with J_{BH} = 120 ± 5 cps (see Figure 1). The ratio of the relative intensities of the two doublets was 4.90:2 (average of seven individual traces). The sample was free of other boron-containing species detectable by nmr spectroscopy in solution, but it was not possible to reisolate the solid salt from the solution totally free of some borate impurity. However, the analysis obtained is in reasonable agreement with the composition $Cs_2B_7H_7$.

Anal. Calcd for $Cs_2B_7H_7$: B, 21.7. Found: B, 20.4.

Method B.—Hydrated $Na_2B_8H_8 \cdot xH_2O$ (2.6 g) was stirred with 300 ml of 1,2-dimethoxyethane at 50–60° for about 10 min. Insoluble material was collected by filtration and converted to $Cs_2B_8H_8$ by dissolution in water and precipitation with cesium hydroxide. A total of 1.3 g of pure $Cs_2B_8H_8$ was recovered. The dark red, almost black, dimethoxyethane filtrate was then saturated with a stream of air for about 2 hr, after which time the color of the mixture had changed to milky white. The addition of 100 ml of 1 *N* cesium hydroxide solution to this mixture precipitated 0.5 g of undegraded $Cs_2B_8H_8$ which was collected by filtration. Methanol (25 ml) was then added to the filtrate, and the resulting mixture was left standing for 24 hr. A total of 0.8 g of $Cs_2B_6H_6$ precipitated from the solution during this time. This crude fraction of $Cs_2B_6H_6$ was contaminated by a small amount of $Cs_2B_{10}H_{10}$ as indicated by its infrared spectrum, but was obtained pure by two subsequent recrystallizations from 20 ml of water. The yield of pure $Cs_2B_6H_6$ was 0.6 g. The aqueous dimethoxyethane filtrate from the crude $Cs_2B_6H_6$ isolation step was then reduced to a volume of about 5 ml on the rotating evaporator at about 10 mm pressure. At this point, 0.3 g of solid precipitated which consisted largely of a mixture of $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12} \cdot CsBH_4$. These species were identified by comparing the infrared spectrum of the mixture with spectra of authentic species. This solid was filtered off from the solution, and 10 ml of methanol was added to the filtrate. A white solid (1.5 g) precipitated, the infrared spectrum of which showed the characteristic features of the anion $B_7H_7^{2-}$. Purification was effected by allowing an aqueous solution of the crude cesium salt to react with an excess of an ammoniacal solution of zinc chloride and recrystallizing the resulting precipitate twice from 30 ml of dilute ammonium hydroxide solution. The final yield was 150 mg of colorless microcrystals of $[Zn(NH_3)_{2.76}(H_2O)_{1.24}]B_7H_7$. Another less pure crop (0.2 g) was isolated from the mother liquor.

Anal. Calcd for $[Zn(NH_3)_{2.76}(H_2O)_{1.24}]B_7H_7$: Zn, 30.1; N, 17.8; H, 8.2; B, 34.9. Found: Zn, 30.1; N, 17.1; H, 8.3; B, 35.2.

The infrared spectrum of this salt (Nujol mull; cation absorption omitted) showed two strong sharp bands at 2500 and 2450 cm^{-1} in the B–H stretching region; other absorption occurred at 1100 (m), 1040 (w), and at 920 (m) cm^{-1}. The spectrum of $Cs_2B_7H_7$ was similar; it had an additional band at 720 cm^{-1} which was masked by NH_3 absorption in the zinc ammine salt. The ultraviolet spectrum of an aqueous solution of $Cs_2B_7H_7$ cuts off at 2000 A.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK 11973

The Crystal and Molecular Structure of Monoiododecaborane[1a]

BY A. SEQUEIRA[1b] AND WALTER C. HAMILTON

Received February 22, 1967

The crystal and molecular structure of the low-melting isomer of monoiododecaborane (mp 98.5–100°) has been determined using three-dimensional X-ray diffraction data. The material crystallizes in space group $P2_1/c$ (C_{2h}^5) of the monoclinic system, with eight molecules in a unit cell of dimensions a = 13.98 (σ = 0.02), b = 12.11 (σ = 0.02), c = 14.34 A (σ = 0.02); β = 120.6° (σ = 0.4). Iodine is at the 1 position in both of the molecules of the asymmetric unit. The structure consists of decaborane-like polyhedral cages that fall in sheets which are roughly parallel to the (120) plane and are held together by the van der Waals interactions between the protruding iodines, as well as by the iodine–hydrogen interactions. The mean B–I bond length is 2.17 A (σ = 0.013), and the B–B bond distances are in good agreement with those found in decaborane and in 1-ethyldecaborane.

