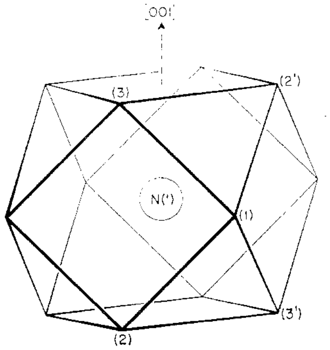

Figure 3.—A perspective view of the distribution of sulfur atoms around an ammonium ion, identifying the [001] direction. The sulfur atoms are located at the vertices of the slightly distorted cuboctahedron.

alent values of 3.48 (3) Å. In addition, there are two sets of four equivalent distances at the larger values of 3.68 (3) and 3.82 (3) Å. While the shortest N–S distance suggests the possibility of N–H···S hydrogen bonds,[17] the angular distribution of these sulfur atoms about the ammonium ion is not favorable for their formation. The larger N–S distances are somewhat greater than the sum of the van der Waals radii of sulfur and nitrogen.[16] The four sulfur atoms nearest any nitrogen lie 0.10 Å in the [001] direction from the corners of a square, the plane of which is parallel to (001) and contains the nitrogen atom. These four sulfur atoms and the other eight can be considered as residing at the vertices of an approximate cuboctahedron which is slightly elongated in the *c* direction and surrounds the ammonium ion, as shown in Figure 3. The cuboctahedra and the tetrahedra share edges only, giving rise to open packing of polyhedra in this structure.[18]

The corresponding tungstate could not be prepared using any of the methods mentioned above. Neither could a nickel, cobalt, or silver ammonium thiomolybdate be obtained. Attempts were made to prepare a cuprous sodium or potassium thiomolybdate using method iii. Sodium or potassium thiomolybdate solutions were prepared by passage of hydrogen sulfide into a solution of molybdenum trioxide in caustic soda or potash. To these were added freshly precipitated cupric sulfide; a deeply colored liquid resulted. Acidification to pH 5 gave a reddish precipitate, difficult to filter, as reported by Debray.[2] The phases present in these precipitates could not be identified by X-ray diffraction due to poor crystallinity. Chemical analysis was not meaningful as the precipitates could not be washed well. Reduction of the cupric copper had probably taken place in the dissolution process. This does not appear to be the case when a 5% excess of cupric sulfate solution is added to ammonium thiomolybdate solution to form a black precipitate. Clark and Doyle[5] showed that this was not cupric thiomolybdate, $CuMoS_4$, as thought by Berzelius[19] but presumably a mixture of molybdenum and cupric sulfides. An unreported and unexplained event in this precipitation is that the pH drops to a final value of 2.0.

Acknowledgments.—We wish to thank Dr. W. W. Harvey for helpful discussions, Dr. R. H. Duff for taking the electron diffraction plates, J. R. Carter for assistance with the measurement of X-ray films, and S. I. Andersen for help with the chemical analysis.

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The Crystal and Molecular Structure of Hexadecaborane(20)

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Received June 30, 1969

The boron hydride hexadecaborane(20), $B_{16}H_{20}$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 5.849$ (9), $b = 13.67$ (2), $c = 16.75$ (3) Å, $\beta = 100.83$ (5)°, $Z = 4$, and $\rho_{calcd} = 0.975$ g/cm^3. The $B_{16}H_{20}$ molecule may be described as an unsymmetrical fusion of a B_{10} icosahedral fragment with a B_8 icosahedral fragment in which the component fragments open in opposite directions and, as such, is the first example of a neutral boron hydride without molecular symmetry. The structure was solved by direct methods and refined by least squares to a conventional R factor of 5.4% for 1095 reflections which were collected by counter methods. Mechanisms for the formation of $B_{16}H_{20}$, chemical properties of $B_{16}H_{20}$, and possible new fused fragment boron hydrides are discussed.

Introduction

The structures of 12 neutral boron hydrides have been determined[2] previously, and in ten of these compounds (all but B_5H_9 and $B_{10}H_{16}$) the boron atoms are arranged such that the frameworks, or portions thereof,

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(2) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963; (b) R. M. Adams in "Boron, Metallo-Boron Compounds and Boranes," Interscience Publishers, New York, N. Y., 1964; (c) M. F. Hawthorne in "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1967.

may be regarded as fragments of an icosahedron. Two of the ten icosahedral fragment boranes may be described as fusions of other simpler icosahedral fragment boranes; n-$B_{18}H_{22}$ and i-$B_{18}H_{22}$ each consist[3] of two $B_{10}H_{14}$ fragments[4] which open in opposite directions and which share a common edge. The $B_{20}H_{16}$ molecule, which consists[5] of two $B_{10}H_{14}$ fragments joined together across the open face of each fragment, is not a fusion of simpler boranes in the same sense as is n-$B_{18}H_{22}$ or i-$B_{18}H_{22}$. We report here[6] the details of an X-ray diffraction study of hexadecaborane(20), $B_{16}H_{20}$, and show that the structure of this new borane may be regarded as a fusion of a $B_{10}H_{14}$ fragment with a B_8H_{12} fragment[7] in such a way that the component fragments open in opposite directions and share a common edge.

Experimental Section

Hexadecaborane(20), $B_{16}H_{20}$, was recently prepared[8] by the pyrolysis of $B_9H_{13}S(CH_3)_2$. A small sample of $B_{16}H_{20}$ was supplied by Dr. Jaromir Plešek and Dr. Stanislav Heřmánek of the Institute of Inorganic Chemistry, Prague-Rez, Czechoslovakia, and small, needlelike single crystals were grown by sublimation. Weissenberg photographs of $0kl$, $1kl$, and $2kl$ layers and precession photographs of $h0l$, $h1l$, $hk0$, $hk1$, and $hk2$ layers, all taken with Mo Kα radiation, showed reciprocal lattice symmetry C_{2h} and systematic absences of l odd for $h0l$ and of k odd for $0k0$, consistent with space group $P2_1/c$ (C_{2h}^5). The lattice constants of $a = 5.849$ (9), $b = 13.67$ (2), $c = 16.75$ (3) Å, and $\beta = 100.83$ (5)° were determined by least-squares refinement of the angular settings of 16 reflections which had been centered on a Picker automatic X-ray diffractometer using standard procedures.[9] The measurements were made at 22° with Mo Kα radiation (λ 0.70926 Å), and a local version of the program PICK2 was used[10] for the least-squares calculations. A density of 0.975 g/cm³ was calculated from the assumption that four molecules occupy the unit cell. This value is in reasonable agreement with experimental measurements (flotation technique) which bracket the density between 0.94 and 1.00 g/cm³. The high solubility of the compound and the limited amount of sample precluded a more accurate density determination. There is one molecule of $B_{16}H_{20}$ in the asymmetric unit, and no molecular symmetry is demanded by the space group.

The intensity data were collected from a crystal of approximate dimensions[11] 0.5 × 0.5 × 1.0 mm (1.0-mm dimension parallel to a) which was sealed in a thin-walled glass capillary and mounted with the a axis approximately coincident with the ϕ axis of the Picker four-circle diffractometer. The moving crystal–moving counter technique was used with a scan rate of 1°/min and a scan range of 1.00° in 2θ (0.40 less and 0.60 greater than the calculated 2θ value). All scans were recorded on a strip chart, and periodic inspection of the tracings indicated that the peaks were properly centered. Background counts of 10 sec were taken at each end of the scan range. Mo Kα radiation was used and the diffracted beams were filtered through Zr foil. The scintillation counter had an aperture of 3.5 × 5.0 mm and was 31.5 cm from the crystal. The takeoff angle was set to 2°, and the pulse height analyzer was set to admit 90% of the Mo Kα peak. Essentially all reflections of significant intensity were below $2\theta = 35°$. Two symmetry-related quadrants of reciprocal space, ($\pm h$, $+k$, $+l$) and ($\pm h$, $+k$, $-l$), were measured in the range $0 < 2\theta < 35°$, and the former quadrant was also explored for $35° < 2\theta < 50°$.

