Lawrence Berkeley National Laboratory

Title
THE CRYSTAL AND MOLECULAR STRUCTURES OF THREE BORON COMPOUNDS

Permalink
https://escholarship.org/uc/item/5g77c26w

Author
DeBoer, Barry Goodwin.

Publication Date
1968-08-01

University of California

Ernest O. Lawrence
Radiation Laboratory

THE CRYSTAL AND MOLECULAR STRUCTURES OF THREE BORON COMPOUNDS

Barry Goodwin DeBoer
(Ph.D. Thesis)
August 1968

Berkeley, California

DISCLAIMER

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE CRYSTAL AND MOLECULAR STRUCTURES OF THREE BORON COMPOUNDS

Barry Goodwin DeBoer
(Ph.D. Thesis)

August 1968

The Crystal and Molecular Structures of Three Boron Compounds

Contents

The Crystal and Molecular Structures of Three Boron Compounds

Barry Goodwin DeBoer

Lawrence Radiation Laboratory
University of California
Berkeley, California

August, 1968

Abstract

The crystal and molecular structures of three boron-containing compounds have been determined by X-ray diffraction studies of single crystal specimens. They are: the rubidium salt of an octadecahydroeicosaborate(2-) photoisomer, $Rb_2B_{20}H_{18}$; the tetramethylammonium salt of a brominated carborane-metal "sandwich" ion, $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$; and tris-difluorobora-borane — phosphorus trifluoride, $B_4F_6PF_3$.

Crystals of $Rb_2B_{20}H_{18}$ are orthorhombic, space group $Pn2_1a$, with $\underline{a} = 12.344 \pm .007$ A, $\underline{b} = 19.014 \pm .010$ A, $\underline{c} = 7.260 \pm .005$ A, and contain four formula units per unit cell. The calculated density is 1.58 g/cc (by flotation, 1.57 g/cc). The structure was determined by Patterson and Fourier techniques and refined by a full-matrix least-squares procedure to a conventional $\underline{R}$ of 0.127 for 1175 scintillation-counter data (0.073 for the 935 non-zero data). The non-centric nature of the space group was demonstrated by the measurement of anomalous dispersion 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 $2/m$ ($\underline{C}_{2h}$) point symmetry. A list of thirteen possible isomers covering reasonable choices of bridge positions is presented together with their point symmetries.

Crystals of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$ are monoclinic, space group $P2_1/c$, with $\underline{a} = 19.893 \pm .010$ A, $\underline{b} = 19.487 \pm .010$ A, $\underline{c} = 15.058 \pm .010$ A, $\beta = 93.15° \pm .05°$, and contain eight formula units and four crystallographically independent anions per unit cell. The calculated density is 1.967 g/cc, in agreement with the measured value of $1.98 \pm .01$ g/cc. The structure was solved by statistical methods and refined by a least-squares procedure to a conventional $\underline{R}$ of 8.7% on 3002 data collected by counter methods. All four independent anions have the same shape to within the accuracy of this determination. The anion, the product of a bromination during which the bis-dicarbollyl·cobalt "sandwich" is believed to remain intact, consists of two substituted icosahedra with the cobalt as their common vertex. In each icosahedron, the carbons are adjacent to each other and to the cobalt, while the three borons bonded to bromine form the corners of a triangular face. Two corners of this face are as far as possible from the carbons, and the third is adjacent to the cobalt. These bromination sites are consistent with a charge distribution in the reactant which is analogous to that in $\underline{o}\text{-}B_{10}C_2H_{12}$, but modified slightly by the presence of the Co(III).

Crystals of $B_4F_6PF_3$ are orthorhombic, space group Pnma, with $\underline{a} = 13.893 \pm .005$ A, $\underline{b} = 10.578 \pm .005$ A, $\underline{c} = 6.075 \pm .005$ A, and contain

four formula units per unit cell. The calculated density is 1.82 g/cc. The structure was solved by statistical methods and refined by full-matrix least-squares to a conventional $\underline{R}$ of 9.3% for 703 data collected by counter methods (6.7% for the 603 non-zero data). The molecule consists of a central boron atom, tetrahedrally bonded to three BF_2 groups and the PF_3 group in such a way that the molecule has approximately 3m (C_{3v}) point symmetry, one mirror of which is required by the crystal symmetry. Distances found (uncorrected for thermal motion) are: B–F, 1.305 A; B–B, 1.68 A; B–P, 1.825 A; and P–F, 1.51 A (all ± .015 A).

I. Introduction

Determinations of molecular structure form a large and important part of chemistry and the study of matter in general. A knowledge of the three-dimensional atomic arrangements in the molecules of substances is a prerequisite to an understanding of many of the physical and chemical properties of those substances. One of the most powerful methods of determining such atomic arrangements is the examination of the diffraction of X-rays by single crystals. The method is powerful because it is applicable to a wide range of compounds and is able to handle molecules composed of many more atoms than those amenable to study by, for instance, spectroscopic methods. Crystal structure studies such as those described here may be thought of as a form of inverted spectroscopy, in which an unknown diffraction grating is examined by the use of a known radiation source, rather than vice versa. Since our crystal "diffraction grating" is composed of units which are arranged with three-dimensional periodicity, the three-dimensional locations of the atoms within the repeated unit may be deduced from the diffraction intensities. These locations provide the desired image of the molecule(s), with the information it carries as to composition, conformation, substitution sites, etc. These locations may also be used to calculate interatomic distances and angles from which inferences may be drawn concerning bonding, electronic structure, non-bonded forces, and other detailed properties of the molecules.

The principle parts of this thesis describe the application of the single-crystal X-ray diffraction technique to three compounds drawn from the rapidly expanding field of boron chemistry. They are, in order, a

borohydride anion, a metallo-carborane, and a novel boron fluoride compound. Each of these compounds was chosen for study because each is the product of a type of reaction which has not previously been observed in the chemistry of boron, and the compounds themselves are likewise unique. They represent opportunities to observe previously unseen facets of boron chemistry and so increase our knowledge of this element. However, since these compounds are not very closely related otherwise, and because the determination of the structure of one crystal is well separated from that of another, the work on each compound is presented separately. Each presentation has its own introduction, descriptions of the experimental procedure and method of solution, and discussions of the results and their implications.

II. The Crystal Structure of the Rubidium Salt of an Octadecahydroeicosa-

   borate(2-) Photoisomer

A. 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.[1-9*] The structure of the parent ion

has been established[5,6] 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.[10]

   Recently, Hawthorne and Pilling[2] 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 photo-

isomerization product. The results prove that the geometry is the

centrosymmetric (2/m or $\underline{C}_{2\underline{h}}$) alternative of the pair suggested by

Hawthorne and Pilling.

B. Experimental

   Crystals of the rubidium salt were received from 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

---

* References and Footnotes for part II are to be found on page 26.

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 CuKα 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 manual General Electric XRD-5 apparatus using molybdenum radiation and a Zr filter at the receiving slit. The components of the alpha doublet $(\lambda(Kα_1) = 0.70926$ A) were resolved. 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 and a large ($\sim 3.5°$) take-off angle from the X-ray tube anode. Coincidence losses were negligible. For each reflection which was seriously affected by streaking from other orders, individual backgrounds were measured by seeking a minimum on the low-2θ side of the peak; otherwise, the background was taken from a plot of background as a function of 2θ for various values of phi and chi. The measurements included reflections to $2\theta = 45°$, 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, this data was used in the early stages of the analysis. When it became evident that the quality of the data was unacceptable, a second crystal about 0.11 X 0.06 X 0.05 mm in size and of much better appearance than the first was selected from the recrystallized material. 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 random fluctuations of the size expected for counting statistics.

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). Standard deviations of five percent of the intensity or one count per second, which ever was greater, were assigned to all the raw intensities, except for the anomalous dispersion data, for which standard deviations were estimated from the scatter between measurements made within the sets $k > 0$ and $k < 0$. Weighting factors were derived from these standard deviations as one over the square of the resulting

standard deviations of the observed structure factors. The calculated absorption coefficient, μ, of 60 cm^{-1}, and the dimensions of this crystal indicate that $\mu\underline{s}$ is limited between 0.3 and 0.5, where $\underline{s}$ is the maximum path length of an X-ray within the crystal. It is estimated 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 distance-and-angle calculations were done by Zalkin's (unpublished) FORDAP and DISTAN programs. The unpublished version of the Ganzel-Sparks-Trueblood least-squares program which was used, minimizes the function $\Sigma\underline{w}(|\underline{kF_o}| - |\underline{F_c}|)^2/\Sigma\underline{w}|\underline{kF_o}|^2$, where $\underline{F_o}$ and $\underline{F_c}$ are the observed and calculated structure factors, respectively, $\underline{w}$ is the weighting factor, and $\underline{k}$ 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 factors[11] for Rb^+ were corrected by $\Delta\underline{f}' = -0.9$ electrons and $\Delta\underline{f}'' = +3.1$ electrons as the real and imaginary parts of the anomalous dispersion. Scattering factors for boron and hydrogen were also taken from standard tables.[11] The anisotropic

temperature factors used have the form: $\exp(-0.25\sum_i\sum_i h_i h_i b_i b_i B_{ii})$,

$i,i = 1, 2, 3$, where b_i is the ith reciprocal axis.

C. <u>Results</u>

Four formula units of $Rb_2B_{20}H_{18}$ are contained in the orthorhombic unit cell with dimensions $a = 12.344 \pm .007$ A, $b = 19.014 \pm .010$ A, $c = 7.260 \pm .005$ A. The calculated density of 1.58 g/cc agrees with the value $(1.57 \pm .01$ g/cc$)$ obtained by flotation in a mixture of carbon tetrachloride and dibromoethane. These measurements apply to room temperature ($\sim 23^\circ$C) and their standard deviations 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 $Pn2_1a$. The positive test for pyroelectricity and the violations of Friedel's rule (presented below) indicate the non-centric $Pn2_1a$, and this choice leads to a successful structure with each atom in the general set of positions: $(x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; -x, \frac{1}{2} + y, -z; \frac{1}{2} + x, y, \frac{1}{2} - z)$.

1. <u>Determination of Structure</u>

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 $R = \Sigma \left| |kF_o| - |F_c| \right| / \Sigma |kF_o|$. 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"

($R = 0.297$, all data). 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 re-

maining 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 possi-

bilities 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 $\sin\theta/\lambda \cong .50$, 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/A^3 in reasonable positions for all eighteen hydrogens. Only eight non-hydrogen peaks larger than 0.46 electrons/A^3 were not explainable by such things as pile-up of errors near the rubidium ions 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 A from its boron (~ 1.3 A in the case of the two bridging hydrogens) and constrained to "ride"[12] 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 $[\Sigma w(|kF_o| - |F_c|)^2/(u-v)]^{\frac{1}{2}}$ where u is the number of data and 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 A, and the greatest difference is 0.11 A.

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

$$\frac{|F(+)| - |F(-)|}{0.5(|F(+)| + |F(-)|)}$$

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.

2. 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.[2] The anion has an approximate $2/\underline{m}(\underline{C}_{2h})$ point symmetry. A calculation of the anion's deviations from perfect $2/\underline{m}$ symmetry gave a root-mean-square deviation of 0.07 A (excluding B5', see below). It is felt 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 arrange-ment (Figure 2) of symmetric pieces. No significance is assigned to the handedness found for the particular sample from which the data were ob-tained, and another crystal would be expected 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. The author does not

Table I. Final Positional and Thermal Parameters in $Rb_2B_{20}H_{18}$

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}^a$
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	1.2
H(4)	.064	.054	.631	1.2
H(5)	-.136	.150	.463	1.2
H(7)	.238	.053	.286	1.2
H(8)	-.017	.022	.214	1.2
H(9)	-.051	.177	.040	1.2
H(10)	.116	.089	-.041	1.2
H(1')	.117	.412	.550	1.2
H(3')	.003	.445	.217	1.2
H(4')	.267	.475	.295	1.2
H(5')	.297	.309	.437	1.2
H(6')	.008	.309	-.047	1.2
H(7')	.173	.440	-.128	1.2
H(8')	.378	.344	.046	1.2
H(10')	.225	.295	-.212	1.2
H(2-2')	.027	.285	.403	1.2
H(6-9')	.210	.215	.114	1.2

(a) The units are A^2.

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

Table I, continued

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

$(\underline{B}_{11}$, 4.1(2); $\underline{B}_{22}$, 2.5(2); $\underline{B}_{33}$, 5.6(2); $\underline{B}_{12}$, 0.7(1);

$\underline{B}_{13}$, 1.4(1); $\underline{B}_{23}$, 0.3(1)) and for Rb(2): $(\underline{B}_{11}$, 4.3(2);

$\underline{B}_{22}$, 3.1(2); $\underline{B}_{33}$, 3.8(2); $\underline{B}_{12}$, -0.7(1); $\underline{B}_{13}$, -1.1(1);

$\underline{B}_{23}$, 1.1(1)), where the units are $\overset{\circ}{A}^2$.

(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.