Introduction

The iodination of decaborane is known to result in two isomers of monosubstituted and two of the disubstituted derivatives.[2a] Of these, one of the diiodo derivatives has been shown to be substituted in the 2 and 4 positions, based on a determination[2b] of the intramolecular I···I distance from a two-dimensional X-ray diffraction study. Based on this result, the B^{11} nmr spectra of the two isomers of $B_{10}H_{13}I$ have been interpreted by Schaeffer, *et al.*,[3] to show that the substitution occurs at the 2 position in the higher melting isomer (mp 119), but not in the lower melting isomer (mp 100°). Their interpretations regarding the exact position of substitution in this lower melting isomer have been varied enough to include the 5, 7, 8, 10, the 1,3, or the 6,9 positions.[4] However, the deuterium tracer studies of Hillman[2a,5] favored the 5 substitution. In addition, high-resolution B^{11} nmr spectra have been interpreted[6] to show that the substitution occurs at the 1,3 or the 6,9 positions, but any further choice between these two sets could not be made, due to the overlap of 1,3 and 6,9 doublets in the spectra. Hence, an X-ray diffraction study seemed to be appropriate.

---

(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission; (b) on deputation from the Atomic Energy Establishment, Trombay, Bombay, India.

(2) (a) M. Hillman, *J. Am. Chem. Soc.*, **82**, 1096 (1960); (b) R. Schaeffer, *ibid.*, **79**, 2726 (1957).

(3) R. Schaeffer, J. N. Shoolery, and R. Jones, *ibid.*, **80**, 2670 (1958).

(4) In particular, see footnote 10 of ref 3.

(5) After the completion of this work, the deuterium tracer studies of Hillman have been shown to be consistent with the 1 substitution: R. L. Williams, private communication.

(6) R. E. Williams and T. P. Onak, *J. Am. Chem. Soc.*, **86**, 3159 (1964).

Crystal Data

Eight formula units of $B_{10}H_{13}I$ are contained in a monoclinic unit cell of dimensions $a = 13.98$ (2), $b = 12.11$ (2), $c = 14.34$ (2) A, and $\beta = 120.6$ (4)°. The calculated and measured densities are 1.565 and 1.59 (2) g/cm^3, respectively. The observed extinctions are consistent with the space group C_{2h}^5-$P2_1/c$. All of the atoms occupy general positions of the type $\pm(x, y, z; x, {}^1/_2 - y, {}^1/_2 + z)$.

Collection and Reduction of the X-Ray Data

The sample of $B_{10}H_{13}I$ (mp 100°), kindly supplied by Dr. M. Hillman, contained many well-formed, colorless, needle-shaped single crystals. Precession photographs and optical goniometry showed that the crystals belonged to the monoclinic system with the direction of the b axis lying parallel to the long needle axis of the crystals. The principal faces were found to be (001), (100) and $(10\bar{1})$. A small crystal of ~0.45-mm length and ~0.033-mm^2 cross section was sealed in a glass capillary, and the intensity data were collected at room temperature by the equiinclination Weissenberg and Buerger precession methods, using Zr-filtered Mo Kα radiation. Layers $h0l$ through $h10l$ were recorded in successive exposures ranging from 48 to 120 hr, using Ilford Industrial G X-ray film and a Nonius Weissenberg camera. The intensities of 1982 independent reflections within the angular range $\theta_{Mo} \leqslant 23°$ were estimated visually. This represents roughly 74% of the possible reflections in this range. In addition, about 670 reflections, in levels $hk0$, $hk1$, $0kl$, and $1kl$, were recorded using the same crystal on a precession camera. The F_o^2 values, where F_o is the observed structure amplitude, obtained after applying the usual Lorentz-polarization corrections, were corrected for absorption. The transmission factors for a linear absorption coefficient of 30.3 cm^{-1} varied from approximately 0.52 to 0.65. Separate absolute scale factors were determined for each layer through a modification of Wilson's[7] procedure.

