)	86 (6)	70 (6)	35 (3)	4 (5)	2 (3)	−2 (3)
$B_{9'}$	0.1715 (6)	0.3498 (6)	0.4698 (4)	94 (6)	97 (8)	40 (4)	8 (6)	11 (4)	9 (5)
B_{10}	0.3303 (5)	0.5534 (6)	0.1780 (4)	74 (5)	87 (6)	34 (3)	−2 (5)	7 (3)	0 (4)
$B_{10'}$	0.0599 (8)	0.3963 (6)	0.3980 (4)	87 (6)	97 (8)	43 (4)	4 (6)	4 (4)	3 (5)
B_{11}	0.2156 (5)	0.5628 (6)	0.2261 (4)	77 (5)	81 (6)	38 (3)	−5 (5)	5 (3)	15 (4)
$B_{11'}$	0.0988 (5)	0.4962 (6)	0.3212 (4)	69 (6)	89 (8)	39 (4)	4 (6)	10 (4)	5 (4)
B_{12}	0.3394 (5)	0.6061 (5)	0.2868 (4)	81 (6)	55 (5)	42 (3)	0 (5)	0 (3)	2 (3)
$B_{12'}$	0.1699 (5)	0.5052 (6)	0.4269 (4)	88 (6)	84 (8)	42 (4)	16 (6)	8 (4)	3 (5)
C_1	0.4845 (5)	0.3118 (5)	0.0654 (3)	84 (5)	99 (6)	43 (3)	−14 (5)	−10 (4)	2 (4)
C_2	0.5482 (5)	0.2674 (6)	0.0030 (3)	105 (6)	154 (8)	38 (3)	−1 (6)	26 (4)	−21 (4)
C_3	0.2278 (4)	0.0522 (5)	0.2216 (3)	86 (6)	81 (6)	41 (3)	−11 (5)	−3 (3)	6 (4)
C_4	0.2508 (5)	−0.0622 (5)	0.1761 (3)	122 (7)	82 (7)	54 (4)	12 (6)	−4 (4)	−24 (4)
C_5[b]	0.8338 (7)	0.3806 (6)	0.0830 (4)	143 (9)	106 (8)	67 (5)	−39 (7)	−5 (5)	2 (5)
C_6[b]	0.9288 (7)	0.3547 (8)	0.0445 (5)	129 (8)	194 (11)	96 (5)	−11 (8)	52 (6)	−5 (6)
N_1	0.4345 (4)	0.3494 (4)	0.1149 (3)	76 (4)	98 (5)	34 (2)	−4 (4)	−1 (2)	−1 (3)
N_2	0.2116 (3)	0.1422 (4)	0.2552 (2)	78 (3)	65 (5)	43 (3)	−13 (4)	−3 (3)	−5 (3)
N_3[b]	0.7580 (6)	0.4026 (6)	0.1143 (4)	165 (9)	167 (9)	87 (5)	−52 (8)	24 (5)	−26 (5)

[a] x, y, and z are in fractional monoclinic coordinates. Thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. Standard deviation of the last significant figure is given in parentheses. [b] Atom is part of the CH_3CN of crystallization.

TABLE V

FINAL ATOMIC PARAMETERS FOR H ATOMS

Atom	x	y	x	β, A^2
H_1	0.294 (5)	0.316 (6)	0.198 (3)	5.5 ± 1.6
H_4	0.492 (3)	0.285 (4)	0.309 (3)	1.2 ± 0.8
$H_{4'}$	0.313 (4)	0.168 (4)	0.435 (3)	2.4 ± 1.0
$H_{5'}$	0.078 (5)	0.137 (5)	0.395 (3)	4.6 ± 1.5
H_6	0.171 (5)	0.418 (5)	0.096 (3)	3.9 ± 1.3
$H_{6'}$	−0.001 (5)	0.312 (5)	0.247 (3)	3.9 ± 1.4
H_8	0.472 (4)	0.498 (4)	0.413 (3)	3.1 ± 1.1
$H_{8'}$	0.361 (4)	0.436 (4)	0.486 (3)	2.6 ± 1.0
H_9	0.531 (5)	0.551 (6)	0.240 (4)	5.8 ± 1.7
$H_{9'}$	0.156 (4)	0.328 (5)	0.540 (3)	3.5 ± 1.4
H_{10}	0.343 (4)	0.628 (5)	0.123 (3)	3.9 ± 1.4
$H_{10'}$	−0.022 (4)	0.419 (5)	0.419 (4)	3.4 ± 1.2
H_{11}	0.142 (4)	0.626 (5)	0.206 (3)	3.4 ± 1.2
$H_{11'}$	0.050 (4)	0.580 (5)	0.291 (3)	3.1 ± 1.1
H_{12}	0.356 (4)	0.700 (5)	0.304 (3)	3.4 ± 1.3
$H_{12'}$	0.170 (5)	0.595 (5)	0.461 (4)	4.9 ± 1.7

