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The Crystal and Molecular Structure of Iodopentaborane-9

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The molecular configuration of 1-iodopentaborane-9 (B_5H_8I) has been determined in a partial three-dimensional X-ray crystallographic study. The unit cell is monoclinic with $a=11{\cdot}24$, $b=10{\cdot}03$, $c=13{\cdot}14$ Å, $\beta=110°5'$, $Z=8$ and the space group is $C2/c$. The structure refined smoothly to R (observed data only) = 13·0% for data taken at −25°C which included 417 observed and 112 unobserved reflections in the $h0l$, $h1l$, $h2l$, and $hk0$ levels. Individual isotropic temperature factors were used for the one iodine and five boron atoms. Hydrogen atom parameters were not included.

Experimental

Iodopentaborane (B_5H_8I) forms colorless crystals melting at 54°C. It is soluble in most common organic solvents and reacts slowly with water vapor and oxygen, forming a fuming mist and giving off odors characteristic of the boron hydrides.

Because of the high vapor pressure of iodopentaborane and its sensitivity to air, single crystals were grown from the melt in small, thin-walled, Pyrex capillary tubes. The tubes were first filled with crystallites of the compound which was prepared according to the procedure of Hall, Subbana & Koski (1964) and then sealed off in a dry box. The unit-cell parameters and space group were determined from precession photographs of the $0kl$, $1kl$, $h0l$, and $h1l$ levels taken at room temperature with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å). The room-temperature cell dimensions were used throughout the structure analysis since the unit-cell dimensions at −25°C agreed with the room temperature values within the estimated standard deviations. The lattice constants reported here agree well with those of Norment, Henderson & South (1960).

The systematic absences observed for this crystal are as follows:

hkl	$h+k=2n+1$
$h0l$	$l=2n+1(h=2n+1)$
$0k0$	$(k=2n+1)$

On this basis the space group is Cc or $C2/c$. The Howells, Phillips & Rogers (1950) statistical test applied to the $0kl$ and $h0l$ data indicated that these projections are centered. Since these results are consistent only with the space group $C2/c$, it was used in the structural determination. The complete determination of the structure showed that $C2/c$ is the correct choice. The assumption of eight molecules in the unit cell gives a reasonable density, 1·80 g.cm^{-3}, a reasonable molecular volume, 174 Å^3, and allows the molecules to be in the general positions of the space group. The final structure verified this assumption. The density of the crystal was not determined because of its high solubility in suitable solvents.

Intensity data were obtained on a Buerger precession camera for the $h0l$ and $0kl$ projections at room temperature and for the $h0l$, $h1l$, $h2l$, and $hk0$ levels at −25°C. The intensities were estimated with the aid of a densitometer. The very weak reflections were estimated by eye and the unobserved reflections were set equal to one half the minimum observed intensity.

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Exposure times varying from 30 minutes to 48 hours were required in order to allow estimation of the intensities for all reflections in each level. The crystal was maintained at −25 °C by passing a stream of dry air through a dry ice bath and then onto the crystal through a nozzle based on a design by Post, Schwartz & Fankuchen (1951).

The data were put on a common scale using the exposure times of each film and corrected for Lorentz and polarization effects. Final scaling was accomplished in the least-squares refinement of the structure. Although absorption effects were not negligible, no absorption corrections were applied because of the difficulties inherent in the geometry of the precession technique and because the capillary axis did not lie close to the rotation axis of the precession camera.

Crystal data

1-Iodopentaborane-9, B_5H_8I; m.p. 54 °C
Monoclinic, space group $C2/c$
Unit cell (room-temperature values):
$a=11{\cdot}24$, $b=10{\cdot}03$, $c=13{\cdot}14$ Å, $\beta=110°5'$
$Z=8$, $\varrho(\text{calc})=1{\cdot}80$ g.cm^{-3}

Based on prior experience with the camera and measuring devices used the standard deviation of each axis is estimated to be ±0·04 Å and that of the angle β to be ±10′.

Structure determination

The structure determination was initiated with the $h0l$ and $0kl$ room temperature data. Patterson syntheses for both these levels revealed approximate positional parameters for the iodine atom. Because the b axis is the shortest axis it was expected that the $h0l$ projection would be less subject to problems of overlap and thus would reveal the boron positions most clearly. Using only the iodine positional parameters and an overall temperature factor of 3·5 an $h0l$ electron density map was calculated with the low temperature data. The $h0l$ R* index using only the iodine atom was 20·7%. Scattering curves for both iodine and boron, as neutral atoms, were taken from *International Tables for X-ray Crystallography* (1962). The dispersion corrections of Dauben & Templeton (1955) were applied to the scattering curve of iodine. On the basis of this map four orientations of a molecular model consistent with the boron framework of pentaborane-9 were developed and an electron density map computed for each. The R values for these four calculations ranged upward from 21·5%.