Table II. Observed and Calculated Structure Factors for $Rb_2B_{20}H_{18}$

Table III. Values of $\dfrac{|\underline{F}(+)| - |\underline{F}(-)|}{0.5(|\underline{F}(+)| + |\underline{F}(-)|)}$ for $Rb_2B_{20}H_{18}$[a]

$\underline{h}$	$\underline{k}$	$\underline{\ell}$	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 $\underline{F}(+)$ and $\underline{F}(-)$ are the structure factors for

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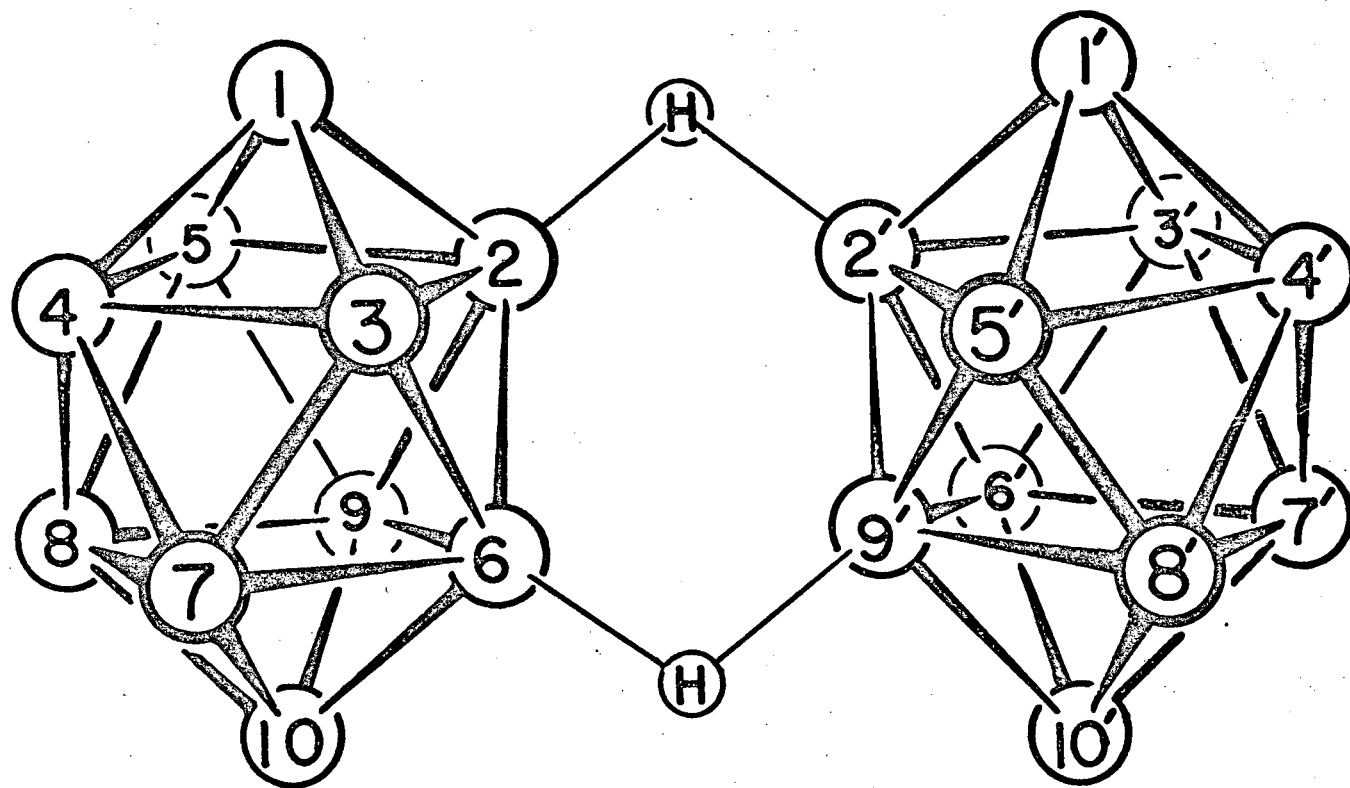
Figure 1. - $B_{20}H_{18}^{2-}$ photoisomer (terminal hydrogens omitted for clarity).
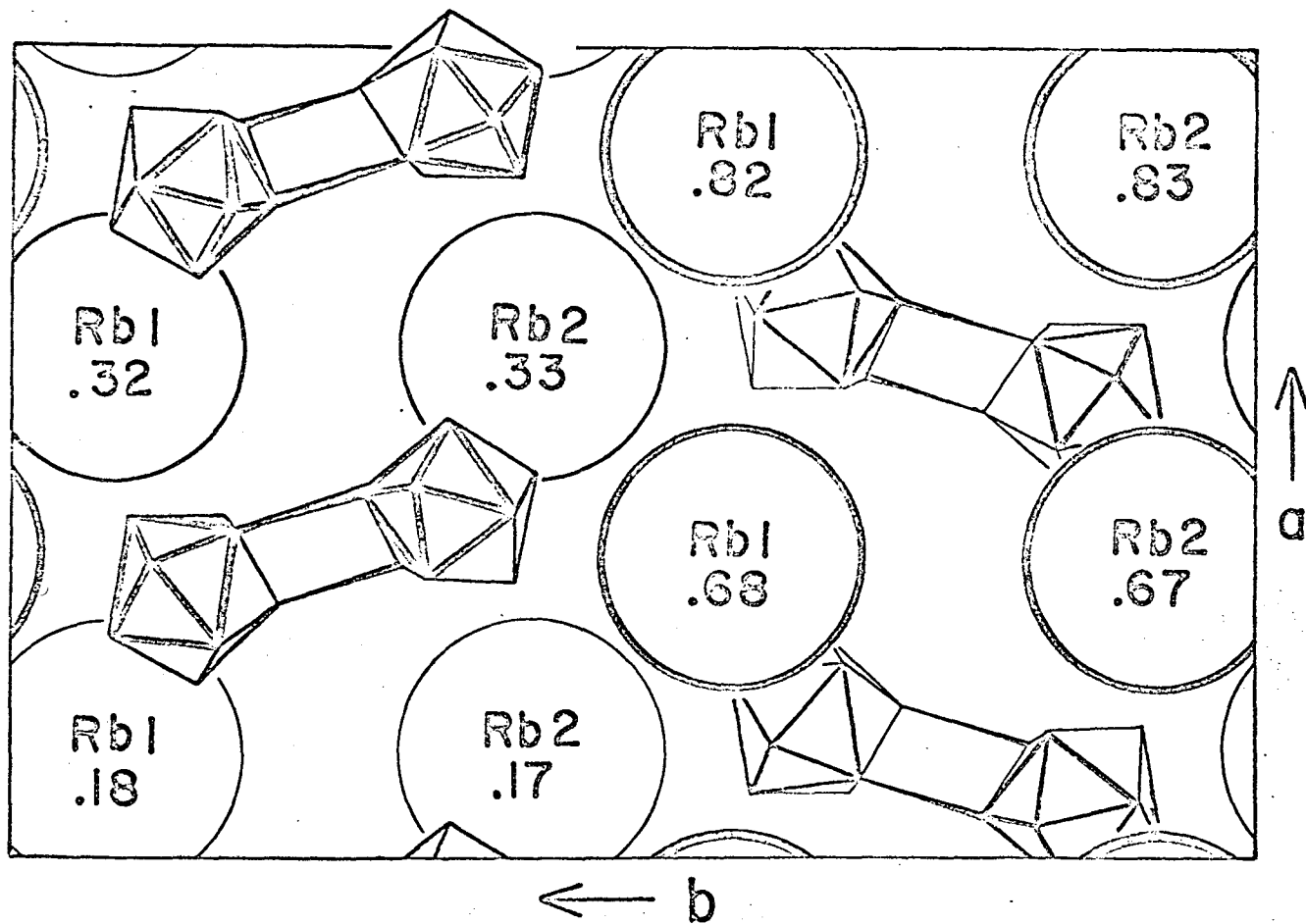
Figure 2. – One unit cell of $Rb_2B_{20}H_{18}$ seen down c axis (hydrogens omitted). Numbers on Rb ions are z coordinates as decimal fractions of c; the centers of the B_{20} units are approximately at $z = \frac{1}{2}$ and $z = \frac{3}{4}$.

Table IV. Distances[a] in $Rb_2B_{20}H_{18}$

apex-ring	A	intra-ring	A	inter-ring	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)	1.73(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)

across bridges	
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 A. However, the author feels that the root-mean-square deviations from the averages given in the text of ~.05 A 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 B_{10} unit which are involved in hydrogen bridges.

Table V. Angles[a] in $Rb_2B_{20}H_{18}$

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° ± 2°			e-e'-e ave. = 61° ± 2°		
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
						6	9'	2'	91

ave. = $90^{\circ} \pm 2^{\circ}$ ave. = $90^{\circ} \pm 3^{\circ}$

(a) Standard deviations for these angles as calculated from the least-squares matrix are ~ 1.5°, but the author feels that the given root-mean-square deviations from the average show that ~ 2.5° would be nearer the truth.

understand how this effect arises but did exclude B5' from the calculation
of the deviations of the anion from $2/\underline{m}$ symmetry and from the calculations
of average boron-boron distances.

The average of 15 apical-equatorial distances (excluding B1'-B5')
is 1.68 ± .04 A and the average of 28 equatorial-equatorial distances
(excluding B5'-B8', B5'-B9', and the inter-bridging-boron distances) is
1.82 ± .05 A. The shortened inter-bridging-boron distances average
1.68_5 ± .05 A and the B-B distances across the B-H-B bridges average
2.04 ± .09 A. The errors quoted are root-mean-square deviations. The
increase in calculated bond distances due to thermal motion is estimated
to be ~.02 A, or about half a standard deviation. These averages may be
compared with those found[13] for the cuprous salt of $B_{10}H_{10}^{2-}$ which are
1.73 ± .02 A for apical-equatorial distances, 1.86 ± .03 A for distances
within the equatorial rings, and 1.81_5 ± $.01_5$ A 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 ($\overline{1}$) of the other's position is 0.062 ± .008 A.
The rubidium-hydrogen distances are normal for van derWaals contacts.
The average of the eight shortest Rb-H distances (four on each rubidium)
is 2.8 A, and the shortest single distance is 2.6 A. The minimum boron-
rubidium distance is 3.3 A.

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 proposed[9] for the structure of the parent $B_{20}H_{18}^{2-}$ ion before it was
shown[5,6] to be linked by a pair of B-B-B three-center bonds rather than
hydrogen bridges. Hawthorne and Pilling mention[2] "the formation of
unidentified metastable intermediates" in the thermal reversion of the
photoisomer studied here to the parent ion. Thus it may be that some or
all of the isomers discussed here also exist.

Table VI. Possible $(B_{10}H_8)$⟩$^{H}_{H}$⟨$(B_{10}H_8)^{2-}$ Isomers

no.[a]	bridge locations[b]	pairs linked[c]	point group[d]
1	(1-2', 2-1')	A-A	$2/m = C_{2h}$
2	(1-1', 2-2')	A-A	$mm2 = C_{2v}$
3	(2-3', 3-2')	E-E	$mm2 = C_{2v}$
4	(2-2', 3-3')	E-E	$2/m = C_{2h}$
5	(2-2', 6-9')	E'-E'	$2/m = C_{2h}$
6a	(2-2', 6-6')	E'-E'	$222 = D_2$
6b	(2-2', 9-9')		
7a	(1-2', 2-3')	A-E	$1 = C_1$
7b	(1-3', 2-2')		
8a	(1-2', 2-6')	A-E'	$1 = C_1$
8b	(1-2', 2-9')		
9a	(2-2', 3-6')	E-E'	$1 = C_1$
9b	(2-2', 3-9')		

(a) The a-b pairs are enantiomers.

(b) Reference 10.

(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)   A description of this work has been published by B. G. DeBoer, A. Zalkin, and D. H. Templeton, Inorg. Chem., 7, 1085 (1968).

(2)   M. F. Hawthorne and R. L. Pilling, J. Am. Chem. Soc., 88, 3873 (1966).

(3)   M. F. Hawthorne, R. L. Pilling, and P. M. Garrett, ibid., 87, 4740 (1965).

(4)   M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, ibid., 87, 1892 (1965).

(5)   R. L. Pilling, M. F. Hawthorne, and E. A. Pier, ibid., 86 3568 (1964).

(6)   B. L. Chamberland and E. L. Muetterties, Inorg. Chem., 3, 1450 (1964).

(7)   M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garret, J. Am. Chem. Soc., 85, 3704 (1963).

(8)   A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, ibid., 84, 3026 (1962).

(9)   A. Kaczmarczyk, R. Bobrott, and W. N. Lipscomb, Proc. Nat'l. Acad. Sci. U. S., 48, 729 (1962).

(10) Numbering according to: R. Adams, Inorg. Chem., 2, 1087 (1963); See Figure 1.

(11) "International Tables for X-ray Crystallography", Vol III, The Kynoch Press, Birmingham, England, 1962, pp. 202, 206, 216.

(12) Each B-H unit was refined as a rigid, non-rotating body.

(13) R. Dobrott and W. N. Lipscomb, J. Chem. Phys., 37, 1779 (1962).

III. The Crystal Structure of a Brominated Carborane - Metal Sandwich

Compound — $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

A. Introduction

Hawthorne and co-workers[1-6*] have recently synthesized a number of π-dicarbollyl metal compounds analogous to the π-cyclopentadienyl "sandwich" compounds. They found[6,7] that one of these substances, $Co(B_9C_2H_{11})_2^{-1}$, could be electrophilically brominated by treatment with neat bromine or bromine in glacial acetic acid to give $Co(B_9C_2H_8Br_3)_2^{-1}$. This is thought[7] to be the first example of a substitution upon the intact bis-dicarbollyl metal "sandwich" compound.

This determination[8] of the crystal structure of the tetramethyl-ammonium salt of the product ion once again establishes the bis-dicarbollyl metal structure as two icosahedra with the metal atom as their common vertex. This work was undertaken in order to ascertain the positions of bromine substitution upon these icosahedra. It was found that the bromines are bonded to three borons in each icosahedron which form a triangular face, one corner of which is adjacent to the cobalt atom. The other two corners of the brominated face are as far as possible from the two carbon atoms, which are adjacent to each other and to the cobalt.