Throughout the data collection the intensities of five standard reflections in diverse regions of reciprocal space were measured at approximately 2-hr intervals. During the first 7 days of measurement the intensities of these reflections did not change noticeably; however there was a uniform decrease in intensity of approximately 3% during the last 3 days of measurement. All data collected during this latter period were corrected by assuming that the decrease was a linear function of elapsed time. After measurements were completed the most intense reflections were rechecked to see if any had exceeded the linear counting capacity. Three such reflections (012, 110, 102) were found and after attenuator calibration with less intense reflections, intensities of these three were corrected.

Approximately 1800 of the 2500 observations represented unique data points, and, after Lorentz and polarization corrections were made,[12] 1046 of the unique reflections had $F_o^2 > 2.5\sigma(F_o^2)$, where σ was defined[13] as

$$\left[\left(C + \frac{60}{20}(B_1 + B_2)\right) + (0.03)^2 \times \left(C - \frac{60}{20}(B_1 + B_2)\right)^2\right]^{1/2}$$

where C is the total integrated counts during the 60-sec scan, and B_1 and B_2 are background counts during the two 10-sec background measurements. These 1046 data were used for the solution of the structure and preliminary refinement and were merged with the reflections with $F_o^2 > 2.5\sigma(F_o^2)$ from the symmetry-related quadrant for the final refinement procedures.

Absorption by crystals of $B_{16}H_{20}$ is insignificant; the linear absorption coefficient is 0.384 cm^{-1} for Mo Kα radiation, and transmission factors for the minimum and maximum possible path lengths are 0.980 and 0.954, respectively.

Solution of the Structure and Refinement

The structure was solved by Sayre's method[14] using programs which had been modified locally for use on the IBM 360 computer. The normalized structure factors

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

were calculated with the program NORMAL[15] for reflections with $\rho = (\sin^2\theta)/\lambda^2 \leq 0.30$, where F_H^2 has been corrected for thermal motion, $\epsilon = 2$ for $0k0$ and $h0l$, and $\epsilon = 1$ for all other reflections in space group

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[3] (a) P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 26 (1963); (b) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *ibid.*, **39**, 2339 (1963).

[4] (a) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, **3**, 436 (1950); (b) C. M. Lucht, *J. Amer. Chem. Soc.*, **73**, 2373 (1951); (c) E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 209 (1957); (d) A. Tippe and W. C. Hamilton, *Inorg. Chem.*, **8**, 464 (1969).

[5] R. D. Dobrott, L. B. Friedman, and W. N. Lipscomb, *J. Chem. Phys.*, **40**, 866 (1964).

[6] A preliminary account of this work has been reported previously: L. B. Friedman, R. E. Cook, and M. D. Glick, *J. Amer. Chem. Soc.*, **90**, 6862 (1968).

[7] R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1659 (1964).

[8] J. Plešek, S. Heřmánek, B. Štíbr, and F. Hanousek, *Collect. Czech. Chem. Commun.*, **32**, 1095 (1967); **33**, 699 (1968).

[9] T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

[10] PICK2, J. A. Ibers' least-squares program for crystal lattice constants and orientations based on W. C. Hamilton's MODE1.

[11] A referee has pointed out the potential error associated with the use of such a large crystal. However, only a few milligrams of sample was available, and since the stability of the compound was uncertain, we chose to collect the data from the first reasonably good crystal which could be prepared. The rather large uncertainties in the cell dimensions may be due, in part, to the large size of the crystal.

[12] DACOR, a program for making Lorentz and polarization corrections, calculating intensity standard deviations, and merging data.

[13] The local program DACOR calculates a σ similar to, but not identical with, that described by P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[14] D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).

[15] NORMAL, a program for calculating normalized structure factors, which originated at Harvard University.

TABLE I

DISTRIBUTION OF E's[a,b]

	Obsd	Theory (centric)
$\langle\|E\|\rangle$	0.869	0.798
$\langle E^2\rangle$	1.000	1.000
$\langle\|E^2 - 1\|\rangle$	0.813	0.968
$\|E\| \geq 3.0$	0.20%	0.3%
$\|E\| \geq 2.0$	3.6%	5.0%
$\|E\| \geq 1.0$	31.5%	32.0%

[a] $E_H^2 = F_H^2/(\epsilon\Sigma_{j=1}^{N}f_{jH}^2)$, 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.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $B_{16}H_{20}$[a]

H= 0,K= 0

L	FO	FC
2	34	34
4	378	383
8	110	112
10	59	64
12	172	175
16	60	73

H= 0,K= 1

L	FO	FC
1	184	183
2	733	759
3	604	613
4	129	134
5	28	8
6	106	103
7	32	33
8	46	35
10	106	109
11	71	72
13	77	81
14	36	31
17	68	61

H= 0,K= 2

L	FO	FC
0	181	182
1	528	522
2	637	639
3	260	279
4	216	211
5	81	75
6	264	254
7	93	86
8	81	81
9	168	166
10	40	38
11	83	84
12	121	125
13	96	93
16	55	56

H= 0,K= 3

L	FO	FC
1	261	258
2	57	55
4	329	318
6	201	197
7	33	24
9	205	206
11	79	80
15	33	29

H= 0,K= 4

L	FO	FC
0	123	128
1	232	225
2	214	212
5	148	147
6	183	179
7	298	298
8	56	55
9	48	39
10	86	85
11	31	19
12	75	81
15	64	64

H= 0,K= 5

L	FO	FC
1	261	258
2	120	116
3	102	101
4	45	46
5	79	76
6	69	63
7	154	156
8	180	179
9	93	96
10	30	16
11	42	33
12	76	79
13	94	96
14	33	28

H= 0,K= 6

L	FO	FC
0	376	364
1	141	135
2	138	132
3	39	36
4	71	75
5	31	38
6	95	102
7	61	64
8	84	88
9	108	114
10	229	235
11	46	44
12	54	50
13	49	46
14	40	34

H= 0,K= 7

L	FO	FC
1	118	118
2	31	25
4	72	77
5	149	152
6	122	129
7	183	183
8	86	86
9	123	125
10	40	35
11	38	41
12	60	66
13	56	64
15	35	37

H= 0,K= 8

L	FO	FC
0	156	158
1	138	138
2	60	60
3	48	49
4	116	117
5	146	156
6	100	106
7	141	138
8	40	42
9	34	21
12	75	76

H= 0,K= 9

L	FO	FC
1	139	141
2	131	137
4	127	129
5	59	53
6	112	115
7	83	81
8	45	47
9	109	113
11	44	40
12	63	64
13	45	42
14	67	57

H= 0,K= 10

L	FO	FC
0	218	217
3	84	90
4	59	55
7	83	84
10	60	56

H= 0,K= 11

L	FO	FC
1	101	102
3	74	77
4	52	56
7	34	32
8	64	59
11	74	60

H= 0,K= 12

L	FO	FC
3	94	94
4	36	34
5	45	44
6	84	72
8	64	60
9	85	76

H= 0,K= 13

L	FO	FC
1	45	48
4	69	67
5	49	59
6	50	43

H= 0,K= 14

L	FO	FC
2	52	44
4	83	94
5	60	48

H= 1,K= 0

L	FO	FC
-14	47	51
-12	99	101
-10	93	105
-8	41	45
-4	424	417
-2	161	170
0	496	491
2	1034	1063
6	83	80
8	104	106
10	154	166
14	53	67
16	72	69
18	43	36

H= 1,K= 1

L	FO	FC
-14	44	39
-13	77	76
-12	59	55
-11	72	75
-10	85	83
-8	106	102
-7	116	109
-5	84	87
-4	430	417
-3	318	329
-2	292	300
-1	537	558
0	906	939
1	284	286
2	273	268
3	28	29
4	23	7
5	81	81
7	122	121
8	198	197
9	103	104
10	55	65
11	30	17
12	184	195
13	89	85
14	32	35
16	63	60
17	42	33
18	58	49