The initial stages of the computations were performed on an IBM 7094 computer and the final stages on a CDC 6600 using programs developed or modified at BNL. In the least-squares refinement the function $\Sigma w(F_o^2 - F_c^2)^2$ was minimized. The weights w were proportional to $1/\sigma^2(F_o^2)$, where the standard deviations, σ, were assigned in the following way: $I > 16$, σ proportional to F^2/I; $I < 16$, σ proportional to $F^2/16$, where I is the value of the raw intensity for each reflection. The atomic scattering factor for H was based on the free atom wave function.[8] The atomic scattering factors for neutral B and I were taken from the Hartree scattering-factor calculations of Cromer, Larson, and Weber.[9] The anomalous parts of the iodine scattering factor given by Cromer[10] were included in the calculation of the structure factors.[11] The anisotropic temperature factors used have the form $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

Solution and Refinement of the Structure

The positions of the two independent iodine atoms were easily derived from the three-dimensional, sharpened, origin-removed Patterson function. The positional parameters of these were refined along with isotropic thermal parameters and separate scale factors for the separate layers. (Any reflection observed on two layers was entered twice in the least squares.) Two cycles of refinement yielded weighted and unweighted R values, R_w and R, of 0.265 and 0.359, where $R_w = [\Sigma w(F_o^2 - F_c^2)/\Sigma w F_o^4]^{1/2}$ and $R = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$. A difference Fourier based on the heavy-atom phases readily yielded the positions of the 20 boron atoms, and two cycles of isotropic least-squares refinement, with the iodine and boron atoms included, gave R values of 0.272 (R_w) and 0.170 (R). At this stage the precession data were added to the Weissenberg data, and two more cycles of least-squares refinement with anisotropic thermal parameters on the iodine atoms and isotropic on the borons reduced R_w and R to 0.174 and 0.135, respectively. A difference Fourier was again calculated to look for the hydrogen peaks, and the positions of the 26 hydrogens were identified. The hydrogen peaks, however, were no stronger than some of the residual peaks around the iodines and borons, or the other spurious ones. The hydrogen atoms were included in the subsequent refinement and their temperature factors were fixed at values corresponding to the adjacent borons. Two more cycles of least-squares refinement with the hydrogen parameters fixed and with anisotropic thermal parameters on the iodine and boron atoms yielded values of $R_w = 0.160$ and $R = 0.108$. Finally, the positional parameters of the hydrogens were also allowed to vary, and after ten cycles (alternate cycles on the two molecules because of limitations of size in the least-squares program), most of the hydrogen parameters converged while a few that were oscillating were fixed at their mean positions. The final R values are $R_w = 0.135$ and $R = 0.100$, the corresponding values of the conventional R factors (on F_o) being 0.071 and 0.060, respectively. The final value of 0.93 of the error-of-fit function[12] $[\Sigma w(F_o^2 - F_c^2)^2/(n - m)]^{1/2}$, where n is the number of observations and m is the number of variable parameters, is fairly close to the expected value of unity, thus suggesting that the absolute scale of the weights is reasonable.

The final parameters and their standard deviations are listed in Table I, while the observed and calculated structure factors are listed in Table II.

Description of the Structure

The molecular structure of $B_{10}H_{13}I$ (shown in Figure 1) is very similar to that of $B_{10}H_{14}$,[13] with the boron

---

[7] A. J. C. Wilson, *Nature*, **150**, 152 (1942).

[8] J. A. Ibers, "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

[9] D. T. Cromer, A. C. Larson, and J. T. Waber, *Acta Cryst.*, **17**, 1044 (1964).

[10] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[11] J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

[12] W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964.

[13] J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS IN $B_{10}H_{13}I^a$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				Molecule 1					
I	0.1495	0.5807	0.4326	92	69	65	−7	27	−3
B_1	0.028	0.478	0.298	63	47	63	8	37	2
B_2	0.022	0.490	0.172	81	70	67	−4	44	10
B_3	−0.093	0.524	0.185	63	73	67	13	32	−3
B_4	−0.099	0.457	0.294	77	89	77	11	50	−4
B_5	0.087	0.372	0.258	64	84	89	9	56	−5
B_6	0.005	0.362	0.112	86	86	81	2	56	−1
B_7	−0.121	0.446	0.075	115	72	63	33	45	3
B_8	−0.194	0.422	0.155	77	71	139	−16	52	−18
B_9	−0.140	0.320	0.257	90	91	121	−41	65	−15
B_{10}	0.005	0.350	0.339	74	73	76	−12	41	−2
				Molecule 2					
I	0.6309	0.0431	0.1926	95	64	113	10	74	4
B_1	0.520	0.142	0.220	65	46	65	−14	27	−7
B_2	0.522	0.131	0.347	84	91	60	8	41	22
B_3	0.402	0.099	0.224	62	74	91	−7	51	−9
B_4	0.388	0.172	0.110	89	87	56	−2	28	−15
B_5	0.583	0.246	0.321	64	95	56	−18	29	−16
B_6	0.517	0.258	0.396	124	106	54	−11	42	−16
B_7	0.394	0.178	0.321	120	55	85	−15	73	−2
B_8	0.300	0.205	0.166	73	92	125	−7	52	−23
B_9	0.351	0.310	0.110	104	106	79	24	47	10
B_{10}	0.493	0.277	0.161	79	63	45	1	18	4