B. Experimental

Crystals of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$ were received from Professor

---

* References and Footnotes for part III are to be found on page 49.

M. F. Hawthorne of the University of California, Riverside. Intensity data were collected from two of these orange-brown crystals, both of which were approximately 0.1 mm square and 0.05 mm thick. The calculated linear absorption coefficient, μ, was 153 cm^{-1} (for CuKα). It is estimated that the absorption effect on intensities may vary by a factor of the order of 1.5 between the extreme cases. Both crystals were mounted by being glued to the ends of Pyrex glass fibers in such a way that the fiber, the instrument φ axis, and the b axis were all perpendicular to the plate. A General Electric XRD-5 X-ray diffractometer equipped with a molybdenum X-ray tube, a manual quarter-circle Eulerian-cradle goniostat, and a Zr filter at the receiving slit was used to measure cell dimensions. They were obtained from carefully measured 2θ (θ is the Bragg angle) values of the h00, 0k0, and 00ℓ reflections. The alpha doublet (λ(MoKα_1) = 0.70926 A) was resolved. The β angle was obtained directly from the angle on the φ circle between the h00 and 00ℓ sets of reflections. A card-controlled version of the same apparatus, using a copper X-ray tube and a Ni filter between crystal and counter, measured intensities by scanning 2θ at the rate of 1°/min., beginning 0.7° below the α_1 peak and ending 0.7° above the α_2 peak (λ(CuKα_1,Kα_2) = 1.5405, 1.5443 A). The take-off angle at the X-ray tube anode was approximately 4°. Coincidence losses were negligible. Ten-second stationary background counts were taken at each end of the scan. Three reflections which were measured at frequent intervals showed no systematic trends over the course of taking either data set. The maximum 2θ was 75° ($\sin\theta/\lambda$ = 0.395).

The first crystal yielded 1598 independent intensities before it

was accidentally destroyed. Of these, ~ 23% were measured once, ~ 64% either two or three times, and the remainder up to six times. These multiple measurements include remeasurements of the same reflection and measurements of equivalent $(-h,k,-l)$ reflections in an irregular pattern caused by the fact that these measurements were made during an initial exploration of the use of the newly-acquired diffractometer. The second crystal gave a complete set of 3002 independent intensities. Approximately 75% of these (those with $|l| \leq 6$) also had their equivalent $(-h,k,-l)$ reflections measured. These figures do not include the space group extinctions which were also measured and found to confirm the extinction rules $(0k0, k \neq 2n$ and $h0l, l \neq 2n)$ obtained from preliminary Weissenberg photographs.

The intensity, I, and standard deviation, $\sigma(I)$, for each measurement was calculated by:

$$I = C - (t_C/2t_B)(B_1 + B_2) \qquad \text{and:}$$

$$\sigma^2(I) = C + (t_C/2t_B)^2(B_1 + B_2) + (0.06 \times I)^2$$

where C is the number of counts accumulated in scanning through the reflection in time t_C, and B_1 and B_2 are the background counts, each obtained in time t_B. Within each data set, multiple measurements (including measurements of equivalent reflections) were averaged and the averages assigned standard deviations equal to the greater of: $(\Sigma_i \sigma_i^2/n^2)^{\frac{1}{2}}$ or $(\Sigma_i \Delta_i^2/n^2)^{\frac{1}{2}}$, where σ_i and Δ_i are the standard deviation and deviation from the average of the ith measurement and n is the number of measurements averaged. The latter expression did give the greater value in 10% of the

cases in the first set and 15% in the second set. Later, it was realized that this procedure tends to "average out" the $0.06 \times \underline{I}$ included in $\sigma(\underline{I})$, but this was approximately corrected when the two data sets were combined as described below. Observed structure factors for reflections which were included in both data sets were larger in the first set about as often as in the second, and corresponding values were typically in disagreement by 5%. There was no statistically valid deviation from equal scaling, and the combined data set was generated by averaging (without scaling) those $\underline{F}_{\underline{o}}$ values[9] which the two sets had in common and setting:

$$\sigma^2(\underline{F}_{\underline{ave}}) = 0.5[\sigma^2(\underline{F}_1) - (0.03\underline{F}_1)^2] + 0.5[\sigma^2(\underline{F}_2) - (0.03\underline{F}_2)^2] + (0.03\underline{F}_{\underline{ave}})^2,$$

where the terms in square brackets were set to zero if they were negative. If the expression: $\sigma^2(\underline{F}_{\underline{ave}}) = 0.5(\underline{F}_1 - \underline{F}_2)^2$ gave a larger number, it was used instead. In no case was any reflection of the combined set allowed to have a standard deviation less than 3% of itself (corresponding to 6% of $\underline{I}$). A plot of the resulting $\sigma(\underline{F}_{\underline{o}})$ versus $\underline{F}_{\underline{o}}$ revealed that the great majority of points fall on or near a smooth curve. This curve starts near 10 electrons for small $\underline{F}_{\underline{o}}$, stays near 3 electrons for $\underline{F}_{\underline{o}} = 40$ to 100 electrons, and follows the 3% of $\underline{F}_{\underline{o}}$ line thereafter. Forty-five percent of the data have $\underline{F}_{\underline{o}} \geqq 70$ electrons, and of these, only about 8% have standard deviations more than three electrons above the curve described, with the 002 reflection by far the worst at 441 ± 66 electrons. These large deviations were, of course, caused by disagreements between the two data sets obtained from the two different crystals. All data were corrected for Lorentz and polarization effects, but no corrections beyond the averaging just described were made for absorption or extinction.

Computations were performed on an IBM 7044 and a CDC 6600. Zalkin's FORDAP and DISTAN programs (unpublished) were used for Fourier syntheses and distance-and-angle calculations. An unpublished Wilson-plot program by Maddox and Maddox gave normalized structure factor magnitudes[10] which were used in Long's sign-determination program[11] as described below. The unpublished version of the Ganzel-Sparks-Trueblood least-squares program which was used, minimizes the function $\Sigma \underline{w}(|\underline{kF}_\underline{o}| - |\underline{F}_\underline{c}|)^2/\Sigma \underline{w}|\underline{kF}_\underline{o}|^2$, where $\underline{F}_\underline{o}$ and $\underline{F}_\underline{c}$ are the observed and calculated structure factors, $\underline{k}$ is the scale factor, and $\underline{w}$ is the weighting factor. Scattering factors[12] for Co^{+3} and neutral Br were corrected for the real part of anomalous dispersion by -2.2 and -0.9 electrons, respectively. The imaginary part of anomalous dispersion was neglected. Scattering factors for neutral nitrogen, carbon, and boron were also taken from standard tables[12]. The anisotropic temperature factors used have the form:

$$\exp(-0.25 \ \Sigma_\underline{i} \Sigma_\underline{j} \underline{h}_\underline{i} \underline{h}_\underline{j} \underline{b}_\underline{i} \underline{b}_\underline{j} \underline{B}_\underline{ij}),$$

$\underline{i},\underline{j} = 1,2,3$, where $\underline{b}_\underline{i}$ is the $\underline{i}$th reciprocal cell length.

C. Results

The monoclinic unit cell, space group $P2_1/c$, $\underline{a} = 19.893 \pm .010$ A, $\underline{b} = 19.487 \pm .010$ A, $\underline{c} = 15.058 \pm .010$ A, $\beta = 93.15 \pm .05°$, contains eight formula units of $N(CH_3)_4[Co(B_9C_2H_8Br_3)_2]$. The calculated density of 1.967 g/cc agrees with the value (1.98 ± .01 g/cc) found by flotation in a mixture of bromoform and ethylene dichloride. These measurements apply to room temperature ($\sim 23°$ C) and the error figures given are estimates. The observed extinctions correspond to space group $P2_1/c$. All four of

the two-fold sets of special positions are occupied by cobalt atoms and all other atoms are in general four-fold positions $\pm(x,y,z; x,\frac{1}{2}-y,\frac{1}{2}+z)$.

1. Determination of Structure

Attempts to interpret the Patterson function calculated from the second (complete) data set failed because of an error in communication which resulted in the mistaken idea that there were four, rather than eight, molecules per unit cell. Normalized structure factor magnitudes,[10] E_h, were calculated and used in Long's sign-determining program[11] which iteratively applies the relation; $sE_h \sim s\Sigma_k E_k E_{h-k}$, where s is to be read "the sign of". After enough of the signs were worked out by hand to yield a good set of "starting reflections" for input, a run of Long's program on 379 E's $\geqq 1.5$ gave one set of signs which was better than any other as judged by the smaller number of passes necessary to reach it and by its high consistency index (0.82 as against the second-best 0.65). The consistency index is defined as: $\Sigma_h \Sigma_k E_h E_k E_{h-k} / \Sigma_h \Sigma_k |E_h E_k E_{h-k}|$. A Fourier synthesis using the signed E's as coefficients showed sixteen largest peaks ranging in relative size from 1.00 to 0.57 with a definite break down to the seventeenth at 0.28. Isotropic bromines at these sixteen positions, four of which were the two-fold special positions, quickly refined to $R = 0.26$ where $R = \Sigma||kF_o| - |F_c||/ \Sigma|kF_o|$. A difference Fourier synthesis phased by these sixteen atoms showed all fifty-four of the non-hydrogen light atoms. Their locations showed that the asymmetric unit contains four half-anions plus two tetramethylammonium ions and that the cobalt atoms are those in the four two-fold sets of

special positions. The refinement beyond this point was routine except that, because of the large number of parameters involved, it was done in a block diagonal fashion. The heavy atoms (four anisotropic cobalts fixed at the special positions plus twelve anisotropic bromines) were refined full-matrix while the light atoms were held fixed, alternately with full-matrix refinements of the fifty-four isotropic light atoms with the heavy atoms fixed. The two carbons in each of the four icosahedral fragments were identified by their low temperature factors when refined as borons and the shorter distance between them. The partial data set from the first crystal was averaged in as described above when the refinement halted at $R = 0.11$ and it was found that the large disagreements were concentrated at low angle (where most of the partial data set had been obtained). Continued refinement using this composite data set changed the structure only slightly, but R fell to nearly its final value and the distribution of large disagreements became more uniform. Six cycles of diagonal-matrix least-squares (all parameters) finished the refinement and gave the final R value of 0.087. The standard deviation of an observation of unit weight, defined as $[\Sigma w(|kF_o| - |F_c|)^2/(u-v)]^{\frac{1}{2}}$, where u is the number of data and v is the number of independent parameters refined, was 2.28. Standard deviations derived from the final diagonal matrix were typically 10% less than those obtained from one cycle of full-matrix refinement which included all parameters, and ranged from approximately 5% larger to approximately 25% smaller.[13] In the last cycle, no parameter shifted more than 4% of the standard deviation calculated for it, except for the tetramethylammonium ions, where a few parameters shifted by as much as 11%

of their calculated standard deviations. The six largest peaks in a final difference Fourier (1.9, 1.8, 1.8, 1.3, 1.1, and 0.9 electrons/A^3) were all judged to be due to errors in the data, since their positions (far from any atom) made no chemical sense. This result made a search for hydrogens unjustified. The final atomic coordinates and thermal parameters are listed in Table I and the values of $|\underline{F}_o|$ and $\underline{F}_c$ are given in Table II.

2. Discussion

All four crystallographically unrelated anions were found to have the same atomic arrangement with corresponding dimensions equal to within the experimental accuracy. Figure 1 illustrates the structure of the $Co(B_9C_2H_8Br_3)_2^{-1}$ anion and the numbering system used in this study. The top and bottom halves of the anion are related by a crystallographic inversion center located at the cobalt. Interatomic distances are presented in Table III and averages thereof in Table IV. The average B-B, B-C, C-C, B-Br, and Br-Br distances are in agreement with those found[14-19] for similar compounds. The Br-B-B angles are all (with one exception) within 5° of their 121° average and show no significant deviations from this value which are systematic over the four anions. The Br(5)-B(5)-Co angles are slightly smaller (116° to 119°) as expected from the protrusion of the icosahedron's cobalt vertex. This protrusion is also shown by the smaller angles (49.4^o with a root-mean-square deviation of $\pm 1.7^o$ about this value) at cobalt. The 120 B-B-B angles necessarily average to exactly 60° and have a root-mean-square deviation of 2°. The sixteen B-C-B and thirty-two C-B-B angles average 63° and $58\frac{1}{2}^o$ while the four C-B-C and