H= 1,K= 2

L	FO	FC
-16	51	45
-13	119	117
-12	61	63
-11	82	85
-10	70	71
-9	28	21
-7	109	111
-6	59	57
-5	36	32
-4	24	19
-3	24	13
-2	69	66
-1	512	512
0	305	296
1	245	250
2	26	27
3	112	112
4	146	144
5	259	249
6	255	246
7	180	175
8	83	75
10	60	61
12	171	174
13	90	91
14	77	73
15	36	39
16	68	61
17	36	29

H= 1,K= 3

L	FO	FC
-13	35	25
-11	64	60
-9	88	91
-8	153	161
-6	136	130
-5	64	61
-4	78	76
-3	107	111
-2	109	107
-1	47	55
0	223	219
1	128	127
2	211	209
3	73	71
4	93	90
5	165	162
6	420	399
7	41	36
8	48	46
9	42	39
10	41	35
11	215	220
12	118	118
13	31	29
17	32	20

H= 1,K= 4

L	FO	FC
-13	31	23
-12	53	52
-11	135	134
-10	123	126
-9	41	42
-6	37	41
-5	52	54
-4	91	89
-3	139	135
-2	50	44
-1	245	238
0	92	91
1	[illegible]	143
2	[illegible]	98
3	184	185
4	53	52
6	127	128
7	158	159
8	128	121
9	281	286
10	123	125
12	84	82
13	76	67
14	33	28

H= 1,K= 5

L	FO	FC
-12	72	75
-11	55	64
-10	48	49
-9	193	193
-7	58	66
-6	40	35
-5	133	134
-4	44	36
-2	113	116
-1	485	470
0	142	140
1	342	339
3	32	32
6	37	42
7	103	97
8	53	52
9	45	40
10	70	73
11	185	191
12	40	35
13	32	36
14	45	41
15	45	48

H= 1,K= 6

L	FO	FC
-15	60	54
-14	31	19
-12	33	36
-11	54	49
-10	71	70
-8	137	140
-7	93	93
-6	67	67
-5	76	76
-3	104	109
-2	115	114
-1	109	107
0	106	108
2	134	126
3	63	70
4	38	39
5	144	142
6	119	125
7	129	133
8	61	67
9	139	140
10	74	81
12	106	104
13	54	.52

H= 1,K= 7

L	FO	FC
-12	48	54
-10	49	59
-9	66	60
-8	142	140
-7	216	222
-6	58	57
-5	76	81
-4	177	178
-3	55	59
-2	37	37
-1	38	35
0	180	181
1	49	45
2	114	111
3	90	97
4	70	72
5	143	149
6	89	95
8	200	199
9	55	51
11	96	94
12	93	92
13	73	78

H= 1,K= 8

L	FO	FC
-13	67	52
-10	89	85
-7	54	54
-6	95	95
-5	205	207
-4	56	50
-3	107	105
-2	135	133
0	121	125
1	103	98
3	166	167
5	174	142
6	75	79
7	96	97
8	35	42
9	56	53
12	39	38
13	44	40
14	43	30

H= 1,K= 9

L	FO	FC
-11	56	45
-9	34	16
-8	63	62
-6	53	58
-4	212	219
-3	69	70
-2	39	47
-1	32	27
0	76	83
1	23	26
2	53	57
3	44	52
4	49	40
5	195	200
6	99	101
7	36	36
9	39	43

H= 1,K= 10

L	FO	FC
-9	32	38
-7	83	86
-6	40	41
-5	50	47
-4	32	31
-3	63	57
-2	102	101
-1	159	162
0	33	37
2	190	192
4	36	27
6	33	21
7	91	91
11	39	35
12	61	61
13	51	41

H= 1,K= 11

L	FO	FC
-6	45	39
-5	36	37
-4	40	36
-3	101	107
-2	55	55
0	67	72
1	123	130
7	54	57
9	34	35
10	73	80
12	60	50

H= 1,K= 12

L	FO	FC
-8	50	52
-7	40	32
-6	30	19
-4	57	58
-3	33	21
-1	110	111
0	62	62
1	37	34
4	61	49
8	93	91
10	69	77

H= 1,K= 13

L	FO	FC
-7	69	64
-6	51	47
-5	52	57
-4	35	5
-3	41	34
0	30	7
1	35	29
3	107	99
6	84	80
8	73	68

H= 1,K= 14

L	FO	FC
-4	40	27
-3	70	63
-2	36	37
0	39	37
4	48	43

H= 2,K= 0

L	FO	FC
-12	39	50
-10	46	56
-8	170	195
-4	159	164
-2	208	210
0	34	37
2	113	115
4	35	33
6	144	144
8	32	35
12	151	156
16	[illegible]	16

H= 2,K= 1

L	FO	FC
-15	36	23
-13	32	32
-11	50	41
-10	97	98
-9	48	49
-8	54	53
-7	217	212
-6	109	106
-5	246	240
-4	171	166
-3	33	31
-2	30	29
-1	56	52
0	38	40
1	38	38
2	111	110
3	229	220
4	17	18
5	109	105
6	80	76
7	55	50
8	39	41
10	76	86
11	181	186
12	126	131
14	31	32

H= 2,K= 2

L	FO	FC
-14	47	42
-12	34	25
-11	154	152
-10	33	19
-8	100	97
-7	193	178
-6	46	42
-5	84	85
-4	158	158
-3	33	32
-1	30	23
0	125	125
1	114	109
2	170	240
3	51	52
4	70	69
5	27	15
6	71	68
7	147	138
8	133	136
9	135	142
10	67	69
11	78	76
12	61	60
13	63	65
14	94	98
15	70	72

H= 2,K= 3

L	FO	FC
-14	72	65
-9	177	181
-8	97	94
-7	52	54
-6	95	97
-5	41	51
-4	102	88
-3	63	61
-2	90	81
-1	112	109
0	113	114
1	134	133
3	52	54
4	210	201
6	165	160
7	91	91
9	51	54
12	78	70
13	187	197
14	44	47
16	31	4

H= 2,K= 4

L	FO	FC
-13	75	80
-12	60	70
-11	43	41
-10	56	52
-9	157	161
-8	140	135
-7	79	86
-6	56	52
-5	32	35
-3	35	37
-2	24	3
-1	172	150
0	140	137
2	132	127
7	152	152
8	115	109
9	33	30
10	32	28
11	137	131
12	36	32
14	32	29

H= 2,K= 5

L	FO	FC
-14	43	36
-11	32	25
-9	34	29
-7	233	233
-5	105	104
-4	42	40
-3	101	105
-2	90	89
-1	33	37
0	96	92
1	272	265
2	35	31
5	133	131
6	65	65
7	41	40
9	33	29
10	52	41
11	50	53
12	31	25
13	98	105

H= 2,K= 6

L	FO	FC
-14	71	66
-12	59	54
-11	62	55
-10	71	80
-9	130	134
-8	105	103
-7	44	46
-6	31	27
-5	123	126
-4	35	32
-3	27	32
-2	199	195
-1	115	116
1	72	73
2	39	35
3	153	150
4	28	24
5	30	24
6	117	122
7	216	225
8	132	136
9	33	38
10	72	75
11	164	175
12	76	77
14	43	31

H= 2,K= 7

L	FO	FC
-13	54	45
-12	58	51
-9	69	72
-8	44	35
-7	53	57
-6	41	42
-5	79	78
-4	29	5
-3	125	125
-2	174	177
-1	50	47
0	64	64
1	195	199
3	89	94
5	70	71
6	104	107
7	87	94
10	37	34

H= 2,K= 8

L	FO	FC
-10	39	26
-9	82	73
-7	68	63
-6	35	35
-4	158	156
-3	106	103
-2	36	32
-1	190	199
0	49	47
1	77	75
2	192	196
3	93	88
4	73	82
5	259	259
7	51	51
8	91	96
9	99	99
10	57	53
13	43	39

H= 2,K= 9

L	FO	FC
-11	56	46
-9	66	57
-7	54	54
-5	35	30
-4	61	57
-2	119	122
0	151	158
1	76	80
3	55	50
4	38	36
5	32	33
7	80	78
10	35	36