Hydrogen atom	Molecule 1				Molecule 2			
	x	y	z	B, A^2	x	y	z	B, A^2
H_2	0.060	0.555	0.155	3.02	0.546	0.073	0.389	2.96
H_3	−0.123	0.625	0.144	2.91	0.397	−0.031	0.240	3.09
H_4	−0.125	0.511	0.341	3.82	0.371	0.151	0.030	3.73
H_5	0.181	0.340	0.313	3.31	0.670	0.262	0.364	3.08
H_6	0.047	0.328	0.056	3.65	0.540	0.273	0.469	4.38
H_7	−0.148	0.509	−0.027	3.67	0.342	0.126	0.347	3.57
H_8	−0.317	0.469	0.080	4.33	0.240	0.168	0.136	4.13
H_9	−0.175	0.262	0.279	3.92	0.274	0.365	−0.001	4.30
H_{10}	0.050	0.310	0.422	3.28	0.547	0.311	0.122	2.83
$H_{6,5}$	0.028	0.280	0.190	3.48	0.546	0.322	0.341	3.73
$H_{6,7}$	−0.113	0.317	0.073	4.00	0.425	0.265	0.348	3.97
$H_{9,8}$	−0.231	0.369	0.147	4.45	0.334	0.286	0.153	4.21
$H_{9,10}$	−0.029	0.275	0.294	3.60	0.454	0.352	0.186	3.56

[a] The β's are in units of 10^{-4} A^2. The standard deviations of the positional parameters are 0.0001 or less for the iodines, 0.001 or less for the borons, and 0.01 or less for the hydrogens. The standard deviations of the thermal parameters are 2 or less for iodines and 16 or less for the borons.

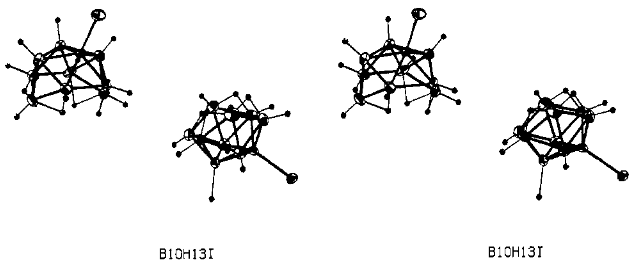


Figure 1.—Stereo view of the two molecules in the asymmetric unit of $B_{10}H_{13}I$.

atoms sitting at ten of the vertices of a slightly distorted regular icosahedron of which two neighboring vertices are unoccupied and with iodine substituting for one of the hydrogens. The substitution takes place at the 1 position[14a] although the charge distribution[14b] is slightly more favorable for electrophilic substitution at the 2,4 positions. As in the case of $B_{10}H_{14}$, the boron framework is conveniently described in terms of two almost regular pentagonal pyramids sharing a common edge (B_1–B_3). The folding angle of 80.2° (averaged over two molecules) between the base planes B_1–B_3–B_5–B_6–B_7 and B_1–B_3–B_8–B_9–B_{10} of the pentagonal pyramids is appreciably larger than the corresponding angle of 76° in $B_{10}H_{14}$ and is probably a steric effect of the substitution. The deviations of the atoms from these least-squares planes are small but significant (0.02 → 0.1 A).