Table I. Final Positional and Thermal Parameters[a] in $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
1 Co	0.	0.	0.	3.1(2)	2.1(2)	3.0(2)	0.7(2)	0.1(2)	0.0(2)
1 Br(5)	.0939(1)[b]	.0812(1)	−.1619(2)	6.1(1)	5.8(2)	5.0(2)	−0.1(1)	0.9(1)	0.6(1)
1 Br(9)	.1640(2)	.1975(2)	.0155(2)	7.9(2)	6.9(2)	8.3(2)	−2.5(1)	−1.2(2)	0.2(2)
1 Br(10)	−.0010(1)	.2408(1)	−.1278(2)	7.6(2)	3.4(1)	8.4(2)	−0.1(1)	−1.5(2)	2.2(1)
2 Co	0.5	0.5	0.	2.2(2)	2.2(2)	2.2(2)	−0.1(2)	0.4(2)	−0.2(2)
2 Br(5)	.3829(1)	.4459(1)	.1533(2)	4.9(1)	4.7(1)	5.4(2)	−0.8(1)	2.5(1)	0.4(1)
2 Br(9)	.3712(2)	.2769(2)	.0308(2)	12.7(2)	8.2(2)	6.5(2)	−7.7(1)	1.4(2)	−1.0(2)
2 Br(10)	.5025(1)	.3069(1)	.2262(2)	8.3(2)	5.0(1)	4.8(2)	−1.0(1)	0.2(1)	2.0(1)
3 Co	0.	0.5	0.	2.1(2)	2.1(2)	3.1(3)	0.3(2)	0.3(2)	0.0(2)
3 Br(5)	.0684(1)	.6171(1)	−.1475(2)	5.1(1)	5.9(1)	8.4(2)	0.1(1)	1.8(1)	4.2(1)
3 Br(9)	.1905(1)	.4844(2)	−.2110(2)	6.2(1)	7.8(2)	6.9(2)	−1.3(1)	3.5(1)	−2.1(1)
3 Br(10)	.2332(1)	.6034(2)	−.0147(2)	4.3(1)	8.4(2)	8.6(2)	−3.1(1)	1.3(1)	−2.1(2)
4 Co	0.5	0.	0.	2.6(2)	2.5(2)	2.9(3)	0.9(2)	0.4(2)	0.2(2)
4 Br(5)	.4304(1)	−.1082(1)	−.1688(2)	5.8(1)	4.2(1)	3.3(1)	−0.5(1)	0.4(1)	−0.6(1)
4 Br(9)	.2666(1)	−.0179(2)	−.1510(2)	4.8(1)	7.5(2)	6.9(2)	0.1(1)	−2.0(1)	1.8(2)
4 Br(10)	.3133(1)	−.1774(1)	−.0066(2)	6.4(1)	4.7(1)	5.0(2)	−1.7(1)	0.6(1)	0.0(1)

atom	x	y	z	B	atom	x	y	z	B
1 C(2)	−.060(1)	.070(1)	.057(1)	3.5(5)	3 C(2)	.068(1)	.463(1)	.088(2)	4.8(6)
1 C(3)	.012(1)	.050(1)	.115(2)	4.7(6)	3 C(3)	.053(1)	.413(1)	.004(1)	4.4(5)
1 B(4)	.079(1)	.058(1)	.058(2)	3.8(6)	3 B(4)	.056(1)	.451(1)	−.099(2)	3.9(6)
1 B(5)	.044(1)	.091(1)	−.055(2)	3.4(6)	3 B(5)	.085(1)	.540(1)	−.067(2)	2.2(5)
1 B(6)	−.040(1)	.092(1)	−.042(2)	3.1(6)	3 B(6)	.090(1)	.546(1)	.052(2)	3.9(6)
1 B(7)	−.034(2)	.124(2)	.141(2)	7.5(9)	3 B(7)	.131(2)	.398(2)	.056(2)	7.0(9)
1 B(8)	.060(1)	.124(1)	.136(2)	4.3(7)	3 B(8)	.122(1)	.399(2)	−.053(2)	5.7(8)
1 B(9)	.079(1)	.150(2)	.029(2)	6.2(8)	3 B(9)	.147(1)	.477(1)	−.096(2)	3.3(6)
1 B(10)	.005(1)	.169(1)	−.036(2)	3.8(6)	3 B(10)	.164(1)	.532(1)	−.009(2)	3.5(6)
1 B(11)	−.068(2)	.151(2)	.033(2)	7.4(9)	3 B(11)	.159(2)	.483(2)	.091(2)	6.2(8)
1 B(12)	.011(2)	.192(2)	.073(2)	7.7(9)	3 B(12)	.185(1)	.445(2)	−.007(2)	5.6(8)
2 C(2)	.580(1)	.435(1)	−.001(1)	4.3(6)	4 C(2)	.447(1)	−.009(1)	.113(1)	3.4(5)
2 C(3)	.522(1)	.422(1)	−.082(1)	4.1(5)	4 C(3)	.425(1)	.060(1)	.053(1)	3.7(5)
2 B(4)	.443(1)	.413(1)	−.048(2)	3.9(6)	4 B(4)	.407(1)	.037(1)	−.064(2)	3.9(6)
2 B(5)	.455(1)	.418(1)	.073(2)	1.8(5)	4 B(5)	.416(1)	−.055(1)	−.063(2)	4.5(7)

2 B(6)	.541(1)	.436(1)	.101(2)	2.9(6)	4 B(6)	.445(1)	-.085(1)	.046(2)	3.7(6)
2 B(7)	.578(2)	.357(2)	-.050(2)	6.7(8)	4 B(7)	.372(2)	.030(2)	.128(2)	6.7(8)
2 B(8)	.438(1)	.342(2)	-.079(2)	6.4(8)	4 B(8)	.346(1)	.060(1)	.018(2)	4.5(7)
2 B(9)	.447(1)	.340(2)	.023(2)	5.7(8)	4 B(9)	.336(1)	-.017(1)	-.052(2)	3.4(6)
2 B(10)	.509(1)	.352(2)	.109(2)	5.4(7)	4 B(10)	.357(1)	-.088(1)	.014(2)	2.9(6)
2 B(11)	.589(1)	.361(1)	.064(2)	4.7(7)	4 B(11)	.378(1)	-.060(1)	.124(2)	4.7(7)
2 B(12)	.527(2)	.301(2)	.019(2)	6.3(8)	4 B(12)	.311(1)	-.020(1)	.060(2)	5.0(7)
1 N	.773(1)	.255(1)	.265(1)	4.9(4)	2 N	.269(1)	.259(1)	.272(1)	6.3(5)
1 Me(1)	.796(2)	.214(2)	.345(3)	14.8(13)	2 Me(1)	.237(2)	.301(3)	.196(3)	17.4(16)
1 Me(2)	.701(2)	.245(2)	.250(2)	11.1(10)	2 Me(2)	.240(3)	.216(3)	.337(5)	24.5(24)
1 Me(3)	.812(1)	.235(1)	.187(2)	8.1(8)	2 Me(3)	.312(2)	.209(2)	.233(3)	17.3(16)
1 Me(4)	.791(2)	.329(2)	.300(3)	12.6(11)	2 Me(4)	.301(2)	.317(2)	.328(3)	14.0(13)

(a) The units are A^2.

(b) The numbers in parentheses are the standard deviations in the least significant digit as calculated from the final diagonal least-squares matrix. They are not significantly different from those obtained from the complete matrix (see text and footnote 13).