H= 2,K= 10

L	FO	FC
-8	54	51
-7	53	53
-4	37	46
-3	30	15
-2	132	136
-1	31	35
0	63	61
1	49	42
2	83	83
4	76	81
5	68	69
10	32	7
11	33	39

H= 2,K= 11

L	FO	FC
-9	77	65
-2	36	38
-1	62	61
0	39	40
2	42	53
3	52	51
5	55	61
6	35	42
9	72	74

H= 2,K= 12

L	FO	FC
-6	66	65
-1	39	19
0	36	39
2	50	51
7	105	96
8	41	38

H= 2,K= 13

L	FO	FC
-3	43	32
-1	36	11
6	72	63

H= 3,K= 0

L	FO	FC
-10	58	63
-8	199	199
-6	258	256
-4	29	26
-2	184	194
0	43	37
2	248	246
4	49	47
6	116	117
8	45	58
10	130	129
12	50	49
16	75	66

H= 3,K= 1

L	FO	FC
-13	49	49
-10	102	131
-9	100	100
-8	103	99
-7	69	72
-5	184	180
-4	134	138
-3	77	72
-2	131	140
-1	107	110
0	29	22
1	29	30
2	243	245
3	249	252
4	101	99
5	152	148
6	69	66
7	128	129
8	88	97
10	114	111
11	56	86
12	59	58
13	64	69

H= 3,K= 2

L	FO	FC
-13	52	56
-11	64	62
-10	62	65
-9	138	135
-8	31	33
-7	178	181
-2	66	67
-1	89	90
1	53	53
2	45	51
3	92	88
4	239	238
5	75	74
7	113	117
11	150	150
12	37	34
13	65	74
14	34	26
15	33	16
17	50	47

H= 3,K= 3

L	FO	FC
-13	60	54
-9	34	26
-8	40	33
-7	109	112
-6	38	39
-5	71	65
-4	55	60
-3	35	19
-2	46	45
-1	44	34
0	160	179
1	115	115
3	105	102
4	34	35
5	107	108
6	23	14
7	64	67
8	32	36
9	78	80
10	38	37
11	41	42
14	31	10

H= 3,K= 4

L	FO	FC
-13	65	58
-12	40	45
-11	116	112
-9	52	60
-8	80	82
-7	142	143
-6	120	113
-5	53	50
-4	53	60
-3	113	113
-2	35	27
-1	193	194
0	38	43
1	56	52
2	97	100
3	125	127
4	62	55
5	125	126
7	53	61
8	109	112
9	205	208
10	32	17
13	71	72
14	34	31
15	31	5

H= 3,K= 5

L	FO	FC
-10	56	61
-9	36	26
-5	42	45
-4	83	88
-3	185	187
-2	58	61
-1	31	29
0	116	122
1	44	44
3	130	135
4	35	32
5	56	53
6	100	104
7	196	199
8	45	40
9	69	70
10	32	32
11	53	59
12	62	55
15	48	37

H= 3,K= 6

L	FO	FC
-12	34	57
-11	57	52
-8	32	30
-7	95	98
-6	127	122
-5	71	75
-4	40	42
-3	117	118
-2	95	95
0	120	123
1	44	45
2	112	111
3	73	75
4	76	81
5	59	60
6	82	89
7	40	51
8	74	70
9	65	60
10	57	69
11	44	41
14	42	34

H= 3,K= 7

L	FO	FC
-11	35	24
-9	35	44
-6	32	32
-4	31	32
-3	50	61
-2	145	150
0	122	123
1	92	97
2	79	63
3	197	205
5	194	192
6	45	45
7	45	44
10	57	52
11	31	3

H= 3,K= 8

L	FO	FC
-9	53	46
-7	50	50
-6	48	47
-3	92	93
-2	53	51
-1	112	114
1	254	253
2	30	29
3	65	58
4	133	136
6	51	51
7	72	63
10	53	55

H= 3,K= 9

L	FO	FC
-9	57	48
-5	67	58
-4	84	89
-2	81	78
-1	42	30
0	41	44
1	69	65
2	125	122
3	64	65
4	41	39
5	58	60
12	34	12

H= 3,K= 10

L	FO	FC
-7	36	27
-3	37	30
-2	60	53
-1	107	106
0	55	57
2	53	48
6	35	41
9	92	85

H= 3,K= 11

L	FO	FC
5	41	42
7	97	92
8	33	32

H= 3,K= 12

L	FO	FC
0	46	43
1	33	19
2	60	54
3	33	30
4	66	66
7	40	33

H= 4,K= 0

L	FO	FC
-10	62	75
-4	127	130
-2	231	237
0	71	76
2	97	93
4	226	225
6	179	182
8	100	108
10	137	141
14	43	28

H= 4,K= 1

L	FO	FC
-11	70	67
-9	32	29
-8	58	63
-7	137	137
-6	61	62
-4	30	23
-2	67	68
-1	83	83
0	150	151
2	43	41
3	44	43
4	80	75
5	94	96
6	131	129
7	33	27
9	59	36
10	51	49

H= 4,K= 2

L	FO	FC
-6	80	93
-4	82	73
-3	94	92
-2	45	41
-1	142	146
0	67	64
1	31	21
2	63	65
3	144	147
4	42	44
5	35	25
6	108	110
7	69	68
8	112	109
9	45	45
10	31	12
11	70	67
14	85	76
15	54	53

H= 4,K= 3

L	FO	FC
-11	84	70
-10	52	56
-9	40	46
-7	36	33
-6	33	25
-5	43	31
-4	31	34
-3	70	72
-2	106	104
-1	37	35
0	75	73
1	57	56
2	152	149
3	43	47
4	120	123
5	152	152
7	111	112
8	43	37
9	31	26
10	36	27
11	42	42
12	49	56
14	42	37

H= 4,K= 4

L	FO	FC
-6	40	50
-4	78	72
-3	153	155
-2	58	60
2	79	82
3	176	177
4	98	99
5	36	33
7	44	50
9	84	82
10	89	96
15	78	63

H= 4,K= 5

L	FO	FC
-9	35	9
-6	57	58
-4	77	80
-1	142	137
2	35	36
3	52	55
4	43	39
5	172	173
6	105	105
7	33	34
10	33	29

H= 4,K= 6

L	FO	FC
-7	49	40
-6	40	31
-5	33	32
-4	101	100
-3	46	45
-2	122	125
-1	55	63
0	72	70
1	37	30
2	53	50
3	85	85
4	81	76
5	79	62
6	74	79
8	92	100
9	35	27
12	33	28
13	46	33

H= 4,K= 7

L	FO	FC
-7	34	23
-6	44	49
-5	48	50
-4	39	41
-2	44	42
0	105	111
3	65	83
4	34	34
5	43	43
6	36	40
7	67	67
8	55	41
9	35	22
10	56	58
12	42	35
13	57	58

H= 4,K= 8

L	FO	FC
-6	44	37
-5	37	32
-4	58	60
-3	45	48
-2	61	62
2	48	50
3	91	96
4	31	31
5	37	32
7	42	40
11	70	60

H= 4,K= 9

L	FO	FC
-6	38	29
-5	36	21
-3	91	87
-1	103	112
1	53	50
4	42	38
7	56	47
8	62	57
9	32	16
10	66	63

H= 4,K= 10

L	FO	FC
-2	43	46
0	68	61
1	34	35
7	72	72

H= 4,K= 11

L	FO	FC
0	48	40
1	63	61
3	38	32
4	81	80

H= 5,K= 0

L	FO	FC
-4	122	125
0	168	170
4	32	26
6	179	185
8	55	56
10	46	47

H= 5,K= 1

L	FO	FC
-5	57	52
-3	55	56
1	73	74
3	108	111
4	63	58
5	62	50
8	[illegible]	44
10	47	45

H= 5,K= 2

L	FO	FC
-7	32	30
-4	42	53
-3	53	63
-2	103	102
-1	123	124
4	52	52
5	117	116
6	37	32
9	33	34

H= 5,K= 3

L	FO	FC
-7	32	37
-6	43	37
-5	33	35
-2	36	23
1	43	45
2	47	51
3	54	54
5	71	70
7	64	66
9	43	37
11	46	44

H= 5,K= 4

L	FO	FC
-2	34	36
2	34	35
4	47	45
5	84	79
9	60	55
10	43	41
11	63	44

H= 5,K= 5

L	FO	FC
-5	72	62
-3	34	12
-1	103	107
3	59	53
5	40	29
7	63	67
11	61	55

H= 5,K= 6

L	FO	FC
-4	72	65
0	72	72
1	51	51
2	36	39
8	33	13
9	70	72

H= 5,K= 7

L	FO	FC
-3	61	64
-2	84	82
-1	36	26
0	52	41

H= 5,K= 8

L	FO	FC
0	33	25
6	39	33
7	55	41

H= 6,K= 0

L	FO	FC
-2	87	74
4	44	33

H= 6,K= 1

L	FO	FC
-1	63	64
1	38	35
5	33	31

H= 6,K= 2

L	FO	FC
-1	35	32
0	34	19
3	43	19
7	56	54

H= 6,K= 3

L	FO	FC
0	36	34
1	54	45
6	34	18
7	46	41

H= 6,K= 4

L	FO	FC
1	70	46
3	46	23
5	64	60
6	56	49

[a] The values for $|F_o|$ and $|F_c|$ are in electrons × 10. $F_{000} = 4000$.

