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September 1967

Contribution from the Department of Chemistry and Lawrence Radiation
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The Crystal Structure of the Rubidium Salt of an Octadecahydroeicosa-
borate(2-) Photoisomer¹

by Barry G. DeBoer,² Allan Zalkin, and David H. Templeton

Abstract

The crystal structure of the rubidium salt of an octadecahydroeicosa-
borate(2-) photoisomer, $\text{Rb}_2\text{B}_{20}\text{H}_{18}$, has been determined by X-ray diffraction
with a single crystal specimen. The orthorhombic unit cell, space group
 $\text{Pn}2_1\text{a}$, with $a = 12.334 \text{ \AA}$, $b = 19.014 \text{ \AA}$, $c = 7.260 \text{ \AA}$, contains four formula
units. The structure was determined by Patterson and Fourier techniques
and refined by a full-matrix least-squares procedure. The non-centric nature
of the space group was demonstrated by the measurement of anomalous disper-
sion effects. The anion consists of two capped-square-antiprismatic B_{10}
polyhedra joined by a pair of hydrogen bridges, one between each pair of
equatorial four-rings, such that the result has an approximate $2/m$ (C_{2h})
point symmetry. A list of thirteen possible isomers covering reasonable
choices of bridge positions is presented together with their point symmetries.

Introduction

In the last few years, there has been considerable interest in the reactions of the $B_{20}H_{18}^{2-}$ ion and proposals have been made for the probable structures of the products.³⁻¹⁰ The structure of the parent ion has been established^{6,7} as a pair of capped-square-antiprismatic B_{10} polyhedra connected by a pair of three-center bonds which join the 1-2 edge of one polyhedron to the 2' position of the other and the 1'-2' edge of the second to the 2 position of the first.¹¹

Recently, Hawthorne and Pilling³ observed the isomerization of $B_{20}H_{18}^{2-}$ in acetonitrile solution when exposed to light from a mercury lamp. They predicted that the photoisomer was one of the two possible structures which result when two B_{10} polyhedra are joined by a pair of B-H-B bridges, one between each pair of equatorial four-rings.

This work was undertaken to determine the geometry of the photoisomerization product. The results prove that the geometry is the centrosymmetric ($2/m$ or C_{2h}) alternative of the pair suggested by Hawthorne and Pilling.

Experimental

Crystals of the rubidium salt were sent to us by Professor M. F. Hawthorne of the University of California, Riverside. Part of this material was recrystallized from water by slow evaporation. Two sets of intensity data were recorded from different crystals, one from the original sample and the other from the recrystallized portion.

A small, colorless crystal fragment from the original sample was glued to the end of a Pyrex glass fiber, with its long direction parallel to the fiber,

the instrument ϕ axis, and the a axis of the crystal. Preliminary oscillation and Weissenberg photographs were taken with $\text{CuK}\alpha$ radiation to find the Laue group, extinction rules, and cell dimensions. More accurate cell dimensions were derived from Bragg angles of the $h00$, $0k0$, and $00l$ reflections measured with a General Electric manual goniostat using molybdenum radiation and a Zr filter at the receiving slit. The components of the alpha doublet were resolved ($\lambda(\text{K}\alpha_1) = 0.70926 \text{ \AA}$). The same apparatus was used to measure intensities of 1153 independent (in the sense of Laue group) reflections, including 283 recorded as zero, but not including space group absences. Each reflection was counted for 10 seconds with crystal and counter stationary. Backgrounds were measured for each reflection which was seriously affected by streaking from other orders; otherwise, the background was taken from a plot of background as a function of 2θ for various values of ϕ and χ . The measurements included reflections to $2\theta = 45^\circ$, or $\sin\theta/\lambda = 0.540$. Repeated measurements of several arbitrarily chosen reflections showed systematic trends in which one reflection actually became slightly stronger and others decreased by various ratios, in one case a factor of two. It is suspected that these changes were caused by a bending or cracking of the crystal induced at least in part by radiation damage. In spite of these inauspicious circumstances, we proceeded with the analysis. When it became evident that the quality of the data was unacceptable, we selected from the recrystallized material a second crystal about $0.11 \times 0.06 \times 0.05 \text{ mm}$ in size and of much better appearance than the first. Cell dimensions and reflection intensities were measured with the same technique as before except that a shutter excluded the X-rays from the crystal except during the actual counting time. The measurements included 1158 Laue-independent reflections, including 240 recorded as zero. The intensities of

several reflections which were measured at frequent intervals showed only small, random fluctuations.