Table II. Observed and Calculated Structure Factors for $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

```
H,K=  0,  0
  L FOB FCA
  2 441 521
  4 224 263
  6 578 615
  8 248 254
 10  32 -31

H,K=  0,  1
  L FOB FCA
  1   7  -4
  2 128-156
  3  65 -92
  4  47 -61
  5  34 -35
  6 217-235
  7 110 136
  8 148-150
  9 159-164
 10  94 -91
 11  34  20

H,K=  0,  2
  L FOB FCA
  0 244 303
  1 149 192
  2 165 114
  3  11  -3
  4 198-212
  5  52 -62
  6 175 160
  7  13 -16
  8  79 -62
  9 112 104
 10  13   6
 11  41 -22

H,K=  0,  3
  L FOB FCA
  1  55 -73
  2 256-308
  3  97-115
  4 159 143
  5 182-151
  6 235 260
  7  53 -51
  8  89 -91
  9  64 -62
 10  51  48
 11 128-120

H,K=  0,  4
  L FOB FCA
  0 269 265
  1  70 -71
  2  58 -33
  3 132 147
  4 115 143
  5 139-150
  6  52 -54
  7  87  66
  8 155 154
  9  52  54
 10 118 121
 11  58 -43

H,K=  0,  5
  L FOB FCA
  1 200 222
  2  79  88
  3 265 264
  4  73 -76
  5  61 -51
  6  45 -43
  7 249 256
  8  59 -55
  9  68  59
 10  63  69
 11  50  40

H,K=  0,  6
  L FOB FCA
  0  70 -64
  1  68  76
  2  99 112
  3  77 -60
  4 318 321
  5  43 -37
  6  23  -4
  7  16  -3
  8 156 157
  9  10  -5
 10 190 166

H,K=  0,  7
  L FOB FCA
  1  20  14
  2  71 -79
  3  42  43
  4  60 -62
  5  18  17
  6  43  52
  7  33  33
  8  17  18
  9  19   6
 10  99 -95

H,K=  0,  8
  L FOB FCA
  0  72  69
  1 143-155
  2  43 -47
  3  39 -38
  4 115-116
  5   5 -17
  6  68  70
  7  60 -64
  8  84  75
  9  79 -64
 10  33  18

H,K=  0,  9
  L FOB FCA
  1  83 -98
  2  46 -33
  3 259-269
  4  15   6
  5 124-131
  6 135 125
  7  42  42
  8 149-142
  9  90 -67

H,K=  0, 10
  L FOB FCA
  0 246 268
  1 123-139
  2  84 100
  3 143 141
  4 279 290
  5 112 118
  6 226 222
  7   0 -18
  8  63  64
  9  60  49

H,K=  0, 11
  L FOB FCA
  1 145 167
  2 193-215
  3   9  22
  4  90  93
  5  39  44
  6  29  31
  7 131 132
  8 112-115

H,K=  0, 12
  L FOB FCA
  0 132 127
  1 116-121
  2 110 110
  3  42 -49
  4 113 116
  5 147 154
  6  53  59
  7  63 -67

H,K=  0, 13
  L FOB FCA
  1   6  16
  2 111 111
  3 139-140
  4  20  21
  5  27 -23
  6  14   2

H,K=  0, 14
  L FOB FCA
  0  44 -54
  1  70 -72
  2  79  65
  3  69  69
  4  60  65

H,K=  0, 15
  L FOB FCA
  1  15  -3
  2  94  97

H,K=  1,  0
  L FOB FCA
-10  27  36
 -8  22  25
 -6  11  23
 -4  24  22
 -2 153-164
  0   0 -10
  2 216 238
  4 451-481
  6  35  40
  8  71  71
 10  20 -41

H,K=  1,  1
  L FOB FCA
-11 108  98
-10   0 -15
 -9  56 -63
 -8  17  25
 -7  49 -53
 -6  16 -19
 -5 214 244
 -4 121 126
 -3  57 -75
 -2 175-223
 -1  71 -67
  0   6  -7
  1  66  75
  2 161 201
  3  66  85
  4  97-106
  5 248-261
  6  91  84
  7  75  76
  8  66  71
  9  43  33
 10  67  91
 11 166-175

H,K=  1,  2
  L FOB FCA
-11 113 104
-10  22 -18
 -9   0  -6
 -8 108 -99
 -7 147-157
 -6 177-202
 -5 201 229
 -4 324 330
 -3 119-125
 -2 180-214
 -1  74-100
  0  20  34
  1  73  66
  2  98 112
  3  21 -39
  4 184 198
  5 195-208
  6  53  59
  7  97  97
  8  24  10
  9  24 -21
 10  76  73
 11  90 -72

H,K=  1,  3
  L FOB FCA
-11 143 139
-10 186 178
 -9 167-166
 -8  49 -42
 -7 145 155
 -6  64  71
 -5  62  93
 -4 279 310
 -3 207-237
 -2 209 253
 -1 237-231
  0 152 149
  1 219-208
  2 172 207
  3  11 -20
  4  17 -20
  5 143-152
  6  87 104
  7 165 169
  8 112 124
  9  13 -14
 10 152-145
 11   6   2

H,K=  1,  4
  L FOB FCA
-11  23 -24
-10  77  66
 -9  70 -73
 -8 115 111
 -7 123-130
 -6  61 -47
 -5 175-173
 -4  51  68
 -3 119-115
 -2  24 -171
 -1 161-176
  0   9   4
  1 115 111
  2  65 -63
  3 258-268
  4 161-165
  5  32  25
  6  64 -64
  7  49  53
  8 133-135
  9   0 -25
 10  63  61
 11  52 -55

H,K=  1,  5
  L FOB FCA
-11  52 -47
-10  41 -48
 -9  98 -83
 -8 135-128
 -7  13  13
 -6  16  -8
 -5 140 146
 -4  36  37
 -3 151-149
 -2 265-319
 -1 143 147
  0 279-237
  1  64  58
  2 181 205
  3 109 115
  4 112 -96
  5 155 151
  6 171-168
  7  81  77
  8  93  96
  9 113 112
 10  16  27
 11   4 -12

H,K=  1,  6
  L FOB FCA
-10  43 -40
 -9  62  60
 -8  70 -64
 -7 151 152
 -6  20 -31
 -5  20  20
 -4  95  84
 -3  79 -91
 -2  16  10
 -1 429 432
  0 157-143
  1  97-107
  2  99  99
  3  82 -91
  4  80  77
  5  57  76
  6   6   0
  7  37 -30
  8 100-101
  9  61 -57
 10  64  61

H,K=  1,  7
  L FOB FCA
-10  80 -79
 -9   6  -7
 -8  49  49
 -7  20 -24
 -6  82 -86
 -5  59 -75
 -4  62  50
 -3 124 125
 -2 107 120
 -1  98 -95
  0 131-138
  1 306-322
  2  10   3
  3 179 188
  4  67 -72
  5  51 -53
  6  23  18
  7  83 -89
  8  33 -29
  9  28  16
 10  62  49

H,K=  1,  8
  L FOB FCA
-10  50 -44
 -9  49  44
 -8  61  70
 -7 126 132
 -6  38 -36
 -5  85 -85
 -4  39  46
 -3  56 -63
 -2 219-247
 -1 260 293
  0 256 215
  1  35 -28
  2  62  66
  3  87 -83
  4 125-117
  5 262 287
  6  17 -15
  7  27  39
  8 192 187
  9  11  23
 10   0  22

H,K=  1,  9
  L FOB FCA
 -9  95 102
 -8  15  -9
 -7  27 -37
 -6  80  62
 -5  15 -16
 -4 145-150
 -3 165 182
 -2  36  22
 -1  23  -5
  0  76  69
  1  97 -81
  2  15 -25
  3 199 220
  4  10   9
  5  23 -31
  6  19  -6
  7  51 -44
  8  19   5
  9  52  60

H,K=  1, 10
  L FOB FCA
 -9 106 -98
 -8  81 -79
 -7  22  19
 -6  74  79
 -5  88  92
 -4  98 105
 -3 120-133
 -2  38 -45
 -1  55 -54
  0  51 -42
  1  72  87
  2 176 185
  3 114-124
  4  85 -87
  5  53 -59
  6  45  42
  7  96-103
  8  36  32

H,K=  1, 11
  L FOB FCA
 -8  55  53
 -7  51 -59
 -6  36 -33
 -5  30  24
 -4  91 -84
 -3   7  -1
 -2  39  60
 -1  45 -45
  0  57  48
  1  67 -70
  2  78-124
  3  30  30
  4 143-154
  5  66 -87
  6 199 202
  7 101-109
  8  84 -72

H,K=  1, 12
  L FOB FCA
 -7 147-147
 -6  11  19
 -5  77  80
 -4  23  -6
 -3 144-152
 -2 122-128
 -1  17 -24
  0  74  66
  1   6  10
  2  45 -37
  3  21  -9
  4  47 -52
  5  65 -67
  6  59  57
  7  65  64

H,K=  1, 13
  L FOB FCA
 -6 155 155
 -5  46 -34
 -4  49  53
 -3 114-121
 -2  32  41
 -1 120 117
  0 147 147
  1 151 151
  2 147 151
  3  27 -35
  4  39  44
  5  23 -15
  6  86  95

H,K=  1, 14
  L FOB FCA
 -4  70  64
 -3  25  30
 -2  28 -25
 -1  29 -26
  0  29 -22
  1 149 171
  2  63 -93
  3  32  31
  4  40  37

H,K=  1, 15
  L FOB FCA
 -2  13   5
 -1  45  50
  0  55 -59
  1  24  23
  2  34 -26

H,K=  2,  0
  L FOB FCA
-10  79 -92
 -8  72 -68
 -6  45 -34
 -4 123-125
 -2  57-137
  0 380 350
  2 433 414
  4 339-326
  6  58 -71
  8 116 122
 10  11  13

H,K=  2,  1
  L FOB FCA
-11  25   0
-10  67 -89
 -9  45  34
 -8 119-124
 -7  36  33
 -6   4 -22
 -5   7  28
 -4 257-255
 -3  34  26
 -2  39 -65
 -1 228 227
  0  75 -92
  1 222-222
  2 132-120
  3  54  60
  4  67  66
  5 151 162
  6 153-151
  7 149-148
  8  77  73
  9  46 -50
 10  43 -36
 11  18  33

H,K=  2,  2
  L FOB FCA
-11   8 -20
-10  65  65
 -9  47  47
 -8  38  46
 -7 201-215
 -6 166 163
 -5 135-144
 -4 391 401
 -3 211 217
 -2 117 133
 -1 445-463
  0 140  91
  1 217-221
  2 412 463
  3  90  91
  4  67  83
  5 165-196
  6 105 105
  7 261-296
  8  55  57
  9 141 139
 10 123 120
 11  37 -22

H,K=  2,  3
  L FOB FCA
-11  62 -46
-10  45 -37
 -9  92  93
 -8 130 121
 -7 166-179
 -6 143-162
 -5 117 127
 -4  62 -57
 -3  49 -44
 -2 168 184
 -1  69  62
  0 172-176
  1  33  31
  2 114-127
  3 209 210
  4  43  43
  5 175 183
  6 106 121
  7  27 -34
  8  55  56
  9 243 249
 10  30  25
 11  42  41

H,K=  2,  4
  L FOB FCA
-11  97  91
-10 170 170
 -9 260 254
 -8 217 215
 -7  45 -61
 -6  45 -49
 -5 220 229
 -4 231 237
 -3 312 424
 -2 370 366
 -1 151 154
  0 155-147
  1  64  75
  2 406 397
  3 441 467
  4 161 171
  5  43 -49
  6 152 156
  7   7  13
  8 168 170
  9 131 129
 10 166 179
 11  25 -14

H,K=  2,  5
  L FOB FCA
-11  67  63
-10  52 -60
 -9  42  40
 -8  54 -59
 -7  14 -21
 -6 210 222
 -5  41 -43
 -4 127 156
 -3  58 -58
 -2  34 -50
 -1 225-208
  0 114  99
  1 257-244
  2 266 289
  3 101-105
  4  35 -12
  5 328-366
  6  82 -81
  7 159-169
  8  76  69
  9  69 -64
 10  23 -31
 11  80 -73

H,K=  2,  6
  L FOB FCA
-10  82  96
 -9  29 -24
 -8 271 272
 -7 136-130
 -6  32 -41
 -5  39 -54
 -4 310 339
 -3 125-134
 -2 257 260
 -1 375-351
  0 188-164
  1  81  73
  2  34 -23
  3 270-263
  4 302 298
  5  55 -64
  6  49 -44
  7  13  13
  8  50 -40
  9  45  49
 10 114  99

H,K=  2,  7
  L FOB FCA
-10  16  -6
 -9  57  62
 -8 197-204
 -7 143-151
 -6  72  67
 -5  36  20
 -4  72 -87
 -3  17 -10
 -2 149-135
 -1  26  16
  0  93 -87
  1 159-150
  2 164-165
  3 110 131
  4 198-211
  5 150 159
  6  36 -40
  7  90-101
  8   9  33
  9 114 114
 10 170-165

H,K=  2,  8
  L FOB FCA
-10  24   6
 -9  54 -46
 -8 220 208
 -7  21 -22
 -6 172 180
 -5  80  78
 -4 103-103
 -3  44 -51
 -2 300 318
 -1 122 109
  0 105  83
  1 162 158
  2 186 189
  3  64 -68
  4  81  67
  5  75  84
  6 295 319
  7  49  57
  8  95  95
  9  50 -46

H,K=  2,  9
  L FOB FCA
 -9  71  73
 -8  96  96
 -7 105 106
 -6 192 197
 -5 106 103
 -4  90  86
 -3  44  44
 -2  56  33
 -1 204 200
  0 151 157
  1  45  47
  2 146 149
  3  12  27
  4  19 -27
  5  56  60
  6  72  64
  7  42 -33
  8  23  18
  9  18  21

H,K=  2, 10
  L FOB FCA
 -8  78  76
 -7   0   2
 -6  56  55
 -5 130 134
 -4 112 110
 -3  69 -74
 -2  25  -6
 -1  68 -73
  0  31  18
  1  74  63
  2 142-135
  3  23  12
  4 156 168
  5  66 -71
  6  80  82
  7  33 -36
  8  63 -73

H,K=  2, 11
  L FOB FCA
 -8  23  -2
 -7  79 -67
 -6  21 -17
 -5  26  28
 -4 119-120
 -3  67 -82
 -2 122 123
 -1  91 -91
  0  73 -69
  1  26  15
  2  63 -73