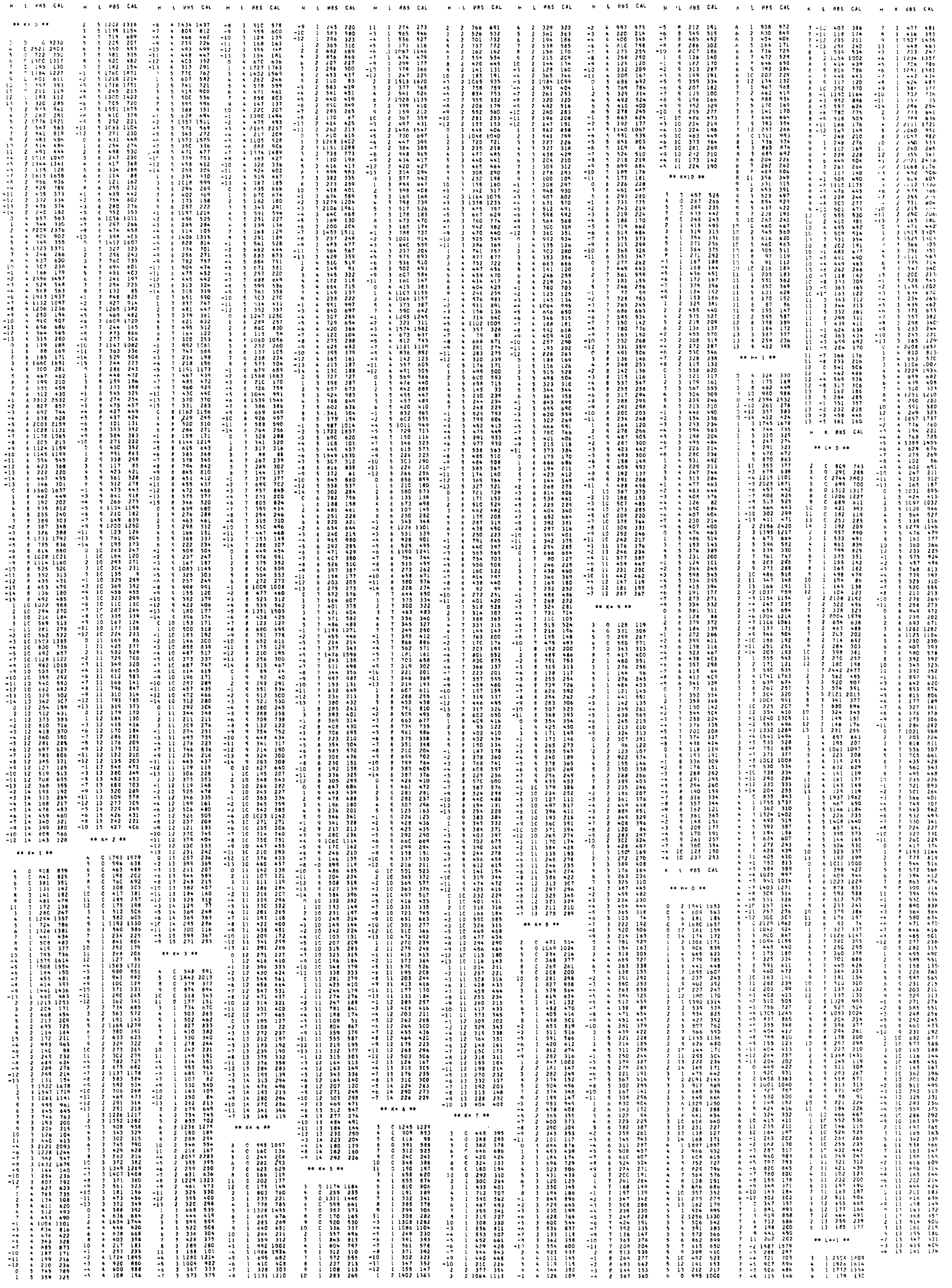
The intramolecular distances and bond angles, shown in Tables III and IV and Figures 2 and 3, are normal. The angles between the B–I bond and four of the adjacent B–B bonds range from 114 to 119°, while the fifth one (I–B_1–B_3) is considerably larger (127°), indicating a significant shift in the position of the iodine atom from the fivefold axis toward the

---

(14) (a) The numbering system suggested by Lipscomb[14b] (shown in Figure 2) has been used throughout this paper; (b) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $B_{10}H_{13}I^a$



---

[a] Note that some of the reflections appear more than once.