$P2_1/c$. The sum over[16] f_{jH}^2 extends over the $N = 144$ boron and hydrogen atoms in the unit cell, and $\langle E_H^2\rangle$ is normalized to 1.000 by adjustment of the scale factor. Experimental and theoretical values of the normalized structure factors are presented in Table I.

Normalized structure factors, E_H, were used as input for a local version of the program REL.[17] The E_H terms were ordered[18,19] in decreasing size of the function

$$|E_H|\sum_K|E_K||E_{H-K}|$$

and then the first three linearly independent E's associated with these terms were fixed in sign in order to determine the origin. The next four reflections were given assumed signs and each of the 16 resulting sets of assumed signs was used in an iterative application of Sayre's relationship with those reflections for which E_H was greater than 1.3 (total of 169 reflections).

In the iterative process newly calculated signs were used immediately to determine signs of all remaining

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[16] The f_j values were obtained from "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1968.

[17] REL, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," R. E. Long, Ph.D. Thesis (Part III), University of California, Los Angeles, Calif., 1965.

[18] Details of the operation of REL recently have been published,[19] and are repeated here only to clarify the steps involved in the solution of the current structure.

[19] T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1076 (1968).

TABLE III

ATOMIC PARAMETERS FOR $B_{16}H_{20}$

Atomic Positional and Isotropic Thermal Parameters[a,b]

Atom	x	y	z	B, Å^2
B1	0.4455 (6)	0.0830 (3)	0.1514 (2)	
B2	0.5193 (7)	0.1999 (3)	0.1858 (2)	
B3	0.4773 (7)	0.1014 (3)	0.2541 (3)	
B4	0.5371 (7)	−0.0160 (3)	0.2074 (2)	
B5	0.6696 (6)	0.1479 (3)	0.0936 (2)	
B6	0.8110 (6)	0.2175 (2)	0.1512 (2)	
B7	0.7175 (7)	0.1807 (3)	0.2529 (2)	
B8	0.7206 (8)	0.0348 (3)	0.2699 (3)	
B9	0.8294 (7)	−0.0359 (3)	0.1819 (3)	
B10	0.6806 (7)	0.0090 (3)	0.1061 (3)	
B1′	0.9238 (6)	0.2042 (2)	0.0498 (2)	
B2′	0.8862 (6)	0.3127 (3)	−0.0065 (2)	
B4′	0.9375 (7)	0.3221 (3)	0.0972 (2)	
B5′	0.7457 (7)	0.4028 (3)	0.0564 (3)	
B6′	0.5953 (7)	0.3343 (3)	−0.0030 (3)	
B7′	0.6891 (7)	0.2096 (3)	−0.0036 (2)	
H1	0.272 (5)	0.074 (2)	0.129 (2)	2.2 (7)
H2	0.393 (4)	0.264 (2)	0.192 (1)	0.4 (5)
H3	0.346 (5)	0.109 (2)	0.199 (2)	2.6 (7)
H4	0.414 (4)	−0.077 (2)	0.226 (1)	1.6 (6)
H7	0.742 (5)	0.228 (2)	0.308 (2)	3.1 (7)
H8	0.734 (5)	0.008 (2)	0.334 (2)	3.7 (8)
H9	0.938 (5)	−0.103 (2)	0.181 (2)	3.0 (7)
H10	0.677 (5)	−0.037 (2)	0.049 (2)	2.6 (7)
H1′	0.085 (4)	0.161 (2)	0.026 (1)	0.9 (6)
H2′	0.017 (4)	0.333 (2)	0.939 (2)	1.6 (6)
H4′	0.095 (5)	0.356 (2)	0.111 (1)	1.7 (6)
H5′	0.771 (5)	0.482 (2)	0.053 (2)	2.5 (7)
H6′	0.512 (4)	0.365 (2)	0.948 (2)	2.5 (7)
H7′	0.677 (5)	0.167 (2)	0.911 (2)	2.0 (6)
H(B6B7)	0.918 (5)	0.178 (2)	0.199 (2)	2.6 (7)
H(B8B9)	0.918 (5)	0.026 (2)	0.223 (2)	2.2 (7)
H(B9B10)	0.883 (5)	0.015 (2)	0.114 (2)	1.7 (6)
H(B4′B5′)	0.765 (5)	0.370 (2)	0.132 (2)	2.7 (7)
H(B5′B6′)	0.529 (5)	0.379 (2)	0.065 (2)	2.5 (7)
H(B6′B7′)	0.505 (5)	0.246 (2)	0.024 (2)	2.4 (7)

Anisotropic Thermal Parameters[c]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B1	290 (15)	57 (3)	40 (2)	−9 (5)	−17 (4)	5 (2)
B2	338 (16)	50 (3)	33 (2)	19 (5)	−9 (4)	2 (2)
B3	340 (15)	70 (3)	37 (2)	19 (6)	0 (4)	9 (2)
B4	357 (17)	52 (3)	49 (2)	−14 (6)	−12 (5)	8 (2)
B5	281 (14)	46 (2)	35 (2)	13 (5)	−25 (4)	−4 (2)
B6	292 (14)	44 (2)	37 (2)	9 (5)	−33 (4)	2 (2)
B7	412 (18)	63 (3)	34 (2)	10 (6)	−22 (5)	1 (2)
B8	424 (19)	62 (3)	47 (2)	9 (6)	−23 (5)	17 (2)
B9	381 (18)	47 (3)	60 (2)	17 (6)	−16 (5)	10 (2)
B10	371 (17)	47 (3)	50 (2)	−32 (6)	−17 (5)	−2 (2)
B1′	254 (14)	47 (2)	38 (2)	0 (5)	−10 (4)	−1 (2)
B2′	295 (14)	57 (3)	38 (2)	−11 (5)	−1 (4)	7 (2)
B4′	322 (17)	50 (3)	45 (2)	1 (6)	−25 (5)	−3 (2)
B5′	386 (17)	50 (3)	54 (2)	−2 (6)	−3 (5)	6 (2)
B6′	346 (16)	73 (3)	44 (2)	5 (6)	−9 (5)	20 (2)
B7′	301 (15)	65 (3)	35 (2)	−12 (5)	−13 (4)	0 (2)

[a] The numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [b] The coordinates are expressed as fractions of the unit cell parameters. [c] Anisotropic temperature factors are multiplied by 10^4. The form of the anisotropic thermal expression is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

unknown reflections. For each of the 16 sign sets the number of cycles and the consistency indices, defined as

$$C = \langle |E_H \sum_K E_K E_{H-K}| \rangle / \langle |E_H| \sum_K |E_K| |E_{H-K}| \rangle$$

where the average is taken over all H, were calculated. Sign set number 6 had the highest consistency index, $C = 0.73$, required five cycles of iteration, phased all 169 input reflections, and yielded the correct structure. The next highest C was 0.59 (after seven cycles), and only one other sign set required fewer than five cycles of iteration (this set had a consistency index of $C = 0.56$). No sign set other than the correct one phased all of the input reflections.