Calculations with the partly refined structure permitted identification of reflections which were most likely to show violations of Friedel's rule. Eleven of these and six others of simple indices were selected. Each member of the sets $\pm h$, k , $\pm l$ and $\pm h$, $-k$, $\pm l$ which was observable with the quarter-circle goniometer in this setting (a axis) was counted at least twice for 100 seconds. These data gave a total of 1175 intensities (independent in the sense of the point group, but including 17 Friedel pairs).

Weighting factors were derived from standard deviations assigned to the raw intensities of five percent of the intensity or one count per second, whichever was greater, except for the anomalous dispersion data, where standard deviations were estimated from the scatter between measurements made within the sets $k > 0$ and $k < 0$. The calculated absorption coefficient, μ , of 60 cm^{-1} , and the dimensions of this crystal indicate that μs is limited between 0.3 and 0.5, where s is the maximum path length of an X-ray within the crystal. We estimate that the variation in intensities due to absorption is not more than twenty percent and is distributed in such a way as to be largely absorbed by temperature factors.

Both data sets were corrected for Lorentz and polarization effects, but no corrections were made for absorption or extinction.

Pyroelectricity was indicated by attraction of a crystal to the side of the glass dewar after the crystal was quickly dipped into liquid nitrogen.

Computations were performed on an IBM 7044 with a 32K memory except for final refinements, which were done on a CDC 6600. Fourier syntheses and dis-

tance-and-angle calculations were done by Zalkin's (unpublished) FORDAP and DISTAN programs. Our unpublished version of the Ganzel-Sparks-Trueblood least-squares program minimizes the function $\sum_w (|\underline{kF}_o| - |\underline{kF}_c|)^2 / \sum_w |\underline{kF}_o|^2$, where $\underline{F}_o$ and $\underline{F}_c$ are the observed and calculated structure factors, respectively, w is the weighting factor, and k is the scale factor. This least-squares program has been modified to handle anomalous dispersion and these effects were included in the later refinements. The atomic scattering factors¹² for Rb^+ were corrected by $\Delta f' = -0.9$ electrons and $\Delta f'' = +3.1$ electrons as the real and imaginary parts of the anomalous dispersion. Scattering factors for boron and hydrogen were also taken from standard tables.¹² The anisotropic temperature factors used have the form: $\exp(-0.25 \sum_i \sum_j h_i h_j b_{ij} B_{ij})$, $i, j = 1, 2, 3$, where b_{ij} is the ij th reciprocal axis.

Results

Four formula units of $\text{Rb}_2\text{B}_{20}\text{H}_{18}$ are contained in the orthorhombic unit cell with dimensions $a = 12.344 \pm 0.007$ A, $b = 19.014 \pm 0.010$ A, $c = 7.260 \pm 0.005$ A. The calculated density of 1.58 g/cc agrees with the value (1.57 $\pm$ 0.01 g/cc) obtained by flotation in a mixture of carbon tetrachloride and dibromoethane. The errors are estimates. The Laue symmetry and observed extinction rules of $0k\ell$, $k+\ell \neq 2n$ and $hk0$, $h \neq 2n$ correspond to both the centric Pnma and the non-centric $\text{Pn}2_1a$. The positive test for pyroelectricity and the violations of Friedel's rule (presented below) indicate the non-centric $\text{Pn}2_1a$, and this choice leads to a successful structure with each atom in the general set of

positions: (x, y, z; 1/2 - x, 1/2 + y, 1/2 + z; -x, 1/2 + y, -z; 1/2 + x, y, 1/2 - z).