  3  55  53
  4  92  92
  5  59 -61
  6   6  15
  7  20 -12
  8  72  74

H,K=  2, 12
  L FOB FCA
 -7  32 -42
 -6  33  26
 -5 122-127
 -4  60  59
 -3  17  13
 -2 164 155
 -1 101-109
  0  94  78
  1  19  17
  2 165 159
  3 108-105
  4  44  40
  5  18  12
  6 107  98
  7  76 -68

H,K=  2, 13
  L FOB FCA
 -6   8 -15
 -5 132 126
 -4  18 -23
 -3  76 -83
 -2  81 -88
 -1  63 -64
  0 167-157
  1 134 131
  2 100 101
  3  19 -15
  4  50  62
  5  66 -72
  6 138-136

H,K=  2, 14
  L FOB FCA
 -4 170 172
 -3 116-119
 -2 103 114
 -1  19 -16
  0  76  75
  1  59  63
  2 197 210
  3  10  10
  4 121 138

H,K=  2, 15
  L FOB FCA
 -2   9  19
 -1  72 -77
  0  67 -64
  1  36 -32
  2 123 118

H,K=  3,  0
  L FOB FCA
-10  82  65
 -8 129 115
 -6 216 237
 -4  89 -73
 -2 229 209
  0  25  23
  2 200 207
  4 411-410
  6  52  50
  8  76  72
 10 246-239

H,K=  3,  1
  L FOB FCA
-11  44  34
-10  85 -75
 -9 149 152
 -8  18  22
 -7 258-273
 -6  53 -51
 -5  68  69
 -4  85 -99
 -3 142 149
 -2 255-277
 -1 160 142
  0 124-123
  1 359 353
  2 133-123
  3  12  12
  4 209-214
  5  86  77
  6  48 -58
  7  39  39
  8 116-115
  9  73  64
 10  56  59
 11  60 -55

H,K=  3,  2
  L FOB FCA
-11  72  59
-10  51 -43
 -9   0 -14
 -8  31 -41
 -7  96 -94
 -6  52 -66
 -5 143 147
 -4 103-119
 -3  55  60
 -2  33  41
 -1  60  47
  0 116-105
  1  45  41
  2 164-167
  3 199 232
  4 124 109
  5   8  -3
  6  69  92
  7  69  77
  8  16 -13
  9  12   6
 10  65 -86
 11  10  18

H,K=  3,  3
  L FOB FCA
-11   8   1
-10  52  50
 -9  15 -11
 -8  42 -51
 -7   9  -1
 -6 105-137
 -5  14  -6
 -4 119-123
 -3  18  35
 -2 178 194
 -1  15   8
  0  55 -64
  1  18  21
  2 237-246
  3  55 -54
  4 159 160
  5  46  42
  6  49  39
  7  51 -54
  8  38 -28
  9  80 -74
 10  34 -34
 11  22  20

H,K=  3,  4
  L FOB FCA
-11  59  47
-10 132-131
 -9  81  80
 -8 154 154
 -7  78  86
 -6  80 -62
 -5  13   1
 -4 385-384
 -3 232 252
 -2 461 451
 -1  90 -79
  0 100  89
  1 187 195
  2 251-269
  3  90 -84
  4  96  89
  5  31  45
  6  79  78
  7  36 -31
  8 105-119
  9  28  20
 10  22 -30
 11  20  -2

H,K=  3,  5
  L FOB FCA
-11 101 -99
-10 127 115
 -9  80  80
 -8  52  48
 -7  41  41
 -6  26 -27
 -5  67 -63
 -4 128 135
 -3 251-251
 -2  86  92
 -1 159 146
  0 289-273
  1 131-149
  2  45  49
  3 289-312
  4 234 220
  5 215 220
  6 186-209
  7 137-139
  8  19 -25
  9  28  24
 10 128 124

H,K=  3,  6
  L FOB FCA
-10  79 -67
 -9  52 -36
 -8   0   5
 -7  61 -55
 -6  24  26
 -5 124-112
 -4 154-177
 -3 161-156
 -2 299 300
 -1  59 -51
  0 190-165
  1  69 -59
  2  22 -26
  3  32  46
  4 235 221
  5 133-134
  6 131 136
  7  94 105
  8 116-121
  9  77  66
 10  72  67

H,K=  3,  7
  L FOB FCA
-10  50  51
 -9  63  55
 -8  44  49
 -7  99  98
 -6 174-184
 -5  65 -65
 -4 152 169
 -3 145 156
 -2 269 274
 -1 265 252
  0 140-119
  1  40 -34
  2   9  -7
  3  38 -31
  4 235 244
  5 223 241
  6  34 -40
  7  25  -5
  8  19 -20
  9  90 -97
 10  75  75

H,K=  3,  8
  L FOB FCA
-10  24  -6
 -9  74  73
 -8  21 -21
 -7  54  43
 -6   7   1
 -5 104-107
 -4  18  18
 -3   7 -14
 -2  86 -96
 -1 182-167
  0  53  56
  1 190-171
  2  20  10
  3 211-225
  4  79 -77
  5  90 -89
  6 111-116
  7  54 -56
  8  93  86
  9  89 -84

H,K=  3,  9
  L FOB FCA
 -9  23  14
 -8  22 -33
 -7  82 -85
 -6 144 151
 -5 159-175
 -4  54 -51
 -3 137-141
 -2  46  35
 -1  33 -19
  0  59  55
  1 128-119
  2  18  21
  3 174-170
  4  78  77
  5  65  67
  6  76 -83
  7   0  13
  8  52  51
  9  37 -48

H,K=  3, 10
  L FOB FCA
 -8 169-157
 -7   0 -11
 -6  16   4
 -5  32  34
 -4 129 120
 -3  95  94
 -2  49 -51
 -1 103 -97
  0 247-241
  1 119 121
  2 157 163
  3  50  52
  4 115-120
  5  76  74
  6  35 -21
  7  11  15
  8  15  30

H,K=  3, 11
  L FOB FCA
 -8  47 -56
 -7   9 -12
 -6  26  22
 -5 112 120
 -4  62 -71
 -3  82  79
 -2  63 -62
 -1  65  49
  0 114 115
  1 114 106
  2 164-165
  3  41  40
  4  60 -49
  5  53  48
  6 155 159
  7  54 -50

H,K=  3, 12
  L FOB FCA
 -7  33 -48
 -6 [illegible]  22
 -5  17   2
 -4  81  88
 -3  76  83
 -2  78  75
 -1  46  52
  0  63  57
  1  72 -57
  2  62  51
  3  53  50
  4  20  21
  5  20   5
  6  52 [illegible]

H,K=  3, 13
  L FOB FCA
 -6  55  62
 -5  27 -31
 -4  64 -59
 -3  47 -48
 -2 115-121
 -1   5   7
  0  46 -40
  1  71  58
  2  42 -31
  3  21 -26
  4  24   6
  5  54 -55

H,K=  3, 14
  L FOB FCA
 -4  27   3
 -3 138 150
 -2   0  18
 -1  30 -30
  0  57 -52
  1  91  87
  2  62 -60
  3  80  83
  4  63  69

H,K=  3, 15
  L FOB FCA
 -1  47 -53
  0  77 -69
  1  99 -91

H,K=  4,  0
  L FOB FCA
-10 153 148
 -8  74  68
 -6 105  99
 -4 124 130
 -2 217-203
  0 311 264
  2  54  56
  4 193 179
  6 112-132
  8 331 344
 10 137 153

H,K=  4,  1
  L FOB FCA
-11 148-139
-10  23  16
 -9  75 -79
 -8  25  -6
 -7  38  44
 -6  66  82
 -5 255-235
 -4  12   7
 -3 135-117
 -2  67  62
 -1  73 -78
  0  25  33
  1  66  64
  2 320 348
  3 230-210
  4 207 204
  5  16   6
  6   0  12
  7  76  81
  8 202 212
  9  49 -57
 10  75  70
 11  23  19

H,K=  4,  2
  L FOB FCA
-11  47 -39
-10 202 197
 -9 167 184
 -8  26  22
 -7  33  18
 -6 317 348
 -5 161-161
 -4 288 268
 -3 565 572
 -2 395 394
 -1 108  94
  0 107 -74
  1  22  12
  2 429 415
  3 382 394
  4 265 253
  5 231 244
  6  80  70
  7  22 -17
  8 113 120
  9 178 183
 10  39  39
 11 102  97

H,K=  4,  3
  L FOB FCA
-11  20  12
-10  57  40
 -9  73  72
 -8  66  70
 -7  72  72
 -6 120-124
 -5 226 216
 -4  14  26
 -3  51 -47
 -2  15  18
 -1  81 -81
  0 116-108
  1 341 318
  2 247-257
  3 189-183
  4 132-109
  5  45 -61
  6  96-102
  7  37  41
  8 107-120
  9   5  12
 10 125-109
 11  62 -51

H,K=  4,  4
  L FOB FCA
-11 112 -99
-10  92  82
 -9  91  81
 -8  63  56
 -7 111-113
 -6 165 158
 -5 321-343
 -4 150-125
 -3 116 -95
 -2  69 -78
 -1  79  70
  0 270 224
  1 532-528
  2 150-165
  3  48  47
  4  67 -57
  5  37 -37
  6 103 104
  7 109-105
  8 174 181
  9  48 -47
 10  26 -14

H,K=  4,  5
  L FOB FCA
-10 112-112
 -9 107-104
 -8 155-149
 -7  62  64
 -6  70 -60
 -5  73  60
 -4  21 -28
 -3  20   9
 -2 223-211
 -1  68 -64
  0  44 -46
  1 417 389
  2  41  53
  3  13 -27
  4  24   6
  5  80 -73
  6  46 -57
  7 219 226
  8  75 -78
  9  52 -29
 10  33  28

H,K=  4,  6
  L FOB FCA
-10  55 -37
 -9   0   8
 -8  31 -20
 -7 270 263
 -6 220 224
 -5  72 -60
 -4  37  30
 -3  81  90
 -2  42  58
 -1 204 201
  0 278 247
  1 148 139
  2  25   8
  3 129-137
  4 153 144
  5 122 126
  6 153 167
  7  46  37
  8  82  91
  9  70 -66
 10  22   8

H,K=  4,  7
  L FOB FCA
-10  96  89
 -9  93  99
 -8  91 -87
 -7  42  32
 -6 142 136
 -5  37  32
 -4 103 106
 -3  22  32
 -2 148 152
 -1  12   9
  0 259 266
  1  62  52
  2   6 -19
  3 123-111
  4 177 172
  5  70  65
  6 177 190
  7  54 -51
  8  70  59
  9  29 -25

H,K=  4,  8
  L FOB FCA
 -9 115-112
 -8 181 168
 -7  51  59
 -6 352 358
 -5  64 -62
 -4  95 -79
 -3 138-133
 -2 224 208
 -1 130 128
  0 302 296
  1  34 -41
  2 130 125
  3 111-114
  4  30  25
  5  67  60
  6 142 146
  7  63  65
  8 123 116
  9 127-117

H,K=  4,  9
  L FOB FCA
 -9  35  20
 -8   9  -4
 -7  27  34
 -6  18  -2
 -5 167-181
 -4  29 -30
 -3  31  31
 -2 232-226
 -1  74  81
  0  95  89
  1  38 -40
  2  39 -40
  3  28 -27
  4 137-150
  5  47  47
  6  23  18
  7  81 -85
  8 111 -99

H,K=  4, 10
  L FOB FCA
 -8  33  48
 -7  30 -31
 -6 162 158
 -5  15  16
 -4 117 103
 -3  21 -16
 -2  91  79
 -1  94 -83
  0 180 171
  1  87 -80
  2  76  77
  3  13   8
  4 198 195
  5 148-152
  6  65  54
  7  54 -65
  8  69  65

H,K=  4, 11
  L FOB FCA
 -7  93 -81
 -6  15 -21
 -5  87 -62
 -4  58 -59
 -3  10   6
 -2  40  39
 -1 221-212
  0  53  53
  1  88 -83
  2 138-146
  3  64  67
  4  12  -6
  5  74 -81
  6  11   7
  7  62 -59

H,K=  4, 12
  L FOB FCA
 -6  36  44
 -5  50 -50
 -4  51  44
 -3 160 181
 -2 148 132
 -1  16   5
  0 228 212
  1  95  90
  2 210 199
  3 140 138
  4  71  75
  5 102 108
  6 105 111

H,K=  4, 13
  L FOB FCA
 -5 149 148
 -4  58  53
 -3  30  36
 -2  66  67
 -1  44 -52
  0  61  60
  1 164 156
  2  20  14
  3  39  34
  4  78  77
  5  44 -49

H,K=  4, 14
  L FOB FCA
 -4  69  61
 -3  75 -69
 -2  18  20
 -1  13 -16
  0  39 -20
  1  35 -31
  2  95  97
  3  15  15

H,K=  5,  0
  L FOB FCA
-10  16   9
 -8 291-303
 -6  99  89
 -4  51  57
 -2 327-283
  0 138 130
  2 420 426
  4 174-144
  6  62  52
  8 261 241
 10  26  33

H,K=  5,  1
  L FOB FCA
-11  24  25
-10 155-156
 -9  59  50
 -8 142 145
 -7 132-134
 -6 144 173
 -5 171-164
 -4  93  83
 -3 127 140
 -2  79  64
 -1 213-185
  0 341 322
  1  52 -39
  2 149 163
  3  11  17
  4  12  16
  5 246-230
  6  67  77
  7  76 -68
  8  65 -63
  9  16 -11
 10  67  68
 11  27 -46

H,K=  5,  2
  L FOB FCA
-11  23 -19
-10 134 140
 -9  79 -76
 -8  49 -35
 -7  70 -77
 -6 114 106
 -5 109-121
 -4 363 352
 -3 137-140
 -2 274-262
 -1  47  53
  0  27  26
  1 317-302
  2  50 -49
  3  42  38
  4  65  67
  5 109 106
  6 139-165
  7  51 -56
  8  74  72
  9  30 -23
 10  11  14

H,K=  5,  3
  L FOB FCA
-11  64  63
-10  71 -69
 -9  45 -46
 -8  70  64
 -7  71  68
 -6  37  38
 -5  50 -55
 -4 305-278
 -3 316 282
 -2 125 133
 -1 115-116
  0 222 205
  1  55  53
  2 320-313
  3 338 315
  4   8  28
  5  88 -94
  6 199 219
  7  38  47
  8  79 -70
  9  53  53
 10   0 -23

H,K=  5,  4
  L FOB FCA
-11   8  17
-10  19 -21
 -9  44 -41
 -8  68  65
 -7  39  42
 -6  28  20
 -5  43 -62
 -4 168-152
 -3  64  55
 -2  47  49
 -1  60 -65