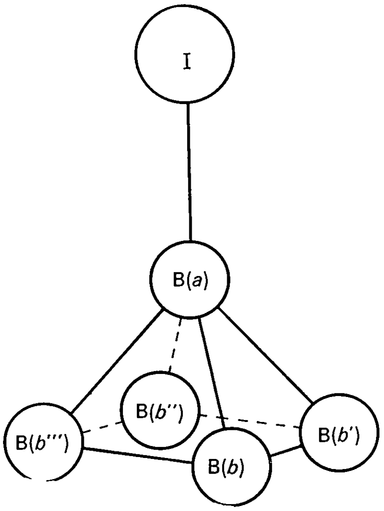

Fig. 1. A model of the B_5H_8I molecule showing only the iodine and boron atoms. The iodine atom is labelled I, the apical boron B(a), and the four basal boron atoms B(b), B(b'), B(b'') and B(b''').

In order to distinguish between these four possible orientations of the molecule an $h0l$ electron density map was computed in which the contribution of the iodine atom was subtracted. Since this difference map suffers less from spurious effects due to termination of series errors, boron positions were more clearly discernible. The molecular orientation which gave an R of 21·5% appeared most consistent with the maxima in the difference map. Thus, this model was refined in the $h0l$ projection using full-matrix least-squares refinement. After three cycles of refinement on the position parameters of the iodine and five boron atoms and one cycle including individual isotropic temperature factors, the R value reduced to 12·8%.

Approximate y parameters for the five boron atoms were calculated by referring to the y parameter of the iodine atom obtained from the $0kl$ Patterson projection and to the known bond distances and angles in pentaborane-9 (Dulmage & Lipscomb, 1952). These parameters were used in calculating a three-dimensional electron density map using all 529 reflections from the low temperature data. All boron maxima were clearly discernible and the R value was 17·3%. This structure was refined by means of three cycles of full-matrix least-squares refinement on position parameters only and three more cycles which included individual isotropic temperature factors. The final R value, based on the 417 observed data, was 13·0% and all the indicated shifts in both position and temperature parameters were less than the indicated errors on each. Refinement was terminated at this point, because it was not felt that the data were adequate to provide meaningful anisotropic factors. Throughout the refinement computations all reflections within one level were given equal weight. The relative weights of the different levels in the final refinement were $h0l=h1l=0{\cdot}878$, $h2l=0{\cdot}244$, and $hk0=0{\cdot}625$.

Discussion

A model of the B_5H_8I molecule including the boron and iodine atoms is shown in Fig. 1. The iodine atom is clearly shown to be bonded to the apical boron in the tetragonal boron pyramid. The final parameters, with their associated errors, are listed in Table 1. In-

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* All R values quoted in this paper are based on observed data only.

Table 1. *Final atomic parameters*

Atom	$x\times10^3$	$\sigma_x\times10^3$	$y\times10^3$	$\sigma_y\times10^3$	$z\times10^3$	$\sigma_z\times10^3$	B	σ_B
I	19·1	0·1	184·9	0·3	68·9	0·1	4·20	0·03
B(*a*)	155	2	350	5	136	1	3·0	0·3
B(*b*)	130	2	505	11	170	2	4·2	0·5
B(*b*′)	215	2	470	5	78	2	4·5	0·5
B(*b*″)	317	2	352	6	172	2	4·9	0·6
B(*b*‴)	220	3	393	7	271	2	5·7	0·8

Table 2. *Interatomic distances and bond angles*

Bonded atom types	Bond distances and angles	Atom designations (Fig. 1)
Iodine – boron	2·20 ± 0·03 Å	I–B(*a*)
Boron (apex) – boron (base)	1·70 ± 0·07	B(*a*)–B(*b*)
	1·72 ± 0·04	B(*a*)–B(*b*′)
	1·72 ± 0·02	B(*a*)–B(*b*″)
	1·71 ± 0·03	B(*a*)–B(*b*‴)
Boron (base) – boron (base)	1·83 ± 0·03	B(*b*)–B(*b*′)
	1·78 ± 0·04	B(*b*′)–B(*b*″)
	1·95 ± 0·03	B(*b*″)–B(*b*‴)
	1·81 ± 0·05	B(*b*‴)–B(*b*)
Boron (base) – boron (apex) – boron (base)	64·7 ± 1·9°	B(*b*)–B(*a*)–B(*b*′)
	62·2 ± 1·5	B(*b*′)–B(*a*)–B(*b*″)
	69·1 ± 1·0	B(*b*″)–B(*a*)–B(*b*‴)
	64·3 ± 1·9	B(*b*‴)–B(*a*)–B(*b*)
Iodine – boron (apex) – boron (base)	130·4 ± 1·2	I–B(*a*)–B(*b*)
	132·8 ± 1·0	I–B(*a*)–B(*b*′)
	131·9 ± 2·3	I–B(*a*)–B(*b*″)
	126·9 ± 1·8	I–B(*a*)–B(*b*‴)