TABLE III

INTERATOMIC DISTANCES IN $B_{10}H_{13}I$[a]

	Distance, A		
	Molecule 1	Molecule 2	Esd[b]
I–B_1	2.195	2.152	0.013
I–B_2	3.405	3.426	0.014
I–B_3	3.511	3.525	0.014
I–B_4	3.352	3.355	0.014
I–B_5	3.345	3.331	0.013
I–B_{10}	3.305	3.317	0.013
B_1–B_2	1.77	1.81	0.02
B_1–B_3	1.73	1.77	0.02
B_1–B_4	1.76	1.75	0.02
B_1–B_5	1.77	1.77	0.02
B_1–B_{10}	1.75	1.78	0.02
B_2–B_3	1.77	1.75	0.02
B_2–B_5	1.81	1.77	0.02
B_2–B_6	1.73	1.71	0.02
B_2–B_7	1.84	1.74	0.02
B_3–B_4	1.80	1.78	0.02
B_3–B_7	1.71	1.73	0.02
B_3–B_8	1.76	1.78	0.02
B_4–B_8	1.79	1.83	0.02
B_4–B_9	1.74	1.76	0.02
B_4–B_{10}	1.80	1.79	0.02
B_5–B_6	1.81	1.75	0.02
B_5–B_{10}	2.02	2.01	0.02
B_6–B_7	1.87	1.78	0.02
B_7–B_8	1.91	1.95	0.02
B_8–B_9	1.76	1.84	0.02
B_9–B_{10}	1.79	1.79	0.02

[a] The average B–H distance is 1.20 ± 0.12 A for the unbridged hydrogens and 1.26 ± 0.13 A for the bridged hydrogens. The closest I–I approaches are 4.298 (1) A. [b] The standard deviations are the same on both molecules.

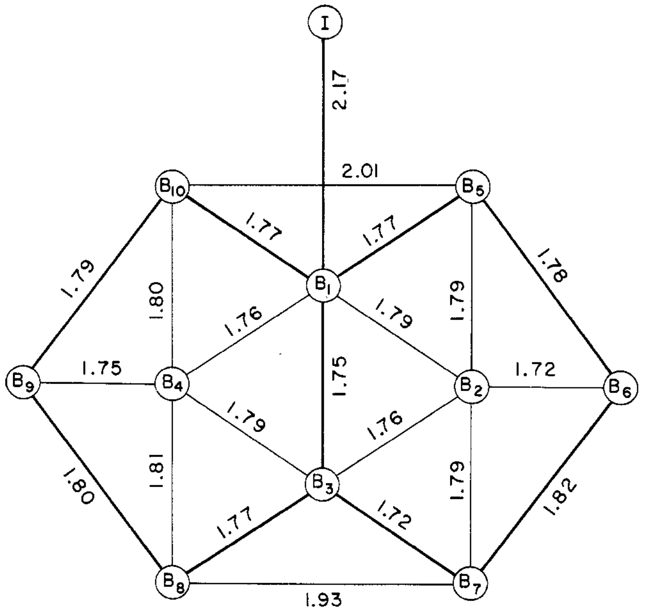


Figure 2.—Bond distances for $B_{10}H_{13}I$ averaged over the two independent molecules.

unoccupied vertex of the icosahedron. The angle between the B–I bond and the normal to the least-squares plane through the atoms B_2–B_3–B_4–B_{10}–B_5 is about 6°. Also, the distance B_5–B_{10} (2.01 A) is somewhat larger than the distance B_7–B_8 (1.95 A) and may be due to the presence of iodine. Table V compares some of