at 1.93 ± 0.04 A are considerably longer, and B_7–B_{12} and B_7–$B_{12'}$ at 1.84 ± 0.01 A are somewhat longer than the 1.77 A found in $B_{12}H_{12}^{2-}$ ion.[11] In association with these distortions we find the interestingly short H···H distances of 2.04 ± 0.06 A for the interactions $H_{11}\cdots H_{11'}$ and $H_8\cdots H_{8'}$. These distances are considerably less than the 2.4 A expected for van der Waals contacts[12] but are not completely unknown among boron hydrides.[13] These H···H contacts would be only 1.6 A if we assumed two regular icosahedra with B–B = 1.77 A and B–H = 1.2 A; also in such an idealized molecule the $B_8\cdots B_{8'}$ and $B_{11}\cdots B_{11'}$ contacts would also be short, about 2.0 A, which is comparable with the "long bond" of 2.01 A in $B_{10}H_{14}$.[14] In the actual $B_{20}H_{16}(NCCH_3)_2$ molecule the $B_8\cdots B_{8'}$ and $B_{11}\cdots B_{11'}$ distances are 2.40 A, so that *both* the B···B and H···H distances are increased by about 0.4 A from the values for an idealized B_{20} polyhedron. The H–B–B angles are reasonably normal, and no systematic variations seem to be present.

Other distances and bond angles are close to expected values. The average B–N distance of 1.50 ± 0.02 A compares well with the 1.523 A distance in $B_{10}H_{12}(NCCH_3)_2$.[13] All of the CH_3CN units are nearly linear, with an average CN distance of 1.16 ± 0.02 A and an average C–C distance of 1.47 ± 0.01 A in accord with 1.15 and 1.46 A, respectively, in the free molecule.[15]

The position of the H atom which is over the open pentagonal face of the molecule is not completely certain. No H_2 is evolved in the reaction. Moreover, there is no other reasonable place for the last H, and this atom appeared at a reasonable density in two successive difference electron density maps. The final individual bond distances of B_2–H_1 = 2.07, B_3–H_1 =

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TABLE VI

BOND DISTANCES (A)[a,b]

Bond	Dist	Av dist
B–B		
1′–5′	1.78 (1)	. . .
1′–4′	1.77	1.79 (2)
1′–6′	1.80	
1′–2	1.76	1.76 (1)
1′–3	1.77	
2–6	1.81	1.79 (2)
2–6′	1.77	
3–4	1.79	
3–4′	1.77	
2–3	1.87 (1)	. . .
2–11	1.86	1.86 (2)
2–11′	1.85	
3–8	1.89	
3–8′	1.84	
2–7	1.80	1.80 (1)
3–7	1.81	
4–8	1.73	1.75 (1)
4′–8′	1.75	
6–11	1.75	
6′–11′	1.76	
4–9	1.77	1.79 (2)
4′–9′	1.82	
6–10	1.79	
6′–10′	1.79	
4–5	1.79	1.80 (3)
4′–5	1.79	
5–6	1.85	
5′–6′	1.78	
5–9	1.76	1.77 (1)
5′–9′	1.77	
5–10	1.77	
5′–10′	1.76	
7–8	1.98	1.93 (4)
7–8′	1.90	
7–11	1.94	
7–11′	1.90	
7–12	1.84	1.84 (1)
7–12′	1.84	
8–12	1.79	1.77 (2)
8′–12′	1.77	
11–12	1.75	
11′–12′	1.79	
9–10	1.77	1.75 (3)
9′–10′	1.73	
9–12	1.83	1.81 (2)
9′–12′	1.80	
10–12	1.83	
10′–12′	1.81	
B–N		
1′–2	1.49	1.50 (2)
5–1	1.52	
C–N		
1–1	1.17	1.16 (2)
3–2	1.14	
5–3	1.17	
C–C		
1–2	1.46	1.47 (1)
3–4	1.48	
5–6	1.46	
B–H		
4–1	1.56	1.82 (37)
6–1	2.08	
5–1	1.38 (6)	. . .
B–H		
4–4	1.12	1.16 (6)
4′–4′	1.19	
5′–5′	1.28	
6–6	1.21	
6′–6′	1.13	
8–8	1.18	
9–9	1.23	
9′–9′	1.21	
10–10	1.22	
10′–10′	1.16	
11–11	1.15	
11′–11′	1.15	
12–12	1.06	
12′–12′	1.11	
2–1	2.07	2.18 (14)
3–1	2.28	