Determination of Structure.— The Patterson function calculated from the first data set was consistent with either one rubidium ion in the eight-fold $Pnma$ or a pair of nearly-centric rubidium ions in the four-fold $Pn2_1a$. The latter was chosen because of the observed pyroelectric effect and the broadening of the Patterson peaks in the a and c directions. Four cycles of least-squares on two slightly non-centric rubidium ions with isotropic temperature factors reduced the R factor for 811 low-angle data of the first set to 0.323 where $\underline{R} = \sum \frac{||\underline{kF}_o| - |\underline{F}_c||}{\sum |\underline{kF}_o|}$. The zero coordinate of the y axis in the polar space group $Pn2_1a$ was defined by requiring the two rubidium ions to have equal and opposite y coordinates in this and all subsequent refinements. A Fourier synthesis phased on the rubidiums was calculated and various choices of peaks refined as boron atoms on a cut-and-try basis. In these trials, the appearance of a large temperature factor was taken as an indication of a poor choice of atomic position. After several trials, a difference Fourier was calculated on the basis of the two rubidium ions and 16 borons which had been "found". This difference Fourier indicated that the rubidium ions were rather badly anisotropic. The same 16 borons plus four more selected from the difference Fourier were refined with the rubidium ions allowed anisotropic temperature factors. R dropped to 0.233 with two of the new borons going to large temperature factors. It was suddenly seen that sixteen of the eighteen "good" borons were arranged in pairs about a pseudo-center (local, non-crystallographic inversion center) and that the addition of two more borons in positions

pseudo-centric to the remaining pair produced two capped square anti-prisms which had a pair of short equatorial-equatorial distances between them.

Two anisotropic rubidium atoms and these twenty borons refined to $R = 0.218$ on all 1153 data of the first set.

An empirical correction for absorption and for degradation of the crystal was attempted, but R was not significantly reduced. The possibilities of disorder in the orientation of the boron structure, of being in the wrong space group, and of having the rubidium atoms "trapped" in the wrong places by false minima were all investigated without improving the agreement.

It was at this time that the second data set was taken and the first set discarded. The structure found from the first data set immediately refined to $R = 0.158$ on the 1158 data of the second set. An inspection of the observed and calculated structure factors revealed a systematic error in the second data set caused by the scattering of the irradiating X-ray beam off a telescope into the counter near a particular value of theta. When the affected data were removed by deleting all data with $\sin\theta/\lambda \geq .50$, R dropped to 0.114 on 925 data.

All the data in the neighborhood of the systematic error (40 to 45 degrees 2θ) were retaken with a lead sheet shielding the counter from the spurious X-rays and other data showing large disagreements were remeasured to check for errors such as mis-set angles and mis-punched cards. At this time, the seventeen reflections were selected and examined for anomalous dispersion effects. These data showed that the wrong alternative had been chosen for the polarity. When the structure was inverted as required, a refinement of

two anisotropic rubidium ions and twenty borons, including anomalous dispersion, gave an R of 0.136 on the 1175 data of the corrected second set. Another difference Fourier showed peaks ranging from 0.78 to 0.46 electrons / $\text{\AA}^3$ in reasonable positions for all eighteen hydrogens. Only eight non-hydrogen peaks larger than 0.46 electrons / $\text{\AA}^3$ were not explainable by such things as series termination ripples about rubidium or ill-fitting borons (e.g. a peak midway between two boron positions). Many attempts at refining the hydrogen positions under various restrictions produced various degrees of agreement, various unacceptable temperature factors and boron-hydrogen distances, and much frustration. The structure was finally refined in two ways: with no hydrogen included, and with each hydrogen in a calculated position 1.2 $\text{\AA}$ from its boron (~1.3 $\text{\AA}$ in the case of the two bridging hydrogens) and constrained to "ride"¹³ on its boron. All hydrogens were also required to have the same temperature factor. Both refinements were done with the weighting scheme described.

In the no-hydrogen case the final R was 0.133 on all 1175 data and 0.079 on the 935 non-zero data. In the last cycle, no parameter shifted by more than 0.04 of the standard deviation calculated for it from the least-squares matrix.

In the case which included hydrogens, the final R was 0.127 on all 1175 data and 0.073 on the 935 non-zero data. In the last cycle, no parameter shifted by more than 0.03 of its standard deviation. The standard deviation of an observation of unit weight, defined as $[\sum w(|\underline{kF}_o| - |\underline{F}_c|)^2 / (\underline{u} - \underline{v})]^{1/2}$ where $\underline{u}$ is the number of data and $\underline{v}$ is the number of independent parameters refined,

was 1.73. The root-mean-square difference in boron positions between the two refinements is 0.05 Å, and the greatest difference is 0.11 Å.