TABLE IV

INTERATOMIC ANGLES IN $B_{10}H_{13}I$

	Angle, deg		
	Molecule 1	Molecule 2	Esd[a]
I–B_1–B_2	117.9	119.5	1.0
I–B_1–B_3	126.3	128.1	1.0
I–B_1–B_4	115.3	118.4	1.0
I–B_1–B_5	114.6	116.0	1.0
I–B_1–B_{10}	113.3	114.7	1.0
B_5–B_1–B_2	61.4	59.1	0.7
B_2–B_1–B_3	60.5	58.7	0.8
B_3–B_1–B_4	61.9	61.0	0.8
B_4–B_1–B_{10}	61.6	61.1	0.7
B_{10}–B_1–B_5	69.8	69.0	0.7
B_1–B_2–B_3	58.7	59.4	0.7
B_3–B_2–B_7	56.6	59.4	0.7
B_7–B_2–B_6	63.0	62.3	0.9
B_6–B_2–B_5	61.6	60.3	0.9
B_5–B_2–B_1	59.3	59.3	0.6
B_8–B_3–B_4	60.6	61.9	0.9
B_4–B_3–B_1	59.9	59.0	0.7
B_1–B_3–B_2	60.8	61.9	0.7
B_2–B_3–B_7	63.8	59.9	0.8
B_7–B_3–B_8	66.7	67.6	0.8
B_1–B_4–B_3	58.3	60.0	0.7
B_3–B_4–B_8	58.6	58.9	0.8
B_8–B_4–B_{10}	60.0	61.6	0.9
B_9–B_4–B_{10}	60.7	60.4	0.9
B_{10}–B_4–B_1	58.9	60.4	0.6
B_6–B_5–B_2	57.1	58.3	0.8
B_2–B_5–B_1	59.3	61.5	0.7
B_1–B_5–B_{10}	54.6	55.8	0.6
B_5–B_6–B_2	61.3	61.5	1.0
B_2–B_6–B_7	61.4	59.7	0.8
B_6–B_7–B_2	55.7	58.0	0.8
B_2–B_7–B_3	59.6	60.6	0.8
B_3–B_7–B_8	57.8	57.3	0.7
B_9–B_8–B_4	58.5	57.2	0.8
B_4–B_8–B_3	60.9	59.2	0.8
B_3–B_8–B_7	55.5	55.1	0.7
B_8–B_9–B_4	61.6	61.2	0.9
B_4–B_9–B_{10}	61.4	60.8	0.8
B_9–B_{10}–B_4	57.9	58.8	0.8
B_4–B_{10}–B_1	59.5	58.5	0.7
B_1–B_{10}–B_5	55.6	55.2	0.6

[a] The standard deviations are the same on both molecules.

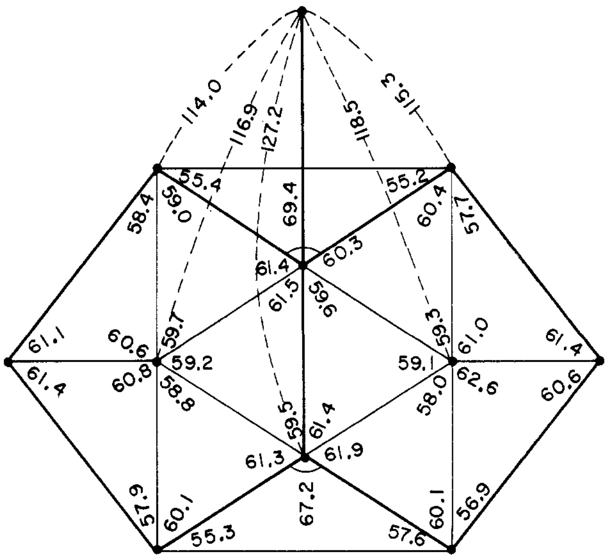


Figure 3.—Bond angles for $B_{10}H_{13}I$ averaged over the two independent molecules.

Table V

Comparison of Bond Distances in $B_{10}H_{14}$, $B_{10}H_{13}(C_2H_5)$, and $B_{10}H_{13}I$

	Distance, A			
	$B_{10}H_{14}$[a]	$B_{10}H_{14}$[b]	$B_{10}H_{13}$-(C_2H_5)[c]	$B_{10}H_{13}I$
B_1–B_3	1.78	1.71	1.78	1.75
B_1–B_4 (B_1–B_2)	1.79	1.80	1.79	1.77
B_1–B_{10} (B_1–B_5)	1.74	1.78	1.77	1.77
B_3–B_4 (B_2–B_3)	1.81	1.78	1.78	1.77
B_3–B_8 (B_3–B_7)	1.74	1.77	1.745	1.74
B_4–B_8 (B_2–B_7)	1.74	1.80	1.79	1.80
B_4–B_9 (B_2–B_6)	1.73	1.72	1.71	1.73
B_4–B_{10} (B_2–B_5)	1.76	1.76	1.775	1.79
B_8–B_9 (B_6–B_7)	1.76	1.77	1.78	1.81
B_9–B_{10} (B_5–B_6)	1.78	1.77	1.78	1.78
B_5–B_{10}	2.01	2.01	1.96	2.01
B_7–B_8	2.01	2.01	1.98	1.93
Av esd	0.03	0.02	0.01	0.02

[a] J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.*, **3**, 436 (1950). [b] E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 209 (1957). [c] A. Perloff, *Acta Cryst.*, **17**, 332 (1964).

the B–B distances in $B_{10}H_{14}$,[13,15] $B_{10}H_{13}(C_2H_5)$,[16] and $B_{10}H_{13}I$. This comparison suggests that there are no important differences in B–B bond lengths among the three structures except possibly for the long B_5–B_{10} and B_7–B_8 bonds. The distances B_2–B_6 and B_4–B_9 appear consistently shorter in all three compounds. Interestingly, according to Lipscomb's three-center model of $B_{10}H_{14}$, this is the only two-center bond in the entire boron framework.