The E map computed[20] from the 169 phased reflections clearly showed positions for 15 of the 16 boron atoms in the asymmetric unit, as well as a probable position for the 16th boron atom. Twelve of these atom positions (two pentagonal pyramids) were used in a structure factor calculation[21] and the resulting electron density map contained the three peaks not used as input and confirmed the expected location for the 16th boron atom. Two cycles of full-matrix least-squares refinement[21] minimizing $\Sigma w(|F_o| - |F_c|)^2$, where the weights w are taken as $4F_o^2/\sigma(F_o^2)$, were carried out for the 16 boron atomic positions with individual isotropic temperature factors giving $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.165$ for 1046 reflections. At this stage a difference map was calculated[20] and all 20 hydrogen atoms were located. Of the 21 largest peaks in the difference map (electron density values 0.54–0.28 e$^-$ Å^{-3}), 20 were assigned to hydrogen atoms and the other peak appeared to be associated with a poorly located boron atom. Further refinement was made for all atomic positions (boron and hydrogen) with individual isotropic temperature factors (two cycles), and then after merging data from the two symmetry-related quadrants, anisotropic temperature factors were introduced for boron atoms and all parameters were refined further (two cycles). The final two cycles of refinement included 225 variables, and the final value of R is 0.054 for the 1095 pieces of merged data. The standard error of an observation of unit weight, defined as $[\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where n is the number of observations (1095) and m is the number of variables (225), is 1.07. Observed and calculated structure factors are compared in Table II. Atomic coordinates expressed in fractions of unit cell dimensions and temperature factors (anisotropic for boron and isotropic for hydrogen atoms) are contained in Table III.

Results and Discussion

The structure of the $B_{16}H_{20}$ molecule and the numbering scheme[22,23] are illustrated in Figure 1. Lipscomb's topological rules[2a] for boron hydrides of general formula $(B_rB_pH_{p+q+c})^c$, where r is the number of boron atoms without terminal hydrogen atoms and c is the electrical charge, yield for $B_{16}H_{20}$ the *styx* numbers (6.10.4.0). The proposed nomenclature rules for

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(20) FORDAP, A. Zalkin's Fourier program.

(21) W. Busing, K. Martin, and H. Levy's ORFLS, a least-squares program, and ORFFE, a function and error program.

(22) The numbering scheme used here differs from that used in the preliminary report of this work[6] and is consistent with the proposed nomenclature rules[23] for boron compounds.

(23) *Inorg. Chem.*, **7**, 1945 (1968).

Table IV
Boron–Boron Bond Distances (Å)

i	j	D_{ij} $B_{16}H_{20}$	Av values[a] $B_{16}H_{20}$	$B_{10}H_{14}$	B_8H_{12}	n-$B_{18}H_{22}$	i-$B_{18}H_{22}$
B1	B2	1.780 (5)	1.777 (14)	1.776 (5)		1.777 (13)	1.778 (16)
B1	B4	1.786 (6)					
B2	B3	1.754 (6)					
B3	B4	1.790 (6)					
B2	B5	1.777 (5)	1.777 (6)	1.786 (5)		1.801 (10)	1.802 (20)
B2	B7	1.780 (6)					
B4	B8	1.775 (6)					
B4	B10	1.779 (6)					
B1	B5	1.722 (5)	1.751 (18)	1.756 (4)		1.758 (14)	1.756 (12)
B1	B10	1.760 (6)					
B3	B7	1.772 (6)					
B3	B8	1.751 (6)					
B5	B6	1.680 (5)	1.680 (5)	1.775 (13)	1.674 (4)	1.838 (5)	1.794 (2)
B6	B7	1.763 (6)	1.773 (7)	1.775 (13)		1.798 (17)	1.787 (5)
B8	B9	1.779 (7)					
B9	B10	1.778 (6)					
B1	B3	1.782 (6)	1.782 (6)	1.772 (6)		1.783 (4)	1.781 (3)
B2	B6	1.713 (6)	1.709 (6)	1.715 (4)		1.754 (35)	1.721 (5)
B4	B9	1.704 (6)					
B5	B10	1.914 (6)	1.965 (50)	1.973 (4)		1.972 (4)	1.974 (19)
B7	B8	2.015 (7)					
B5′	B6′	1.723 (6)	1.723 (6)		1.707 (4)		
B2′	B5′	1.725 (6)	1.721 (6)		1.720 (4)		
B2′	B6′	1.717 (6)					
B2′	B4′	1.821 (6)	1.818 (6)		1.809 (5)		
B2′	B7′	1.816 (6)					
B1′	B4′	1.806 (5)	1.790 (15)		1.792 (4)		
B1′	B7′	1.775 (6)					
B4′	B5′	1.797 (6)	1.794 (6)		1.806 (6)		
B6′	B7′	1.791 (6)					
B4′	B6	1.779 (5)	1.799 (19)		1.822 (4)		
B5	B7′	1.818 (6)					
B1′	B2′	1.794 (5)	1.794(5)		1.830 (4)		
B1′	B5	1.712 (5)	1.712 (6)		1.710 (4)		
B1′	B6	1.712 (6)					

[a] The deviations listed for the average values are either the mean of the standard deviations or the root-mean-square deviation, whichever is larger in each case. Distances for B_8H_{12}, n-$B_{18}H_{22}$, and i-$B_{18}H_{22}$ are those obtained[3,7] in the X-ray studies, while those for $B_{10}H_{14}$ are from the neutron diffraction study[4d] of $^{11}B_{10}{}^2H_{14}$.

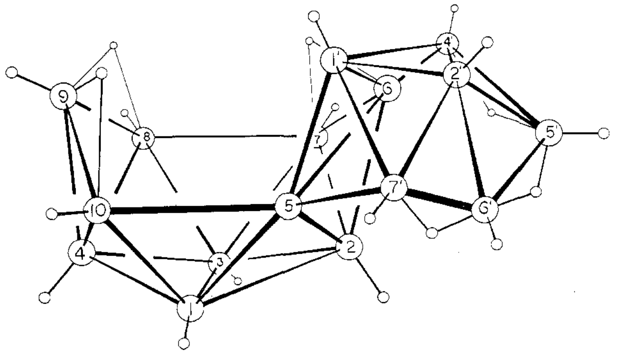

Figure 1.—The molecular structure and numbering scheme for $B_{16}H_{20}$.

boron compounds[23] yield the name hexadecaborane(20), or octaborano(12)[3′,8′:5,6]decaborane(14). The latter name for the compound seems particularly appropriate since positions of boron and hydrogen atoms, bond distances, and bond angles in $B_{16}H_{20}$ are, with but a few exceptions, remarkably similar to the corresponding positions, distances, and angles observed[4,7] in $B_{10}H_{14}$ and B_8H_{12}. The formal fusion of the $B_{10}H_{14}$ and B_8H_{12} fragments is along the B5–B6 edge of $B_{10}H_{14}$ and the B3–B8 edge of B_8H_{12}, with the two fragments opening in opposite directions. Bridge hydrogen atoms along these edges in the component boranes are not present in the $B_{16}H_{20}$ molecule, and terminal hydrogen atoms on B5 and B6 of $B_{10}H_{14}$ and B3 and B8 of B_8H_{12} are also not present in $B_{16}H_{20}$. The symmetries of $B_{10}H_{14}$ (C_{2v}) and B_8H_{12} (C_s) are lost in the unsymmetrical fusion of the two units into $B_{16}H_{20}$, the first structurally characterized neutral boron hydride without molecular symmetry.