[a] Standard deviations for individual bonds computed from the variance–covariance matrix associated with the final atomic coordinates are: $\sigma_{B-B} = 0.008$–0.010; $\sigma_{B-N} = 0.008$; $\sigma_{C-N} = 0.006$–0.011; $\sigma_{C-C} = 0.008$; $\sigma_{B-H} = 0.04$–0.06 A. [b] Average distances are for chemically equivalent bonds, assuming C_{2v} symmetry for two fused B_{11} icosahedral fragments. Standard deviations for the average bond distances are given in parentheses and were computed by applying the equation

$$\sigma_{av} = \left(\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1} \right)^{1/2}$$

σ_{av} is never allowed to be less than the maximum standard deviation of individual bonds within the group.

2.28, B_4–H_1 = 2.08, B_5–H_1 = 1.38, and B_6–H_1 = 1.56 A suggest that H_1 is most strongly associated with B_5, and somewhat strongly with B_6, with lesser association with the other atoms of the pentagonal face. If, on the other hand the isolated molecule really does have C_s symmetry, then the distances are B_5–H_1 = 1.38 ± 0.06, B_4–H_1 = B_6–H_1 = 1.82 ± 0.37, and, finally, B_2–H_1 = B_3–H_1 = 2.18 ± 0.14 A. Hence, we conclude that H_1 is associated primarily with the B_4, B_5, B_6 end of the face, and probably most strongly with B_5, but

TABLE VII

B–B–B BOND ANGLES (DEG)[a]

Atoms	Angle	Av
2–1′–3	64.0 (3)	. . .
2–1′–6′	59.7	59.9 (6)
3–1′–4′	60.1	
5–1′–6′	59.6	60.0 (6)
4′–1′–5′	60.5	
7–2–3	59.2	58.8 (6)
7–3–2	58.4	
7–2–11	64.1	63.5 (10)
7–2–11′	62.8	
7–3–8	64.5	
7–3–8′	62.6	
6–2–11	56.9	57.3 (10)
6′–2–11′	58.1	
4–3–8	56.1	
4′–3–8′	58.0	
1′–2–3	58.2	58.0 (3)
1′–3–2	57.8	
3–4–8	64.9	63.4 (10)
3–4′–8′	62.9	
2–6–11	62.7	
2–6′–11′	63.1	
8–4–9	58.8	59.2 (4)
8′–4′–9′	59.0	
10–6–11	59.2	
10′-6′-11′	59.7	
5–4–9	59.3	59.0 (4)
5′–4′–9′	59.0	
5–6–10	58.4	
5′–6′–10′	59.2	
4–5–9	59.8	60.3 (9)
4′–5′–9′	61.4	
6–5–10	59.2	
6′–5′–10′	60.7	
9–5–10	60.1	59.4 (10)
9′–5′–10′	58.7	
8–7–12	55.6	56.1 (8)
8′–7–12′	56.5	
11–7–12	55.2	
11′–7–12′	57.0	
8–12–9	56.8	58.2 (10)
8′–12′–9′	59.0	
10–12–11	58.4	
10′–12′–11′	58.8	
3–2–6	107.7	109.4 (13)
2–3–4	111.0	
2–7–3	62.4 (3)	. . .
3–8–7	55.9	56.9 (9)
3–8′–7	58.0	
2–11–7	56.5	
2–11′–7	57.2	
7–8–12	58.5	59.6 (8)
7–8′–12′	60.2	
7–11–12	59.8	
7–11′–12′	59.9	
9–8–12	62.9	62.0 (10)
9′–8′–12′	61.2	
10–11–12	62.9	
10′–11′–12′	61.1	
4–8–9	61.7	61.6 (5)
4′–8′–9′	62.3	
6–11–10	61.6	
6′–11′–10′	60.9	
3–8–4	58.9	59.3 (7)
3–8′–4′	59.1	
2–11–6	60.4	
2–11′–6′	58.8	
4–9–8	59.4	59.2 (3)
4′–9′–8′	58.7	
6–10–11	59.2	
6′–10′–11′	59.4	
8–9–12	60.3	59.7 (7)
8′–9′–12′	59.7	
11–10–12	58.7	
11′–10′–12′	60.1	
10–9–12	60.9	61.1 (3)
10′–9′–12′	61.5	
9–10–12	61.1	
9′–10′–12′	61.0	
5–9–10	60.2	60.3 (4)
5′–9′–10′	60.3	
5–9–10	59.6	
5′–10′–9′	61.0	
4–9–5	60.8	60.8 (12)
4′–9′–5′	59.7	
5–10–6	62.4	
5′–10′–6′	60.1	
7–12–8	65.9	64.4 (14)
7–12′–8′	63.3	
7–12–11	65.1	
7–12′–11′	63.0	
9–12–10	58.0	57.8 (4)[b]
9′–12′–10′	57.5	
2–6–5	103.2	103.2 (4)[b]
3–4–5	103.2	
4–5–6	114.7 (4)	. . .