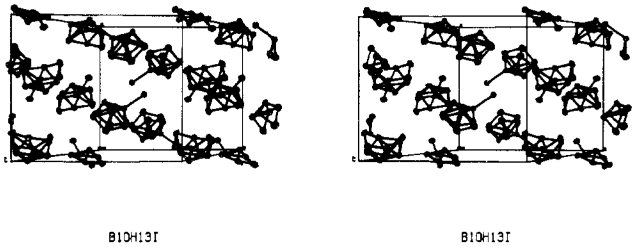


Figure 4.—Contents of one unit cell of $B_{10}H_{13}I$. The hydrogen atoms are not shown.

The average unbridged B–H distance is 1.20 (12) A as against that of 1.26 A in $B_{10}H_{14}$ and 1.11 A in $B_{10}H_{13}$-(C_2H_5). The average bridged B–H distance of 1.26 (13) A is closer to the value of 1.27 A observed in $B_{10}H_{13}$-(C_2H_5) than to that of 1.39 A in $B_{10}H_{14}$. The exact positions of the hydrogen atoms in this series of compounds must await a neutron diffraction investigation.

The crystal structure consists of the packing of discrete polyhedral cages of $B_{10}H_{13}I$ molecules which fall in sheets almost parallel to the (120) planes (see Figure 4). The iodine atoms protrude from the sheets, and pairs of iodines are in van der Waals contact at a distance of 4.3 A. The stacking of the sheets however is not entirely dependent on the I–I interactions, but on the I–H interactions as well. The cage opening in each molecule faces an iodine atom from a neighboring molecule, and the iodine seems to be in van der Waals contact with the bridge hydrogens of the former. The shortest I–H distances are ~3.4 A and are in good agreement with the sum of the van der Waals radii (3.35 A).

Acknowledgment.—We wish to thank Dr. M. Hillman of the Nuclear Engineering Department of Brookhaven National Laboratory for providing us with the crystals. We are also grateful to Mr. Sam J. La Placa for many useful suggestions. A. S. thanks the International Atomic Energy Agency for a Fellowship.

---

[15] E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 209 (1957).

[16] A. Perloff, *Acta Cryst.*, **17**, 332 (1964).

Contribution from the Department of Chemistry,
University of South Florida, Tampa, Florida 33620

Nuclear Magnetic Resonance Study of Aluminum Borohydride

By P. CALVIN MAYBURY and JOSEPH E. AHNELL[1]

Received November 1, 1966

The nuclear magnetic resonance spectrum of aluminum borohydride has been studied at a temperature range −40 to 90°. A freshly distilled sample of $Al(BH_4)_3$ at room temperature has a single broad spectrum. Heating a sample in the liquid state leads to one of two changes in the nmr spectrum: (1) a reversible conversion from the broad spectrum to a quartet spectrum and (2) an irreversible conversion from a broad spectrum to a quartet spectrum. The experimental conditions contributing to these conversions are reported. A mechanism is proposed to account for the spectral observations and involves the formation of a new structure of $Al(BH_4)_3$.

Introduction

In exchange studies of aluminum borohydride with deuterium[2] and deuteriodiborane[3] results were obtained which might be explained on the basis of a structural change of the aluminum borohydride molecule when a sample is heated in the temperature range 50–80°. These results led us to examine critically the nuclear magnetic resonance spectrum of $Al(BH_4)_3$. Ogg and Ray[4] first reported the nmr spectrum of

---

[1] Student participant sponsored by National Science Foundation Undergraduate Science Education Grant No. G-1210.

[2] P. C. Maybury and J. C. Larrabee, Abstracts of Papers, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p 28M.

[3] P. C. Maybury and J. C. Larrabee, *Inorg. Chem.*, **2**, 885 (1963).

[4] R. A. Ogg and J. D. Ray, *Discussions Faraday Soc.*, **19**, 215 (1955).