  0 264 229
  1  15 -26
  2 107-100
  3  51 -50
  4  15  -5
  5  41  29
  6  13  17
  7 104 -97
  8  56  62
  9  21   1
 10  30  41

H,K=  5,  5
  L FOB FCA
-10   0   1
 -9  49 -40
 -8 132 134
 -7   3   6
 -6  40  63
 -5  12  -2
 -4  11  20
 -3  13  22
 -2  74  74
 -1  72 -62
  0  95  78
  1  11  16
  2  11   3
  3  51  49
  4  33  36
  5  43 -42
  6  23   2
  7  28 -28
  8  59 -60
  9 106 105
 10  19  -3

H,K=  5,  6
  L FOB FCA
-10  12  -4
 -9  48 -40
 -8  97 -86
 -7   0   6
 -6  28  -6
 -5 171 163
 -4  52 -58
 -3  88 -60
 -2  69 -70
 -1  17   8
  0 240-197
  1  92  82
  2 190-193
  3 155 129
  4  32  21
  5 193-194
  6 115-117
  7 114 113
  8 161-159
  9 101 103
 10   0  -3

H,K=  5,  7
  L FOB FCA
-10   0 -10
 -9 137-123
 -8  26  19
 -7  87  95
 -6 248-258
 -5  48 -26
 -4  23  27
 -3  31 -37
 -2  52 -49
 -1  66 -58
  0 100 -92
  1  30  40
  2  44 -47
  3  43 -40
  4  69 -79
  5  32 -30
  6 120 127
  7 139 137
  8   0  14
  9  54 -44

H,K=  5,  8
  L FOB FCA
 -9  18   6
 -8  25 -36
 -7  26 -23
 -6  21  15
 -5 130 144
 -4 164 169
 -3  52  45
 -2 115 -98
 -1  15 -12
  0 198 190
  1 145 137
  2  17  17
  3  16  18
  4  74  64
  5  79 -79
  6  50 -52
  7 118 125
  8  74  70
  9  14  17

H,K=  5,  9
  L FOB FCA
 -9   6 -13
 -8  33 -47
 -7 159 161
 -6  72  79
 -5 123 125
 -4  48 -49
 -3  65 -71
 -2 237-239
 -1  20  -4
  0  17  16
  1  89  99
  2  56  60
  3 157-154
  4 170-161
  5  48 -50
  6  95 -96
  7 116 115
  8  54  60

H,K=  5, 10
  L FOB FCA
 -8 143-132
 -7  41  44
 -6  73 -76
 -5  12  11
 -4 103 103
 -3  85 -78
 -2   9   7
 -1  39 -44
  0 169-[illegible]
  1  15 [illegible]
  2 114 117
  3  41 -43
  4  81  77
  5  26   9
  6  41  37
  7  59  62

H,K=  5, 11
  L FOB FCA
 -7  60 -65
 -6  82  75
 -5  74  69
 -4 109 106
 -3  13  -1
 -2  39 -33
 -1  96-106
  0 222 223
  1  46  38
  2  68  68
  3  61  61
  4  97-103
  5  18  -8
  6 165 161
  7  42 -42

H,K=  5, 12
  L FOB FCA
 -6  84 -60
 -5  29 -23
 -4  21  -9
 -3 106-103
 -2  42  34
 -1 185 183
  0  20 -34
  1 116-120
  2 121-113
  3  62 -56
  4  21 -17
  5  15  12
  6 100-104

H,K=  5, 13
  L FOB FCA
 -5  46 -39
 -4  26 -29
 -3  29  39
 -2 170-139
 -1  60 -72
  0  14 -14
  1  44 -38
  2   2  -2
  3  42  36
  4  51 -62

H,K=  5, 14
  L FOB FCA
 -3 111-108
 -2  62  57
 -1  18  -8
  0  30 -29
  1  30  26
  2   6 -14

H,K=  6,  0
  L FOB FCA
-10 269 264
 -8 407 422
 -6 165-159
 -4 331 336
 -2 373 367
  0  64  56
  2  50  35
  4 460 496
  6  22  -5
  8 102  96
 10 250 247

H,K=  6,  1
  L FOB FCA
-11  52  47
-10  50  40
 -9  48  57
 -8  96 -96
 -7 125 141
 -6  78  91
 -5  56 -58
 -4  50 -57
 -3 236 225
 -2 227-230
 -1 196 183
  0  65 -69
  1 116-107
  2  43  35
  3 336 333
  4  92 -66
  5  66  50
  6 184-204
  7  23   7
  8  63  50
  9  66  71
 10  67 -67

H,K=  6,  2
  L FOB FCA
-11  11 -16
-10  66  66
 -9  53  46
 -8 116 114
 -7  15  -8
 -6 219-241
 -5 169-108
 -4  95  94
 -3  13  -4
 -2 101  87
 -1  68 -61
  0 349-304
  1 107 -94
  2  21   2
  3 182-169
  4 295 279
  5  11  14
  6 111 112
  7  73 -72
  8  66 -67
  9  40 -34
 10 160 175

H,K=  6,  3
  L FOB FCA
-10  31 -10
 -9  61 -75
 -8  22 -25
 -7 145-145
 -6 140-142
 -5  31 -33
 -4 183 161
 -3 126-129
 -2  99  99
 -1 196-195
  0  14   3
  1 261-243
  2 240 250
  3   9   0
  4  90  80
  5 111-114
  6 135 142
  7 126-138
  8  42  49
  9  26 -17
 10  10 -12

H,K=  6,  4
  L FOB FCA
-10 116 103
 -9  31  38
 -8 207 204
 -7  53  46
 -6 211 217
 -5  47 -32
 -4 167 178
 -3 136-135
 -2 189 196
 -1 232 195
  0 545 494
  1 104-104
  2  56  68
  3   8  14
  4  36  16
  5  43  41
  6 250 249
  7  95  96
  8  26  28
  9   0  14
 10  17  27

H,K=  6,  5
  L FOB FCA
-10  24  22
 -9 166-163
 -8  36  39
 -7   0   7
 -6  40 -37
 -5  13  -5
 -4  63  47
 -3  58 -48
 -2  31 -39
 -1  13   6
  0 221-187
  1  59  60
  2  79  60
  3 106 115
  4  74  86
  5  14  -0
  6  63 -72
  7 124 129
  8  23 -16
  9  61 -64
 10  79  63

H,K=  6,  6
  L FOB FCA
-10  55  42
 -9 102-102
 -8  54  59
 -7  66  92
 -6 195 191
 -5  99  96
 -4 384 384
 -3  76 -74
 -2 127  95
 -1 166 142
  0 451 439
  1 246 226
  2 223 205
  3  62 -54
  4 278 271
  5  61  61
  6 233 232
  7  29 -12
  8  56  60
  9  30  24

H,K=  6,  7
  L FOB FCA
 -9   0   4
 -8   0   7
 -7  10   2
 -6  90 -95
 -5  32 -21
 -4  16  -6
 -3  24 -15
 -2  88  94
 -1  41  51
  0 251-253
  1 171-173
  2 161-155
  3  44 -50
  4  21 -22
  5  45 -26
  6  93 -94
  7 149-152
  8 107-108
  9 126-118

H,K=  6,  8
  L FOB FCA
 -9  92 -91
 -8  57 -45
 -7  81 -85
 -6  21  16
 -5  20  17
 -4  27  26
 -3 126-129
 -2  49 -40
 -1  46 -51
  0  45 -53
  1  82 -66
  2 134 137
  3  65 -70
  4  69 -96
  5  29 -32
  6  15 -17
  7  22 -12
  8   0  17

H,K=  6,  9
  L FOB FCA
 -8   7   6
 -7  36  21
 -6  49 -42
 -5 196-185
 -4  81  88
 -3  14  19
 -2 145-147
 -1 115 111
  0  90 -77
  1 106-114
  2 221 225
  3  66  56
  4  26 -20
  5  65  69
  6  35 -30
  7  16 -12
  8  83  79

H,K=  6, 10
  L FOB FCA
 -8  53  52
 -7 123-124
 -6  18  -9
 -5 193 197
 -4 309 297
 -3  93  97
 -2 100  94
 -1  36 -22
  0 129 123
  1  40  43
  2 195 190
  3 181 182
  4 271 264
  5  55 -50
  6  25 -28
  7  16   6

H,K=  6, 11
  L FOB FCA
 -7 101  99
 -6  57  62
 -5  47  43
 -4 123 138
 -3 239 233
 -2  19  27
 -1  94  87
  0  34 -26
  1  62 -65
  2 126 127
  3 196 190
  4 125-123
  5  77  77
  6  34 -34

H,K=  6, 12
  L FOB FCA
 -6  26  24
 -5  25  11
 -4  20   4
 -3  85  80
 -2  69  67
 -1 203-203
  0 108 101
  1 106-108
  2  86  85
  3  56 -62
  4  32 -10
  5  66 -71

H,K=  6, 13
  L FOB FCA
 -4  14   3
 -3  67 -75
 -2  39 -59
 -1  69 -64
  0  16   1
  1  40 -41
  2  69  68
  3  19  -7
  4  43 -50

H,K=  6, 14
  L FOB FCA
 -2  45  45
 -1  10 -12
  0  66  71
  1  14 -30

H,K=  7,  0
  L FOB FCA
-10  37 -34
 -8  41  21
 -6  65 -61
 -4  40 -45
 -2  94  80
  0 139-132
  2  78  65
  4 185-175
  6 104  66
  8  68 -62
 10  49  35

H,K=  7,  1
  L FOB FCA
-10 154-156
 -9  31  25
 -8   0   9
 -7 130 126
 -6  64  66
 -5  69 -59
 -4  65 -64
 -3 193-197
 -2 142-155
 -1 486 466
  0 116 110
  1  42 -56
  2  61  74
  3 157-155
  4  15 -10
  5 221 231
  6  41  36
  7  17  25
  8  30 -16
  9  54 -59
 10  98  99

H,K=  7,  2
  L FOB FCA
-10  55 -43
 -9 125 120
 -8  36  36
 -7 132 139
 -6  68 -81
 -5  12 -13
 -4 132 119
 -3 119 127
 -2  27 -22
 -1 365 373
  0  75 -62
  1 167-150
  2  93 -65
  3  67  98
  4  20   4
  5 190 189
  6  15 -21
  7  79 -80
  8 108-100
  9  66 -62
 10  17 -11

H,K=  7,  3
  L FOB FCA
-10 119-113
 -9  31 -33
 -8  49 -52
 -7  22 -23
 -6  46  61
 -5 148-150
 -4 267-275
 -3  63 -60
 -2  18   2
 -1  30  21
  0  12 -16
  1 266-279
  2 255-235
  3  72 -66
  4  56 -45
  5  33 -23
  6  40  35
  7  77 -77
  8  15 -30
  9  76 -81
 10  39 -45

H,K=  7,  4
  L FOB FCA
-10  63 -64
 -9   8   4
 -8 148 141
 -7   0 -11
 -6  93 -66
 -5 157-167
 -4 140-125
 -3 141 141
 -2  39  36
 -1  66  95
  0 139 137
  1  11  21
  2  54  56
  3  14  -5
  4 136-136
  5 257 269
  6 142 150
  7 116-103
  8 109 126
  9  21  -9

H,K=  7,  5
  L FOB FCA
-10  74 -73
 -9  67  65
 -8  54 -52
 -7  63 -72
 -6  56  50
 -5 166 162
 -4 108-113
 -3  51  47
 -2  13 -34
 -1 176 173
  0  64  61
  1  27  31
  2  12   6
  3  40  41
  4  24 -17
  5  19 -22
  6  18 -14
  7  50 -54
  8  21 -31
  9  46  47

H,K=  7,  6
  L FOB FCA
 -9  47  44
 -8  52  54
 -7 133-136
 -6  52  51
 -5 110  96
 -4  64  65
 -3  21 -10
 -2 127 116
 -1 137-131
  0  36  26
  1  77 -78
  2 111 117
  3  44  36
  4  13  -3
  5 157-166
  6 151 156
  7  79 -73
  8  30 -21
  9  10   5

H,K=  7,  7
  L FOB FCA
 -9  93 -77
 -8 104  98
 -7  45 -46
 -6  17 -13
 -5   0  -4
 -4  99 100
 -3 145-142
 -2 142 144
 -1  64 -64
  0  35 -36
  1  36 -36
  2  24  22
  3  53 -52
  4  14  16
  5  43 -53
  6  80  81
  7  99  98
  8   0  14

H,K=  7,  8
  L FOB FCA
 -8   0  16
 -7 229-231
 -6  99-103
 -5  36 -42
 -4  96 -82
 -3 102  97
 -2  67 -56
 -1  71 -70
  0 107 103
  1  60  79
  2 144-155
  3  75  76
  4  87 -87
  5  61  61
  6  60  50
  7  42  36
  8  22 -22

H,K=  7,  9
  L FOB FCA
 -8  26 -31
 -7  68  75
 -6  65  65
 -5 163 163
 -4   7  12
 -3 106-105
 -2  23  25
 -1 130 131
  0  51 -43
  1 136 132
  2 196 197
  3  61 -55
  4 123 120
  5  38  39
  6 107-111
  7  99 103

H,K=  7, 10
  L FOB FCA
 -7  57 -49
 -6  19  -6
 -5  81 -76
 -4  44 -50
 -3  12  22
 -2 102 103
 -1  77 -83
  0  56 -53
  1  61 -78
  2  61 -77
  3 115-107
  4  67 -73
  5  40 -48
  6  42  41
  7 146-142

H,K=  7, 11
  L FOB FCA
 -6  95-102
 -5  46  54
 -4  45 -41
 -3  11 -11
 -2  25  30
 -1  22 -29
  0 149-139
  1  52 -49
  2  40 -32
  3  61  77
  4  28  40
  5  90  95
  6  39 -29

H,K=  7, 12
  L FOB FCA
 -5  18  -1
 -4  98 -92
 -3  27  14
 -2  83  86
 -1 175 176
  0  97 108
  1  41 -41
  2  38 -34
  3  30  27
  4  16   5

H,K=  7, 13
  L FOB FCA
 -3  46  57
 -2 113 111
 -1  58 -52
  0  33 -36
  1 102 -96
  2  37  34
  3  46  44

H,K=  8,  0
  L FOB FCA
-10  11  16
 -8 260 257
 -6  32  48
 -4  55  11
 -2 148 131
  0 109  79
  2  51  35
  4  25  12
  6  12   9
  8 132 126

H,K=  8,  1
  L FOB FCA
-10   0   9
 -9  37  40
 -8 127-123
 -7  79 -92
 -6  95 110
 -5  16 -16
 -4  76 -75
 -3 141-132
 -2 203-194
 -1 166-169
  0 108-100
  1  14 -10
  2  19  21
  3  64 -63
  4 119-134
  5  99-103
  6 114-122
  7  23  -1
  8   0   0
  9  63  70
```