[a] Standard deviations for individual bond angles are $\sigma_{B-B-B} = 0.3$–$0.4°$. [b] Standard deviation set equal to the maximum standard deviation of individual bond angles in the group.

TABLE VIII

AVERAGE BOND ANGLES (DEG)

No. of measurements	Atoms	Largest	Av	Smallest	Std dev
9	B–B–N	122.3	119.7	115.8	2.0
2	B–N–C	176.4	175.2	173.9	1.8
3	C–C–N	179.3	178.7	178.1	0.6
73	B–B–H	131.5	121.6	111.5	4.4

its position in relation to B_4 and B_6 is quite uncertain. These conclusions from the distances are confirmed by a three-dimensional electron density difference map in which all B, C, and N and 15 terminal H atoms have been subtracted. The section of electron density through the maximum of H_1 in a plane parallel to that of the open pentagonal face (Figure 6) shows that H_1 is definitely nearer the B_5 end of the face, but, with its coordinate in the $B_4 \cdots B_6$ direction somewhat uncertain, possibly even disordered. Movement of H_1 to a point midway between B_4 and B_6, but still at a distance of 1.38 A from B_5, followed by two cycles of least-squares refinement resulted in the movement of H_1 to the final position found earlier. However, refinement of such a small percentage of the scattering matter of a structure can be misleading.[16]

No unusual intermolecular contacts occur in the crystal. The $B_{20}H_{16}(NCCH_3)_2$ molecules lie primarily in the (202) plane, while the CH_3CN of crystallization fit into holes of the crystal structure (Figure 5).

We turn now to the relation of this structure to other parts of boron chemistry. The conceptual replacement of a ligand, such as acetonitrile, by H^- has many analogies[1a] among known derivatives and boron hydride ions. Such an analogy in $B_{20}H_{16}(NCCH_3)_2$ would predict two isomers of $B_{20}H_{17}(NCCH_3)^-$ and would suggest a new boron hydride ion, $B_{20}H_{18}^{2-}$, with a structure different from the known ion of this formula.[17] Another structural analogy, in which the presumed[18] bridging H^- of $B_9C_2H_{12}^-$ is conceptually replaced by BH to give the icosahedral carborane $B_{10}C_2H_{12}$, can be applied to $B_{20}H_{18}^{2-}$ to predict the completed polyhedron of the formula $B_{21}H_{18}^-$. Use of CH^+ in place of BH in this analogy predicts the neutral carborane $B_{20}CH_{18}$. A third extrapolation continues the triangular B_3 joining: consider that $B_{21}H_{18}^-$ is formed conceptually from $B_{12}H_{12}^{2-} + B_9H_6^+$ and then continue the procedure with $B_{21}H_{18}^- + B_9H_6^+$ to give $B_{30}H_{24}$, a neutral boron hydride composed of three icosahedra which share two trianglular faces. Three isomers are possible, but there are severe $H \cdots H$ interactions in joining polyhedra, as discussed above. $B_{20}H_{16}(NCCH_3)_2$ has two short $H \cdots H$ interactions, but $B_{21}H_{18}^-$ would have three, and $B_{30}H_{24}$ would have six. Of course, it is not easily predictable where these interactions would limit stability.