Table 3. *Observed and calculated structure factors of low-temperature data used in the final refinement*

h0ℓ

ℓ	$\lvert s_1F_o\rvert$	F_c
h=0		
2	188	198
4	90	-83
6	193	-202
8	165	-176
10	59	-55
12	36	46
14	43	54
16	27	26
h=2		
-16	35	37
-14	44	51
-10	75	-79
-8	165	-185
-6	198	-192
-4	16	33
-2	323	373
0	266	276
2	152	134
4	122	-102
6	184	-180
8	141	-131
10	17	-11
12	45	44
14	41	40
16	14	14
h=4		
-18	11	12
-16	18	34
-14	38	54
-10	98	-100
-8	159	-186
-6	149	-142
-4	99	86
-2	280	281
0	265	250
2	74	75
4	102	-92
6	208	-185
8	92	-82
12	47	39
14	42	28
h=6		
-16	38	45
-14	25	36
-12	12	-21
-10	107	-121
-8	152	-160
-6	45	-50
-4	136	133
-2	221	204
0	192	178
4	167	-145
6	118	-101
8	34	-30
10	16	16
12	32	29

h0ℓ

ℓ	$\lvert s_1F_o\rvert$	F_c
h=8		
-18	13	21
-16	15	34
-14	9	17
-12	34	-39
-10	78	-88
-8	85	-95
-6	8	-12
-4	106	98
-2	180	160
0	97	81
2	52	-36
4	98	-79
6	82	-59
8	9	-17
10	8	13
12	13	22
h=10		
-16	17	22
-12	9	-30
-10	74	-82
-8	63	-60
-6	8	12
-4	102	94
-2	117	103
0	40	32
2	37	-39
4	72	-52
6	44	-38
h=12		
-16	7	16
-12	35	-37
-10	39	-49
-8	20	-25
-6	24	31
-4	77	62
-2	47	44
2	30	-23
4	51	-35
6	18	-16
h=14		
-12	16	-26
-10	25	-26
-6	13	18
-4	36	35
-2	34	25
2	30	-20

h1ℓ

ℓ	$\lvert s_0F_o\rvert$	F_c
h=0		
-17	13	21
-16	7	10
-15	7	2
-14	9	19
-13	43	-49
-11	91	-100
-9	63	-75
-8	82	-82
-7	15	26
-6	72	-75
-5	224	240
-3	315	336
2	152	150
3	269	-278
5	153	-173
6	92	-95
8	44	-50
9	81	99
11	68	83
12	9	15
14	7	19
15	7	-13
h=3		
-17	7	16
-16	7	18
-14	9	23
-13	44	-55
-11	79	-100
-10	45	-47
-9	71	-72
-8	79	-81
-7	105	105
-6	69	-68
-5	240	244
-4	52	40
-3	243	233
-2	131	108
-1	16	14
0	187	170
1	212	-195
2	38	34
3	239	-237
4	87	-74
5	117	-111
6	69	-73
7	17	26
8	28	-35
9	85	92
11	61	64
13	9	9
14	7	16
h=5		
-17	7	14
-16	7	15
-13	56	-69
-11	81	-93
-10	31	-44
-9	11	-19
-8	61	-60

h1ℓ

ℓ	$\lvert s_1F_o\rvert$	F_c
h=5		
-7	117	117
-5	224	227
-3	141	133
-2	109	113
-1	23	-27
0	81	74
1	192	-176
2	18	-12
3	206	-181
4	49	-38
5	62	-58
6	36	-36
7	62	59
8	34	-30
9	69	70
11	39	33
12	9	15
h=7		
-15	13	-26
-13	50	-67
-11	47	-62
-10	29	-40
-8	36	-51
-7	122	114
-6	27	-33
-5	145	146
-4	70	57
-3	112	94
-2	84	76
-1	82	-70
0	55	46
1	161	-149
3	120	-101
4	44	-33
6	50	-46
7	49	42
9	51	45
h=9		
-15	26	-30
-13	35	-48
-12	9	-21
-11	27	-34
-10	33	-38
-9	8	20
-8	25	-29
-7	88	96
-6	8	8
-5	127	110
-4	45	47
-3	13	22
-2	46	45
-1	72	-65
1	121	-96
2	8	-11
3	61	-50
4	36	-34
6	13	-18
7	40	32
9	38	28