There are six bridging hydrogen atoms in $B_{16}H_{20}$, three of which, H(B6B7), H(B8B9), H(B9B10), occupy positions corresponding to those found in $B_{10}H_{14}$ and the other three, H(B4′B5′), H(B5′B6′), H(B6′-B7′), occupy positions corresponding to those in B_8H_{12}. The 14 terminal hydrogen atoms are distributed one per boron atom, with the two boron atoms (B5 and B6) connecting the two icosahedral fragments lacking terminal hydrogens. Each boron atom in $B_{16}H_{20}$ is six-coordinate, and B5 is coordinated to boron atoms only. In the n-$B_{18}H_{22}$ molecule[3a] there are two boron atoms each surrounded by six boron atoms; however these atoms also participate in bridge hydrogen bonding and are therefore seven-coordinate. The i-$B_{18}H_{22}$ molecule also has [3b] two seven-coordinate boron

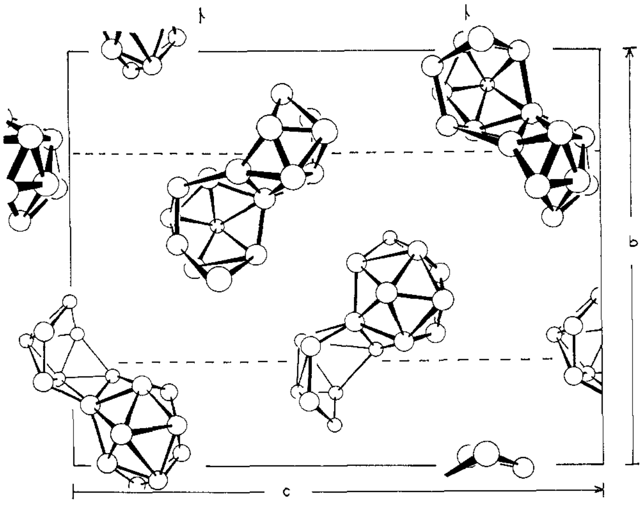

Figure 2.—The molecular packing of $B_{16}H_{20}$ as seen in the 0*kl* projection. Hydrogen atoms are omitted for the sake of clarity.

atoms; one is surrounded by one hydrogen and six boron atoms, and the other is surrounded by seven boron atoms.

Table IV lists all bonded B–B distances in $B_{16}H_{20}$ and compares the appropriate average values with those found[3,4,7] in $B_{10}H_{14}$, B_8H_{12}, *n*-$B_{18}H_{22}$, and *i*-$B_{18}H_{22}$. Especially noteworthy is the B5–B6 distance of 1.680 (5) Å which is considerably shorter than the corresponding distance in $B_{10}H_{14}$, *n*-$B_{18}H_{22}$, and *i*-$B_{18}H_{22}$ but which is almost identical with the corresponding value of 1.674 (4) Å found in B_8H_{12}. In addition, the B5–B10 and B7–B8 distances of 1.914 (6) and 2.015 (7) Å, respectively, indicate a *slight* distortion in the symmetry of the B_{10} fragment of $B_{16}H_{20}$ as compared with $B_{10}H_{14}$ or the B_{10} fragments of *n*-$B_{18}H_{22}$ and *i*-$B_{18}H_{22}$.

TABLE V

BORON–HYDROGEN BOND DISTANCES (Å)

B–H, terminal			B–H, bridge		
B	H	B–H	B	H	B–H
B1	H1	1.15 (3)	B6	H(B6B7)	1.23 (3)
B2	H2	1.13 (2)	B7	H(B6B7)	1.34 (3)
B3	H3	1.08 (3)	B8	H(B8B9)	1.28 (3)
B4	H4	1.11 (3)	B9	H(B8B9)	1.26 (3)
B7	H7	1.16 (3)	B9	H(B9B10)	1.31 (3)
B8	H8	1.15 (3)	B10	H(B9B10)	1.22 (3)
B9	H9	1.11 (3)	B4′	H(B4′B5′)	1.36 (3)
B10	H10	1.16 (3)	B5′	H(B4′B5′)	1.25 (3)
B1′	H1′	1.12 (2)	B5′	H(B5′B6′)	1.29 (3)
B2′	H2′	1.11 (3)	B6′	H(B6′B7′)	1.36 (3)
B4′	H4′	1.09 (3)	B6′	H(B5′B6′)	1.29 (3)
B5′	H5′	1.09 (3)	B7′	H(B6′B7′)	1.20 (3)
B6′	H6′	1.12 (3)		Av	1.28 (5)
B7′	H7′	1.10 (3)			
	Av[a]	1.12 (3)			

[a] Root-mean-square deviations are listed for the average values.

TABLE VI

BORON–BORON–BORON ANGLES (DEG)

Atoms	Angle	Atoms	Angle
B2–B1–B3	59.0 (2)	B3–B8–B4	61.0 (3)
B2–B1–B5	61.0 (2)	B3–B8–B7	55.6 (2)
B3–B1–B4	60.2 (2)	B4–B8–B9	57.3 (2)
B4–B1–B10	60.2 (2)	B7–B8–B9	115.6 (3)[a]
B5–B1–B10	66.7 (2)	B4–B9–B8	61.2 (2)
B1–B2–B3	60.6 (2)	B4–B9–B10	51.4 (2)
B1–B2–B5	57.9 (2)	B8–B9–B10	104.9 (3)[a]
B3–B2–B7	60.2 (2)	B1–B10–B4	60.6 (2)
B5–B2–B6	57.5 (2)	B1–B10–B5	55.7 (2)
B6–B2–B7	60.6 (2)	B4–B10–B9	57.3 (2)
B1–B3–B2	60.4 (2)	B5–B10–B9	116.9 (3)[a]
B1–B3–B4	60.0 (2)	B5–B1′–B6	58.8 (2)
B2–B3–B7	60.6 (2)	B5–B1′–B7′	62.8 (2)
B4–B3–B8	60.2 (2)	B6–B1′–B4′	60.7 (2)
B7–B3–B8	69.8 (3)	B2′–B1′–B4′	60.8 (2)
B1–B4–B3	59.8 (2)	B2′–B1′–B7′	61.2 (2)
B1–B4–B10	59.2 (2)	B1′–B2′–B4′	59.9 (2)
B3–B4–B8	58.8 (2)	B1′–B2′–B7′	58.9 (2)
B8–B4–B9	61.5 (3)	B4′–B2′–B5′	60.8 (2)
B9–B4–B10	61.3 (3)	B5′–B2′–B6′	60.1 (2)
B1–B5–B2	61.1 (2)	B6′–B2′–B7′	60.8 (2)
B1–B5–B10	57.6 (2)	B6–B4′–B1′	57.1 (2)
B2–B5–B6	59.3 (2)	B6–B4′–B5′	117.2 (3)[a]
B6–B5–B1′	60.6 (2)	B1′–B4′–B2′	59.3 (2)
B10–B5–B7′	124.2 (3)[a]	B2′–B4′–B5′	56.9 (2)
B1′–B5–B7′	60.3 (2)	B2′–B5′–B4′	62.2 (2)
B2–B6–B5	63.2 (2)	B2′–B5′–B6′	59.7 (2)
B2–B6–B7	61.6 (2)	B4′–B5′–B6′	108.0 (3)
B5–B6–B1′	60.6 (2)	B2′–B6′–B5′	66.2 (2)
B7–B6–B4′	138.2 (3)[a]	B2′–B6′–B7′	62.3 (2)
B1′–B6–B4′	62.3 (2)	B5′–B6′–B7′	109.4 (3)
B2–B7–B3	59.2 (2)	B5–B7′–B1′	56.9 (2)
B2–B7–B6	57.8 (2)	B5–B7′–B6′	118.0 (3)[a]
B3–B7–B8	54.6 (2)	B1′–B7′–B2′	59.9 (2)
B6–B7–B8	114.2 (3)[a]	B2′–B7′–B6′	56.8 (2)

[a] External angle.

The boron–hydrogen bond distances are listed in Table V, and the average values are 1.12 (3) Å for terminal hydrogen atoms and 1.28 (5) Å for bridge hydrogen atoms, in general agreement with values found[2a] for other boranes. The B–B–B angles are contained in Table VI and a careful inspection of comparable angles indicates that the molecule is not significantly distorted. The crystal structure as projected onto the 0*kl* plane is illustrated in Figure 2, and a projection drawing and valence structure for $B_{16}H_{20}$ is included in Figure 3.