As there is no official nomenclature for boron hydrides composed of icosahedra sharing a triangular face, we have proposed[3] that such compounds be generally called polyicosahedral boranes and that the compound $B_{20}H_{16}(NCCH_3)_2$ be named as an ollyl[18a] derivative of the unknown diicosahedral ion, $B_{21}H_{18}^-$, described above. We therefore suggest the name (1)-1′,5-bisacetonitrileollyldiicosahedralborane for $B_{20}H_{16}(NCCH_3)_2$.

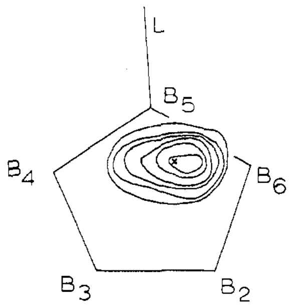

Figure 6.—Projection of the section of maximum electron density through H_1 onto the open pentagonal face, indicating that H_1 is nearer the B_5 end of the face and that H_1 may be disordered between B_4 and B_6. Contours start at 0.125 e A^{-3} and are at intervals of 0.042 e A^{-3}. × is the position of H_1 after final refinement.

Although not necessarily unique, a mechanism combining least motion with the cuboctahedron mechanism[1a] yields a very simple account of the rearrangement of $B_{20}H_{16}$: (a) let the first CH_3CN add at B_5'' (see Figure 2), (b) form a B_5–B_5' bond, (c) apply the dsd mechanism[1a,4] to the faces 5′ 4 2′ 3′, 5‴ 3′ 1′ 4′, 5 3 2 4′, and 1 2′ 1′ 2, (d) break B_4–B_5'', $B_{3'}$–B_5'', and B_3–B_4, (e) move H_1 into the open bridging position, and (f) add the second CH_3CN to B_1. The proposed cuboctahedron intermediate is shown in Figure 3. Of course, we cannot be sure at which stage the second CH_3CN is added, but the other steps are built around the probable mechanism[1a] for the rearrangement of o-$B_{10}C_2H_{12}$ to m-$B_{10}C_2H_{12}$. In addition, a mechanism initiated by nucleophilic attack at a belt B is favored by molecular orbital calculations,[19–21] which indicate that the belt B atoms are considerably more positive than the other B atoms.

The question of the generality of the framework rearrangement observed in the reaction of $B_{20}H_{16}$ with CH_3CN requires further study. In $B_{10}H_{14}$ chemistry only $(CH_3)_2S$ is a weaker nucleophile than CH_3CN.[22] Assuming the same basic strength is exhibited toward other boranes, it appears that a milder reaction, which may not cause framework rearrangement, is the reaction between $B_{20}H_{16}$ and $(CH_3)_2S$. We have carried out this reaction, which has been independently reported,[2b] and preliminary crystallographic studies[23] indicate the formulation $B_{20}H_{16}[S(CH_3)_2]_2$ for the reaction product. The ^{11}B nmr spectrum of $B_{20}H_{16}[S(CH_3)_2]_2$ is virtually identical with that of $B_{20}H_{16}(NCCH_3)_2 \cdot CH_3CN$, which suggests that framework rearrangement does occur in this system as well and thus is probably a general feature of $B_{20}H_{16}$ chemistry. However, any definite generalization must await the com-

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(19) Neglecting zero overlap,[20] $B_1 = B_2 = -0.11$, $B_3 = B_4 = -0.05$, $B_5 = +0.36$.[21] Using slightly different molecular orbital parameters,[20] $B_1 = B_2 = -0.13$, $B_3 = B_4 = -0.09$, $B_5 = +0.42$. If zero overlap[20] is included and the molecular orbital parameters of ref 21 are used, $B_1 = B_2 = +0.02$, $B_3 = B_4 = -0.04$, $B_5 = +0.93$.

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