h1ℓ

ℓ	$\lvert s_0F_o\rvert$	F_c
h=11		
-15	9	-23
-14	7	-2
-13	19	-36
-11	9	-18
-10	13	-19
-9	15	34
-7	65	72
-5	59	57
-4	19	24
-2	15	24
-1	70	-54
0	9	15
1	65	-52
2	13	-13
3	21	-25
4	13	-18
5	7	10
6	7	-7
7	41	24
9	38	15
h=13		
-14	7	-2
-13	13	-23
-12	7	-10
-11	7	-2
-10	7	-18
-9	25	31
-8	7	-7
-7	36	43
-5	19	21
-4	21	22
-3	9	-9
-2	13	17
-1	37	-32
0	7	-2
1	42	-32
2	9	-12
3	7	-8
5	9	11
7	17	13
h=15		
-10	7	-8
-9	7	19
-8	7	1
-7	7	22
-6	10	8
-5	7	12
-4	7	9
-3	7	-11
-2	7	5
-1	29	-21
1	15	-14

h2ℓ

ℓ	$\lvert s_0F_o\rvert$	F_c
h=0		
5	171	-169
6	116	129
8	96	99
9	74	78
10	16	31
11	45	67
h=2		
-11	80	-89
-10	27	38
-9	36	-51
-8	114	135
-7	55	60
-6	144	139
-5	172	168
2	146	-125
3	218	-202
4	70	77
5	116	-124
6	128	134
7	20	25
8	74	81
9	78	74
11	40	53
h=4		
-13	35	-53
-11	43	-69
-10	72	79
-8	115	126
-7	78	75
-6	53	58
-5	184	180
-4	53	-60
-3	155	149
-2	208	-180
-1	27	-15
0	214	-167
1	148	-153
2	18	-18
3	184	-170
4	78	85
5	20	-36
6	94	93
7	22	29
8	37	53
9	46	59
11	18	38
h=6		
-13	31	-49
-11	36	-52
-10	58	72
-8	80	87
-7	75	84

h2ℓ

ℓ	$\lvert s_0F_o\rvert$	F_c
h=6		
-6	28	37
-5	149	146
-4	49	-54
-3	101	92
-2	154	-141
-1	71	-57
0	118	-108
1	96	-118
3	80	-88
4	61	64
5	16	-37
6	77	72
7	30	35
8	18	29
9	26	47
h=8		
-12	17	28
-11	37	-49
-10	51	63
-8	67	64
-7	92	92
-5	93	97
-4	80	-83
-2	121	-112
-1	63	-43
0	56	-46
1	100	-91
3	66	-64
4	64	59
6	31	46
7	26	34
8	19	6
h=10		
-10	30	44
-9	23	26
-8	23	40
-7	92	92
-5	50	53
-4	54	-60
-2	61	-53
-1	54	-44
0	17	-19
1	65	-57
3	40	-30
h=12		
-8	18	20
-7	31	38
-5	18	35
-4	30	-37
-2	40	-32
-1	51	-37

hk0

h	$\lvert s_4F_o\rvert$	F_c
k=1		
1	122	115
k=2		
0	194	-211
2	243	-246
12	13	-10
k=3		
1	309	-318
3	220	-230
5	160	-174
7	77	-90
9	45	-53
11	13	-12
k=4		
0	32	-30
4	32	-18
8	15	3
10	12	1
14	7	1
k=5		
1	199	203
3	183	180
5	127	130
7	71	66
9	39	32
11	20	13
k=6		
0	182	183
2	142	135
4	98	95
6	76	82
8	29	40
k=7		
1	53	-50
3	38	-27
5	30	-21
7	44	-25
9	24	-7
11	10	1
k=8		
0	124	-117
2	137	-122
4	113	-100
6	70	-59
8	36	-30
10	18	-15
12	11	-4

hk0

h	$\lvert s_4F_o\rvert$	F_c
k=9		
1	63	-55
3	49	-41
5	32	-32
7	9	-19
k=10		
0	46	41
2	55	45
4	44	34
6	33	18
8	30	15
10	20	6
k=11		
1	73	56
3	67	48
5	48	38
7	25	21
9	17	10
k=12		
0	21	11
2	14	9
k=13		
1	36	-27
3	32	-20
5	25	-14
k=14		
3	15	-18

tramolecular bond distances and angles are shown in Table 2. The final results are identical with those reported in a preliminary note (Hall, 1964), but are presented here in greater detail.