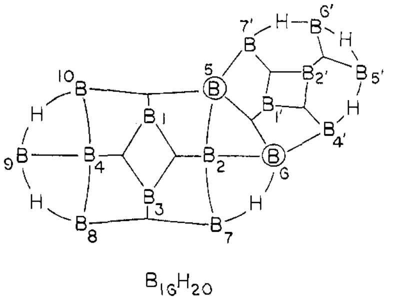

Figure 3.—Projection drawing, valence structure, and numbering scheme for $B_{16}H_{20}$ (6.10.4.0). All boron atoms are bonded to terminal hydrogen atoms except those circled.

We consider now the chemical implications of this structural study. The pyrolysis of $B_9H_{13}S(CH_3)_2$ produces[8] a relatively large yield of $B_{10}H_{14}$ and *n*-$B_{18}H_{22}$, as well as small amounts of $B_{16}H_{20}$. Plešek, *et al.*, have proposed[8,24] that the first step of this py-

[24] S. Heřmánek and J. Plešek, private communication.

rolysis involves the loss of dimethyl sulfide and the generation of an intermediate B_9H_{13} which then (i) dimerizes to $B_{18}H_{26}$ which, in turn, cleaves to yield $B_{10}H_{14}$ and B_8H_{12}, (ii) dehydrogenates to B_9H_{11}, which then dimerizes to give n-$B_{18}H_{22}$, and (iii) eliminates a BH_3 group to yield an unstable B_8H_{10}. We add here a proposal for the dimerization of a possible B_8 fragment which yields, in a very simple way, the observed *boron* framework of $B_{16}H_{20}$.

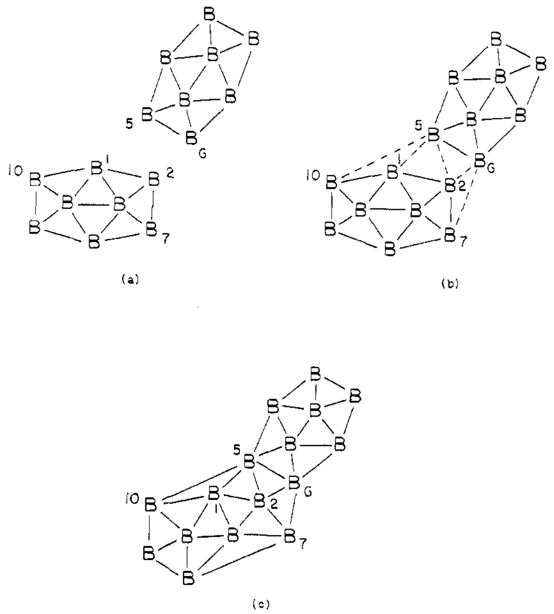

Figure 4.—A proposed dimerization of two B_8 fragments (a) to yield the boron framework of $B_{16}H_{20}$ (c).

Consider two B_8 icosahedral fragments (Figure 4), each with boron atoms arranged as in the known B_8H_{12}. Assume the fragments, one opening upward and the other opening downward, approach each other in such a way that an end of one fragment (5–6) approximately straddles a corner (1–2–7) of the other (Figure 4a). Assume bonding interaction between one edge of the first fragment and three edges of the second (5 to 10, 5 to 1, 5 to 2, 6 to 2, 6 to 7) (Figure 4b). Slight shifts by each of several boron atoms yield the boron atom framework observed in $B_{16}H_{20}$ (Figure 4c).[25]

There is, of course, the possibility that $B_{16}H_{20}$ arises from a more complex series of reactions. For example, some of the n-$B_{18}H_{22}$ produced in the pyrolysis may lose boron atoms 8′ and 9′ which, after minor shifts in the positions of the remaining boron atoms and appropriate rearrangement of bridging hydrogen atoms, would yield $B_{16}H_{20}$. A similar degradation of i-$B_{18}H_{22}$ (which is not a product of the pyrolysis reaction which produces $B_{16}H_{20}$) would also yield $B_{16}H_{20}$.[26]

Only a few chemical properties of $B_{16}H_{20}$ have been reported[8] and they are all consistent with the structure now established. Dimethyl sulfide and triphenylphosphine react with $B_{16}H_{20}$ to give first decaborane(14) and then the corresponding base adducts of decaborane, $B_{10}H_{12}[S(CH_3)_2]_2$ and $B_{10}H_{12}[P(C_6H_5)_3]_2$, respectively. It seems reasonable to assume that the base simply cleaves the $B_{16}H_{20}$ molecule in such a way as to produce a B_{10} fragment and a B_6 fragment. The boron–boron bond distances in $B_{16}H_{20}$ do not, however, indicate special weakness for the B5–B7′, B5–B1′, B6–B1′, or B6–B4′ bonds, which require cleavage for the simplest route to a decaborane-type fragment. Such a cleavage suggests formation of base adducts of the B_6 fragment, and it is noteworthy that other, as yet unidentified, products indeed are obtained[8] in the reaction of $B_{16}H_{20}$ with dimethyl sulfide.

The observed acidic character of $B_{16}H_{20}$ and the resulting yellow anionic conjugate base are reminiscent of the acid character[2,27] of $B_{10}H_{14}$, n-$B_{18}H_{22}$, and i-$B_{18}H_{22}$. It is tempting to speculate that the conjugate base of $B_{16}H_{20}$ is structurally similar (in the B_{10} fragment) to the $B_{10}H_{13}^-$ ion,[2] as the n-$B_{18}H_{21}^-$, n-$B_{18}H_{20}^{2-}$, i-$B_{18}H_{21}^-$, and i-$B_{18}H_{20}^{2-}$ ions are presumed[27] to be. Unfortunately, the structure proposed[2a] for the $B_{10}H_{13}^-$ ion has not been confirmed by X-ray diffraction.

The establishment of the structure of $B_{16}H_{20}$, the third neutral borane with a fused icosahedral fragment structure, suggests that numerous additional fused icosahedral fragment boranes may be capable of existence. In $B_{16}H_{20}$, n-$B_{18}H_{22}$, and i-$B_{18}H_{22}$ the fused-fragment structures may formally be generated from the component fragment boranes by removal of one bridge and two terminal hydrogen atoms from each component fragment and reduction of the sum of boron atoms from the components by two. For component fragments B_nH_m and $B_{n'}H_{m'}$, the fused-fragment formula is $B_{n+n'-2}H_{m+m'-6}$. Application of this formal procedure to the simple icosahedral fragment boranes (B_4H_{10}, B_5H_{11}, B_6H_{10}, B_8H_{12}, B_9H_{15}, and $B_{10}H_{14}$) implies the generation of 123 fused-fragment boron hydrides (235 including enantiomers) each made up of two-component icosahedral fragments. Especially interesting are possible B_{11}, B_{12}, B_{13}, B_{14}, B_{15}, and B_{17} neutral boranes which, as of this writing, have not been characterized. There is also, of course, the possibility that three or more simple borane fragments may (formally) be fused to give even more new structures.

Acknowledgment.—We thank Dr. Plešek and Dr. Heřmánek for the sample of $B_{16}H_{20}$ and for helpful communications, Dr. John H. Enemark for help with the program REL, and Professor W. N. Lipscomb for helpful discussions. This research was supported by funds made available from Oakland University, Wayne State University, and Wellesley College. We gratefully acknowledge the contribution of the Wayne State University Computing Center and a grant from the Petroleum Research Fund administered by the American Chemical Society (841-G).

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(25) S. Heřmánek, J. Plešek, and B. Štíbr proposed a structure for $B_{16}H_{20}$ based upon their chemical studies and the structural principles observed for the previously characterized boranes. This proposal, presented at the 5th Czechoslovak Conference on Inorganic Chemistry, Oct 1967, described $B_{16}H_{20}$ as a symmetric B_8 dimer with six bridge hydrogen atoms, a structure which is actually closely related to the structure established here.

(26) Recent studies by S. Heřmánek and J. Plešek show n-$B_{18}H_{22}$ to be thermally stable up to 190°. Since $B_{16}H_{20}$ is obtained by pyrolysis at much lower temperatures, an intermediate role for n-$B_{18}H_{22}$ seems unlikely.

(27) F. P. Olsen, R. C. Vasavada, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 3946 (1968).