The results of the refinement which included hydrogen are believed to be more accurate on the basis of better agreement and smaller scatter in both the boron temperature factors and in boron-boron distances. All results presented hereinafter refer to the refinement on the corrected second data set which included hydrogens. The final positional and thermal parameters are presented in Table I, while Table II lists the observed and calculated structure factors. Observed and calculated values of the function

$$(|F(+)| - |F(-)|) / 0.5 (|F(+)| + |F(-)|),$$

where $F(+)$ and $F(-)$ are structure factors for $k > 0$ and $k < 0$, are tabulated in Table III for the seventeen anomalous dispersion data. The agreement of magnitudes and signs clearly establishes the non-centric space group and is strong evidence of the correctness of the structure.

Discussion.— The structure of the photoisomeric $B_{20}H_{18}^{2-}$ anion found in this study is shown in Figure 1. This structure is the more symmetric one of the two possibilities postulated by Hawthorne and Pilling.³ The anion has an approximate $2/m$ (C_{2h}) point symmetry. A calculation of the anion's deviations from perfect $2/m$ symmetry gave a root-mean-square deviation of 0.07 Å (excluding B5', see below). We feel that this is nearly, if not entirely, within the accuracy of the determination. Thus the non-centric nature of the space group is a result of an unsymmetrical arrangement (Figure 2) of symmetric pieces.

Table I

Final Positional and Thermal Parameters in $\text{Rb}_2\text{B}_{20}\text{H}_{18}$

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u> ^a
Rb(1)	-.3714(2) ^b	-.0801(1)	.3225(4)	(c)
Rb(2)	.3688(2)	.0801(1)	-.3299(4)	(c)
B(1)	.039(2)	.176(1)	.566(4)	4.4(6)
B(2)	.052(1)	.219(1)	.369(3)	1.1(4)
B(3)	.158(2)	.167(1)	.457(3)	2.7(5)
B(4)	.069(2)	.092(1)	.499(3)	3.0(5)
B(5)	-.044(1)	.146(1)	.407(2)	0.8(3)
B(6)	.140(2)	.181(1)	.218(3)	1.8(4)
B(7)	.162(2)	.091(1)	.315(4)	3.2(5)
B(8)	.022(2)	.075(2)	.275(4)	4.8(7)
B(9)	.000(2)	.160(1)	.174(3)	2.3(4)
B(10)	.096(2)	.111(1)	.110(4)	3.0(5)
B(1')	.138(2)	.389(1)	.400(3)	2.9(4)
B(2')	.095(2)	.316(1)	.293(3)	2.8(5)
B(3')	.077(2)	.405(1)	.195(3)	2.3(5)
B(4')	.229(1)	.421(1)	.239(2)	0.9(4)
B(5')	.241(2)	.329(1)	.312(3)	2.4(4)
B(6')	.081(2)	.330(1)	.048(3)	2.8(5)
B(7')	.172(2)	.403(1)	.005(4)	3.1(5)
B(8')	.287(2)	.350(1)	.104(3)	3.1(5)
B(9')	.188(2)	.284(1)	.153(3)	4.0(5)
B(10')	.204(2)	.318(1)	-.062(3)	3.2(5)

Table I, continued

H(1) ^d	.019	.197	.717	1.2
H(3)	.229	.187	.556	"
H(4)	.064	.054	.631	"
H(5)	-.136	.150	.463	"
H(7)	.238	.053	.286	"
H(8)	-.017	.022	.214	"
H(9)	-.051	.177	.040	"
H(10)	.116	.089	-.041	"
H(1')	.117	.412	.550	"
H(3')	.003	.445	.217	"
H(4')	.267	.475	.295	"
H(5')	.297	.309	.437	"
H(6')	.008	.309	-.047	"
H(7')	.173	.440	-.128	"
H(8')	.378	.344	.046	"
H(10')	.225	.295	-.212	"
H(2-2')	.027	.285	.403	"
H(6-9')	.210	.215	.114	"

(a) The units are $\text{\AA}^2$.

(b) The number in parentheses is the standard deviation in the least significant digit as derived from the least-squares matrix.

(c) The anisotropic temperature factors for Rb(1) are:

(B_{11} , 4.1(2); B_{22} , 2.5(2); B_{33} , 5.6(2); B_{12} , 0.7(1); B_{13} , 1.4(1); B_{23} , 0.3(1)) and for Rb(2): (B_{11} , 4.3(2); B_{22} , 3.1(2);

Table I, continued

(c) continued

B_{33} , 3.8(2); B_{12} , -0.7(1); B_{13} , -1.1(1); B_{23} , 1.1(1)), where the units are $\text{\AA}^2$.