It was expected that the molecule would possess a fourfold axis along the boron–iodine bond in analogy to that found in the parent compound, B_5H_9. However, the bond distances and angles listed in Table 2 show some departure from fourfold symmetry. The greatest discrepancy is in the long boron–boron basal bond, 1·95 Å. This unexpected departure from fourfold symmetry may be due to the lack of complete data and to the absorption problem which was not taken into account.

It is also possible that the long B–B bond may be a consequence of the molecular packing which is shown in Fig. 2. The closest intermolecular boron–boron approach of 4·32 Å is between B(b''') of one molecule and B(b'') from another molecule related by a 2_1 axis. However, if the hydrogen atoms are assumed to have the same distances and angles relative to the basal boron atoms as in the B_5H_9 compound, this short intermolecular B–B distance does not require an intermolecular H–H distance shorter than 2·6 Å. Since this exceeds the normal 2·4–2·5 Å van der Waals distance for H–H contact there seems to be no reason to anticipate any undue strain in the molecule from only the boron end of the molecule. There is a relatively short intermolecular I–I approach of 4·00 Å (expected van der Waals distance, 4·3 Å) across the centers of symmetry which are in the planes $y=0$ and $y=\frac{1}{2}$. Similar halogen–halogen interactions have been observed in many other crystal structures (Voet & Lipscomb, 1964). This intermolecular I–I interaction, in conjunction with the molecular packing, would seem to be sufficient cause to explain the observed distortion from the fourfold symmetry expected for the isolated molecule.

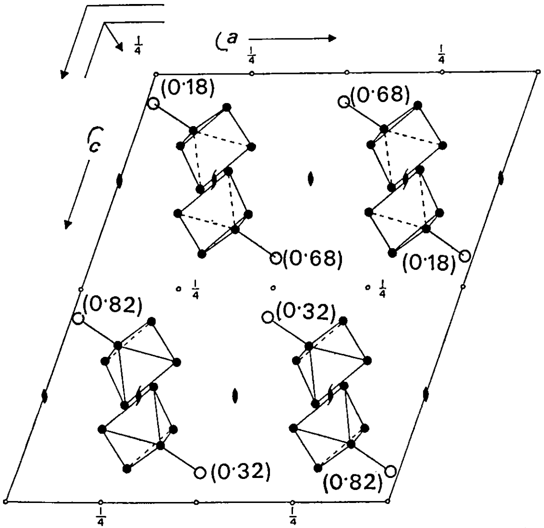

Fig. 2. Molecular packing of B_5H_8I as seen in the projection along the b axis. Open circles indicate the iodine atoms and solid circles indicate boron atoms. Hydrogen atoms have been omitted. Iodine y parameters are shown in parentheses.

Although the errors on the bond distances are rather large, the boron (apex)–boron (base) bond distances compare well with those in other boron hydrides (Dulmage & Lipscomb, 1952; Lavine & Lipscomb, 1954; Nordman & Lipscomb, 1953; Hirshfeld, Eriks, Dickerson, Lippert & Lipscomb, 1958; Kasper, Lucht & Harker, 1950) which fall in the range of 1·70 to 1·80 Å. The boron–iodine bond distance of 2·20 Å in B_5H_8I is somewhat longer than the 2·10 Å distance found in BI_3 (Ring, Donnay & Koski, 1962). It is believed that conditions for multiple bonding which would shorten the boron–iodine bond are more favorable in BI_3 than in B_5H_8I.

Thus, it appears that B_5H_8I is formed from B_5H_9 and I_2 by electrophilic attack by iodine. The apical boron atom of B_5H_9 is believed to be more negative than the basal boron atoms (Eberhardt, Crawford & Lipscomb, 1954) and the apical boron atom is shown to be the position of substitution, in agreement with conclusions derived from nuclear magnetic resonance studies by Schaeffer, Shoolery & Jones (1958).

The sample of B_5H_8I was prepared and purified by one of the authors (LHH) at the Department of Chemistry of the Johns Hopkins University. The computations carried out in this study were performed on an IBM 7094 computer utilizing the X-ray 63 system of crystallographic programs developed at the University of Washington and the University of Maryland (1964).

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