(d) H(1) is on B(1) and similarly. H(2-2') and H(6-9') are the two bridging hydrogens. No standard deviations are given for the positional parameters since these are assumed positions.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80																				

Table III

Values of $\frac{|F(+)| - |F(-)|}{0.5(|F(+)| + |F(-)|)}$ for $\text{Rb}_2\text{B}_{20}\text{H}_{18}$ ^a

<u>h</u>	<u>k</u>	<u>l</u>	Obs.	Calc.
1	1	1	-0.13	-0.15
9	3	2	-0.13	-0.14
1	17	3	0.11	0.10
1	9	5	0.10	0.14
6	3	1	-0.10	-0.12
8	3	0	-0.10	-0.11
1	3	1	0.06	0.07
5	9	2	-0.05	-0.07
1	2	3	0.05	0.05
0	1	1	0.05	0.03
1	3	3	-0.04	-0.03
0	14	0	0.04	0.03
3	3	3	-0.03	-0.04
0	18	0	0.03	0.03
0	2	0	0.01	0.01
0	2	2	0.	-0.01
0	3	1	0.	0.01

(a) Where $F(+)$ and $F(-)$ are the structure factors for $(\underline{h}, \underline{k}, \underline{l})$ and $(\underline{h}, -\underline{k}, \underline{l})$, respectively.

We assign no significance to the handedness found for the particular sample from which the data were obtained, and would expect another crystal to have an equal chance of having either handedness.

An examination of the boron-boron distances given in Table IV shows that B5' is apparently mis-located in a position too far from the apex and too close to the opposite equatorial ring. We do not understand how this effect arises but did exclude B5' from the calculation of the deviations of the anion from $2/m$ symmetry and from the calculations of average boron-boron distances.

The average of 15 apical-equatorial distances (excluding B1'-B5') is 1.68 ± 0.04 Å and the average of 28 equatorial-equatorial distances (excluding B5'-B8', B5'-B9', and the inter-bridging-boron distances) is 1.82 ± 0.05 Å. The shortened inter-bridging-boron distances average $1.68_5 \pm 0.05$ Å and the B-B distances across the B-H-B bridges average 2.04 ± 0.09 Å. The errors quoted are root-mean-square deviations. The increase in calculated bond distances due to thermal motion is estimated to be ~ 0.02 Å, or about half a standard deviation. These averages may be compared with those found¹⁴ for the cuprous salt of $B_{10}H_{10}^{2-}$ which are 1.73 ± 0.02 Å for apical-equatorial distances, 1.86 ± 0.03 Å for distances within the equatorial rings, and $1.81_5 \pm 0.01_5$ Å for distances between equatorial rings.

The two rubidium ions are nearly centrically located, as can be seen from the table of atomic coordinates. The distance between one rubidium ion and the invert ($\bar{1}$) of the other's position is 0.062 ± 0.008 Å. The rubidiums' nearest neighbors are hydrogens, none closer than 2.6 Å. There are no borons nearer than 3.3 Å.

Table IV

Distances^a in $\text{Rb}_2\text{B}_{18}\text{H}_{20}$

<u>apex-ring</u>	A	<u>intra-ring</u>	A	<u>inter-ring</u>	A
B(1)-B(2)	1.66(3)	B(2)-B(3)	1.77(3)	B(2)-B(6) ^c	1.72(3)
-B(3)	1.67(3)	B(3)-B(4)	1.82(3)	B(6)-B(3)	1.78(3)
-B(4)	1.70(3)	B(4)-B(5)	1.87(3)	B(3)-B(7)	1.77(3)
-B(5)	1.64(3)	B(5)-B(2)	1.85(3)	B(7)-B(4)	1.76(3)
B(10)-B(6)	1.64(3)	B(6)-B(7)	1.86(3)	B(4)-B(8)	1.76(4)
-B(7)	1.73(4)	B(7)-B(8)	1.78(3)	B(8)-B(5)	1.85(4)
-B(8)	1.65(4)	B(8)-B(9)	1.80(4)	B(5)-B(9)	1.80(3)
-B(9)	1.58(3)	B(9)-B(6)	1.80(3)	B(9)-B(2)	1.91(3)
B(1')-B(2')	1.68(3)	B(2')-B(3')	1.86(3)	B(2')-B(6')	1.80(3)
-B(3')	1.70(3)	B(3')-B(4')	1.93(3)	B(6')-B(3')	1.79(3)
-B(4')	1.73(3)	B(4')-B(5')	1.83(3)	B(3')-B(7')	1.82(3)
-B(5') ^b	1.82(3)	B(5')-B(2')	1.83(3)	B(7')-B(4')	1.88(3)
B(10')-B(6')	1.73(3)	B(6')-B(7')	1.82(3)	B(4')-B(8')	1.82(3)
-B(7')	1.73(3)	B(7')-B(8')	1.88(3)	B(8')-B(5') ^b	1.66(3)
-B(8')	1.70(3)	B(8')-B(9')	1.79(3)	B(5')-B(9') ^b	1.58(3)
-B(9')	1.70(4)	B(9')-B(6')	1.76(3)	B(9')-B(2') ^c	1.65(3)
<u>across bridges</u>					
		B(2)-B(2')	1.98(3)		
		B(6)-B(9')	2.10(3)		

Table IV, continued

- (a) These distances are not corrected for thermal motion. The terminal digits in parentheses are the standard deviations as estimated from the least-squares matrix in units of .01 Å. However, we feel that the root-mean-square deviations from the averages given in the text of ~.05 Å are a better measure of the accuracy of these distances.
- (b) Evidence that B(5') is displaced from its "true" position.
- (c) Pairs of borons in the same B₁₀ unit which are involved in hydrogen bridges.

Table V

Angles^a in $\text{Rb}_2\text{B}_{20}\text{H}_{18}$

Angle, B-B-B Numbers	degrees, unprimed	degrees, primed	Angle, B-B-B Numbers	degrees, unprimed	degrees, primed
2 1 3	64	67	6 2 9	59	61
3 1 4	65	68	6 3 7	63	61
4 1 5	68	62	7 4 8	61	61
5 1 2	68	63	8 5 9	59	67
6 10 7	67	63	2 6 3	61	62
7 10 8	63	66	3 7 4	62	63
8 10 9	68	63	4 8 5	62	63
9 10 6	68	62	2 9 5	60	69
e-a-e ave. = $66^\circ \pm 2^\circ$			e-e'-e ave. = $61^\circ \pm 2^\circ$		
1 2 3	58	57	3 2 6	61	59
1 2 5	55	62	5 2 9	57	54
1 3 2	58	56	2 3 6	58	59
1 3 4	58	57	4 3 7	59	60
1 4 3	57	55	3 4 7	59	57
1 4 5	55	61	5 4 8	61	54
1 5 2	56	55	2 5 9	63	57
1 5 4	58	57	4 5 8	57	63
10 6 7	59	58	2 6 9	66	55
10 6 9	55	58	3 6 7	58	60
10 7 6	54	58	3 7 6	58	59
10 7 8	56	56	4 7 8	60	58
10 8 7	60	57	4 8 7	60	61

Table V, continued

10 8 9	54	58	5 8 9	59	55
10 9 6	57	60	2 9 6	55	64
10 9 8	58	58	5 9 8	62	59
a-e-e ave. = $57^{\circ} \pm 2^{\circ}$			e-e-e' ave. = $59^{\circ} \pm 3^{\circ}$		
2 1 4	102	101	3 2 2'	115	
3 1 5	101	97	9 6 9'	116	
6 10 8	100	99	2 2' 5'	112	
7 10 9	103	94	6 9' 6'	110	
ave. = $100^{\circ} \pm 3^{\circ}$			ave. = $113^{\circ} \pm 3^{\circ}$		
2 3 4	93	88	5 2 2'	155	
3 4 5	88	89	7 6 9'	154	
4 5 2	89	92	2 2' 3'	157	
5 2 3	90	91	6 9' 8'	153	
6 7 8	88	89	ave. = $155^{\circ} \pm 2^{\circ}$		
7 8 9	93	86	6 2 2'	93	
8 9 6	89	95	2 6 9'	86	
9 6 7	90	89	2 2' 9'	91	
ave. = $90^{\circ} \pm 2^{\circ}$			6 9' 2'	91	
			ave. = $90^{\circ} \pm 3^{\circ}$		

- (a) Standard deviations for these angles as calculated from the least-squares matrix are $\sim 1.5^{\circ}$, but we feel that the given root-mean-square deviations from the averages show that $\sim 2.5^{\circ}$ would be nearer the truth.

The $B_{20}H_{18}^{2-}$ ion described above is not the only one which might be constructed by joining two B_{10} polyhedra with two B-H-B bridges involving adjacent borons in each B_{10} unit. There are thirteen isomers which may be so constructed, five of which are symmetric and the remaining eight of which form four enantiomorphic pairs. Other isomers involving bridging to non-adjacent atoms were not considered because of the drastic crowding of the pair of B-H groups which lie between any such non-adjacent pair. The thirteen isomers are listed in Table VI, together with the point groups to which they belong and an indication of which pairs of atoms in each polyhedron are involved in the hydrogen bridges. The isomer found in this investigation is the fifth listed in Table VI, while number 1 was proposed¹⁰ for the structure of the parent $B_{20}H_{18}^{2-}$ ion before it was shown^{6,7} to be linked by a pair of B-B-B three-center bonds rather than hydrogen bridges. Hawthorne and Pilling mention³ "the formation of unidentified metastable intermediates" in the thermal reversion of the photo-isomer studied here to the parent ion. Thus it may be that some or all of the isomers discussed here also exist. We thank Professor M. F. Hawthorne of the University of California, Riverside for helpful discussions and for providing the crystals which made this work possible.

Table VI

Possible $(B_{10}H_8)_{\text{H}}^{\text{H}}(B_{10}H_8)^{2-}$ Isomers

no. ^a	bridge ^b locations	pairs ^c linked	point ^d group
1	(1-2', 2-1')	A-A	$2/\underline{m} = \underline{C}_{2h}$
2	(1-1', 2-2')	A-A	$\underline{mm}2 = \underline{C}_{2v}$
3	(2-3', 3-2')	E-E	$\underline{mm}2 = \underline{C}_{2v}$
4	(2-2', 3-3')	E-E	$2/\underline{m} = \underline{C}_{2h}$
5	(2-2', 6-9')	E'-E'	$2/\underline{m} = \underline{C}_{2h}$
6a	(2-2', 6-6')	E'-E'	$222 = \underline{D}_2$
6b	(2-2', 9-9')		
7a	(1-2', 2-3')	A-E	$1 = \underline{C}_1$
7b	(1-3', 2-2')		
8a	(1-2', 2-6')	A-E'	$1 = \underline{C}_1$
8b	(1-2', 2-9')		
9a	(2-2', 3-6')	E-E'	$1 = \underline{C}_1$
9b	(2-2', 3-9')		

(a) The a-b pairs are enantiomers.

(b) Reference 11.

(c) A denotes an apex-equatorial pair, E denotes a pair in the same equatorial ring, and E' denotes a pair which has one member in each ring.

(d) In Hermann-Mauguin and Schoenflies notations, respectively.

References and Footnotes

- (1) Work done under the auspices of the U. S. Atomic Energy Commission.
- (2) National Science Foundation Graduate Fellow.
- (3) M. F. Hawthorne and R. L. Pilling, J. Am. Chem. Soc., 88, 3873 (1966).
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- (10) A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, Proc. Nat'l. Acad. Sci. U. S., 48, 729 (1962).
- (11) Numbering according to: R. Adams, Inorg. Chem., 2, 1087 (1963); See Figure 1.
- (12) "International Tables for X-ray Crystallography," Vol III, The Kynoch Press, Birmingham, England, 1962, pp. 202, 206, 216.
- (13) Each B-H unit was refined as a rigid, non-rotating body.
- (14) R. Dobrott and W. N. Lipscomb, J. Chem. Phys., 37, 1779 (1962).

Figure Captions

1. $B_{20}H_{18}^{2-}$ photoisomer (terminal hydrogens omitted for clarity).
2. One unit cell of $Rb_2B_{20}H_{18}$ seen down c axis (hydrogens omitted). Numbers on Rb ions are z coordinates as decimal fractions of c ; the centers of the B_{20} units are approximately at $z = 1/4$ and $z = 3/4$.

XBL 678-4463

Fig. 1

Fig. 2

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