XBL 6711-6070

Table II, continued

```
H,K= 8, 2      2 119-111    3  96 -93    1 102  94   -4  70  55    2  73  67   -5  99 102   -4 266 261    2  62  66    0 218 218    0  65 -69   -7  39 -34   H,K= 13, 0     2  44  41
  L FOB FCA    3 176-169    4  70  65    2  81  83   -3 177 185    3  38 -39   -4 154 152   -3 214 218    3  26  27    1  33  37    1  18  12   -6  36 -30     L FOB FCA    3  26  18    H,K= 14, 4
-10   3  27    4  42  37    5  42 -37    3 190-191   -2 142-147    4  67  51   -3  65 -61   -2 227 222   H,K= 11, 0    2  94  85    2  60 -54   -5  45  43   -4 102 102    4  19  13     L FOB FCA
 -9 118-109    5 133-130    6  15   1    4  70 -75   -1 114-108    5  14   2   -2  88  88   -1 102-101     L FOB FCA    3 100 -69    3  26  27   -4  49 -33                     -4  41  48
 -8 146 153    6  16  35    7  63  63    5   4   9    0 105 106    6  70 -72   -1  43 -49    0  23  19   -8 105 100    4  76 -89   H,K= 13, 6   -4  49 -35                     -3  19   6
 -7  23  -4    7  44 -45                 6  67 -69    1 119 107                 0  23  19    1  15  17   -6  48 -50    5  29 -15    L FOB FCA   -2 149 165   H,K= 13, 0    -2 203 214
 -6 247 265    8 101-100   H,K= 8, 10    7  16 -20    2 125 126   H,K= 9, 10    1 142 136    2  87  79   -4 291-290    6  70  71   -3  13 -12    0 103 111     L FOB FCA    -1  33  37
 -5  25 -25    9 112-121     L FOB FCA   8  12  22    3 111 111     L FOB FCA    2  62  63    3 218 225    4 293 296    7  36 -39   -2  30 -24   -1  99  98    3 207 213     0  22  20
 -4  27 -24                -7  11 -31    9  12  -5    4  51 -55   -6  93 104    3 118-129    4 140 142   -2  55  59                 -1  49  43    0  81  77    4  14  -5     1 126-129
 -3 104-113   H,K= 6, 6    -6  42  30                 5  38 -39   -5  31 -19    4 140 142    5  10  12   H,K= 11, 10   H,K= 11, 5    0  53 -55    1  26 -30    6  53  59     2  15   9
 -2 182 191     L FOB FCA  -5  58 -43   H,K= 9, 2     6  30  23   -4  66 -59    5  44 -45    6  37  44     L FOB FCA    L FOB FCA    1  30 -38    2 188 181                 3  10 -16
 -1  35 -34   -9 126-114                  L FOB FCA   7  36 -38   -3 115 117    6  75  79    7  50 -52   -3  13 -12   -7  65 -70    2  16 -14    3  67  57   H,K= 13, 1
  0  34 -19   -8 122-112   H,K= 9, 2    -4 289 290    8  97 100   -2  87  88    7  39  42               -2  30 -24   -6  82 -75    3   5 -10    4  58  58     L FOB FCA    0 117-113
  1 220 206   -7  60 -71     L FOB FCA  -3  39  39                -1  65  58    8  58 -55   H,K= 10, 7   -1  49  43   -5 137-142                5  71  73   -1  62 -72     1  40 -46
  2 217 204   -6  79  76   -9  74 -74   -2 141 140   H,K= 9, 6     0  24  14                 L FOB FCA    0  53 -55   -4  10   9   H,K= 12, 5    6  53  58                 2  69  74
  3 172-166   -5 111-112   -8 103 -96   -1   0   6    L FOB FCA    1  87  83   H,K= 10, 3   -7  43 -38    1  30 -38   -3 116-112    L FOB FCA                H,K= 13, 2    -5  89  80
  4 110 117   -4  88  79   -7  16   4    0  30 -12   -8 129-130    2  23  16    L FOB FCA   -6  76 -79    2  16 -14   -2  29 -18   -4  98 113   H,K= 13, o    L FOB FCA    -4  84  77
  5  87  72   -3  62 -88   -6  28 -30    1  19  11   -7  31  20    3  54  47   -9  59  54   -5  31  20    3   5 -10   -1  24 -33   -3  48  46    L FOB FCA   -7 122-134    -3  22 -19
  6 219 232   -2 124-113   -5 179-176    2 176 167   -6  60  57    4  23  13   -8  26 -37   -4  72 -69               0  80 -74   -2  36  46   -8 105 102   -6  17  -3    -2  72 -82
  7 153 160   -1 232-234   -4  64  56    3   0 -10   -5  79  88    5  31 -34   -7  17 -28   -3  53  52   H,K= 12, 0    1 138-139   -1 150-145   -6 115 113   -5  89  80    -1  26 -15
  8 148 147    0  32 -31   -3 148-156    4 168 174   -4  88  77                -6  25  31   -2 104  93    L FOB FCA    2  13 -11   -5  41 -45   -4 280 304                 0  58 -63
  9  16  -5    1  21  32   -2 108 105    5  12   6   -3  44 -36   H,K= 9, 11   -5 211-215   -1 114-108  -8 105 102    3 133-133   -4  10  24   -2  22  20   H,K= 13, 2     1  89 -87
               2  69  72   -1 132 110    6  58 -53   -2  43 -45    L FOB FCA   -4  65  61    0  23 -17  -6 115 113    4  49 -53   -3  69  70    0 283 283    L FOB FCA     2  62  51
H,K= 8, 3      3 150-137    0  75 -71               -1  13   8   -5  15  10   -3  90  88    1  22  25  -4 280 304    5  73 -77   -2  32 -19    5  73 -77   -7  61 -70     3  73 -68
  L FOB FCA    4  52 -48    1  91-101   H,K= 8, 11    0 161-155   -4  70  72   -2  87 -95    2  63 -54  -2  22  20    6  84 -86   -3  69  70    6 103 104   -6  28 -26
-10  26  19    5  57 -56    2  33  32     L FOB FCA   1  30  36   -3  16  26   -1  23  22    3  84  96   0 283 283                0  54  68                -5  71  75   H,K= 15, 0
 -9 110 113    6  22 -10    3  55 -57   -6  47  58    2 161 163   -2  16  14    0  35  36    4  50  50   5  73 -77   H,K= 11, 6    1   8  -6   H,K= 12, 6   -4  98 113    L FCB FCA
 -8  45 -48    7  52 -48                -5  46 -37    3  25  31   -1  40 -38    1 178-170    5  25  24   6 103 104    L FOB FCA    2 153 148    L FOB FCA   -3  54 -66    4  90-100
 -7  69 -63    8  55  50   H,K= 8, 12   -4  20  -6    4  11   5    0  22 -25    2  14 -15    6  61  57              -7  36 -12    3 120 120   -6  28 -13   -2  56 -59    -2 141-136
 -6  12  -4                  L FOB FCA  -3  29 -34    5  92 -91    1 100 -96    3  50 -44             H,K= 11, 2   -6  21  20   3 120 120   -5  27 -26   -1 192-192     0  47 -44
 -5 240 239   H,K= 6, 7    -6  47  58   -2  60 -63    6  76 -72    2  46 -42    4 105-104   H,K= 10, 8    L FOB FCA  -5  76  72   -2  83 -69                -1  24  -3     2   0 -12
 -4  18 -11    l FOB FCA   -1  39 -34   -1  39 -34    7  47  48    3  33 -34    5  79  74    L FOB FCA  -8  89  88   -4  82  77   -1  74  74   -4 132 140    0 126-109
  3  11     -9  36 -35     0  42 -42                 8  21  30    4  39  39    6 116 121   -7   0  -4  -7  55  64   -3  87 -78   u  47 -44   -3 104 109    1  15  11   H,K= 15, 1
 -2  95 -77   -8  14  44    1 116-101   H,K= 9, 3                              7 108-110   -6  17 -25  -6  32 -19   -2  76 -80    1  20  -9   -2 139 145    1 118 117    L FOB FCA
 -1 147 141   -7  59 -63    2  91 -93   -9  17  23   H,K= 9, 7    H,K= 9, 12    8  22 -15   -5  44 -49   -5 114 116  -1  74  74   2  60  60    2  48 -50   -1  66 -64   -4  30 -32
  0  67  60   -6  80 -83    3  39 -43   -8  42 -42    L FOB FCA    L FOB FCA                -4  72  69  -4  18  -8   0 126-109   3  69  96    3  47 -38    0  95  97   -3 113 120
  1 218 203   -5 145 149    4  87 -93   -7  36 -39   -9  97 -93   -3  64 -67   H,K= 10, 4   -3 142 143    -3   8 -13  1 118 117    4  27  29    4  71 -68    1  81 -84   -2  52 -45
  2  74 -90   -4 193-196    5  32 -16   -6 120 120   -8  42 -42   -2  22 -16    L FOB FCA   -2 242 234    -1  50  38  2  48 -50   5 105 106    5  94 -97    2 110 114   -1  22 -17
  3  46  62   -3 107-101                -5  20 10    -7  62 -65   -1  49 -30   -9 121-107   -1  50  38    0  44  29  3  69  96    6  40  41    6  87 -90    3  49 -48    0  19  13
  4  10  -2   -2 263 264   H,K= 8, 12   -4 190 190   -6  32 -19    0 107 113   -8  22  39   -4  18  -8    1  49 -50                           7  91  85    4 131 139
  5 158 164   -1  40  29   -1  60  63   -3 191 179   -5  26  21    1  92 -90   -7 168-164   -3   8 -13    2 100  93  H,K= 11, 7    L FOB FCA              5 113  13   H,K= 15, 2
  6 146 144    0  11   2    0  24  24   -2  55  59   -4  24 -13    2  11  13   -6 158 160   -2  63 -66    3 214 214    L FOB FCA  -6   7  -3   H,K= 12, 2                  L FOB FCA
  7  24  35    1 163 169    1   9 -24   -1  67 -73   -3 142 138                -5  21  26   -1  84  74    4 127 133  0 116 117   -5  24 -23    L FOB FCA  H,K= 13, 3    -5  83  92
  8  23 -16    2 207-216               -2 157-153                H,K= 10, 0    -4  47  38               5  38  39  1  97  91   -5  24 -23   -7  60  65   -6  97 -94    1   8  14
  9 112 113    3   6  15   H,K= 9, 13    0  83  90   H,K= 10, 0   -8  63 -57   -3 116-107   H,K= 10, 8    6  59  69  2 196-200   -4  40  44   -6  62 -67   -5  24 -23    2  26  -8
               4 279 282   -2  96 -99    1 126 124    0  16  15   -7  37  27   -2  93 102    L FOB FCA             3  82  83   -3  96 -95   -5  51  52   -4  55 -54
H,K= 8, 4      5  48  42   -1  60  63    1  74  74    1  74  74   -6  37 -27   -1 125-107   0 230 223  H,K= 10, 9    4  30  25   -2 176 169   -4 203 218   -3  68 -67   H,K= 15, 3
  L FOB FCA    6 109 114    0  24  24    2  55  55    2 129-137   -5  91  85                1 112-116    L FOB FCA  5  40 -39   -1  71  73   -3  20  15   -2  33  38    L FOB FCA
-10  70 -64    7  41  34    1   9 -24    4  19   6    3  91  85    4  26  -9   H,K= 10, 1    2  39  30   -6 119-106  6  62  59   0 106 104   -2  36  39   -1  99 -97   -4  47  44
 -9  24 -25    8  33  20               5  13  -6    4 136-130   5  84 -87    L FOB FCA    3  22 -10   -5 101 102  7  76  75   1  31 -28   -1  33  49   0  51 -57   -3  14 -17
 -8  86  88              H,K= 9, 13    7  22  39    6  62  65   6  62  65   -9  33  30    4  39  36   -4  39  36             2  35 -37   0  50  34   1  66 -70   -2  85  84
 -7  56  57   H,K= 6, 12   -2  96 -99    8  55  67    7  44 -44   7  44 -44   -8  50 -52    6 120 118   -3  30  17  H,K= 11, 3   -1  33  49   1  77  77   2  24 -19   -1  14  11
 -6 282 293   -2  96 -99   -1  60  63    9  19  26               6 120 118   -7  88  82    8 154 145   -2  96 -86    L FOB FCA  0  50  34   2  62 -57   3  13  10   0  40  48
 -5 202 195   -1  60  63    0  24  24               H,K= 9, 8    8 154 145   -6  29  32               -1 108-111  -8  86 -85   1  77  77   3  87  84   4  63  61   1  67  60
 -4  59 -43   -6 120 122    1   9 -24   H,K= 9, 4    L FOB FCA    L FOB FCA   -6  12   4              8  68  55  -7 119 122  2 241 234   4  85 -91             2  64 -63
 -3  63 -62   -5  47 -44              -9  22   6   -7  15 -22   -7  15 -22   H,K= 10, 5              H,K= 10, 5  1  75  72   3  82 -86              H,K= 13, 4
 -2  67  55   -4 269 265   H,K= 9, 0   -8  47 -48   -6  23  18    L FOB FCA    L FOB FCA              L FOB FCA  2  31 -15   4  29  23   H,K= 12, 8    L FOB FCA   H,K= 15, 3
 -1 235 220   -3  86  93    L FOL FCA  -7 150 147   -5  46 -48   -9  33  30   -6 224-240   H,K= 11, 4  -8  27  36  3  55 -61   5  22  13   -5  99-112   -6  43 -51    L FOB FCA
  0 364 364   -2 291 284  -10  36  41   -6  10   6   -4  28 -32   -8  50 -52   -5  29 -27    L FOB FCA  -7  29  32  4  46 -37   6  61  73   -4  77 -70   -5  39  29   -4  47  44
  1 161 171   -1  32  30  -8  52  40   -5  52 -53   -3  33  28   -7  88  82   -4  58  59   5 128-138  -6  12   4  5 128-138              -3  97-100   -4  33 -17   -3  22 -16
  2 181 184    0  71  61  -6  73  70   -2 17 -27   -2  17 -27   -6 100 174   -3  30  29             -2  71  67  H,K= 11, 8  H,K= 12, 3   -2  39  38   -3  43  37   -2  85  84
  3  21 -18    1  67 -63  -4 121-124   -1 `1 -41   -1 `1 -41   -5  64 -69   H,K= 11, 8              -1  43  36   L FOB FCA  L FOB FCA   -1 185-185   -2  39  38   -1  14  11
  4 109-100    2 324 292  -3 127-124    0   86    0   86    -4 144 137   L FOB FCA              0 229-226  -8  44  38  -7  22 -12   0  46 -45   -1 185-185   0  40  48
  5  17 -15    3  -2  -7   0 111-119   1   7  12   -3 145 141   -3 145 141              -5  81 -84  -7  64  63  -6  22 -15   1  65 -48   0  46 -45   1  67  60
  6 208 202    4  76  71   2 392 386   2 152 46    -2 18  14   -2 110-108   H,K= 10, 10              -4  50  50  1  17 -17  -5  16  -3   2  64  66   1  91  85   2  64 -63
  7 113 114    5  16 -12   4  92  92   1  77  75   -1  26  21   0 204 193   L FOB FCA              -3 143-150  2  37  30  -4  44  34   3  45 -49   2  62  61
  8 157 169    6  58  54   5 129-130   2  43  41   0  47  44   H,K= 10, 10   0 229-226              -2  37 -35  3  13 -12  -1  66  62   4 127 144   3  43  36   H,K= 15, 4
  9  93 -91    7  35 -33                3  95 -89   1 229 232   L FOB FCA    1  17 -17   4  44  34  -1  66  62  4  44  34  H,K= 12, 9  H,K= 13, 5    L FOB FCA
                           H,K= 8, 9    4 170-173   5  16   6   H,K= 9, 9    2  37  30              5  63 -65   5  57  54   L FOB FCA   -3  33 -19   -2  26  16
H,K= 8, 5     H,K= 8, 9    L FOB FCA   5  71  73   4 124 122    L FOB FCA    3  58 -55   1  96 -96  2 109-107   L FOB FCA  -5 122 126   -2 190 195   -1  21 -10
  L FOB FCA -10  72 -66   -7  45  48   6 179-179   5  16   6   -7  23 -23   3 143-150   3  66 -71  -8  44  38   -3  33 -19  -4  34 -32   -1  63  67   0  96 104
 -9  33 -31  -8 133 137   -6  51 -46   7   0   6   6  43  47   -6  83  67   -2  37 -35   4  19 -7  -7  64  63   4  59 -72  -3  30  15   0  23   8   1  29 -31
 -8 133 137  -7  45  48   -5  23  28   8 111 107   7  22  20   -5  37 -48   H,K= 10, 11   5  85  84  -6  44  46  -1  65 -77  0  82  74   1  44  33
 -7  27  15  -6  46  55   -4  26  34              8 121 119   -4   0  14   L FOB FCA    H,K= 11, 9   -5  68  65  -4  75 -76  2  40  30  -1 171 174
 -6  87  93  -5  23  28   -3  97 -99              -3  72 -75              -8  44  38    L FOB FCA   -4  96 100  -3  27 -21  0  49  43   2  19   9
 -5  59  66  -4  26  34   -2  41  27   H,K= 9, 5   -2  73 -75   H,K= 10, 6  -7  64  63   -5  19 -33  -3  27 -21  -2  20  14  1  80  85   3   0 -29
 -4  77 -79  -3  97 -99   -1  24 -19  -9 121 115   H,K= 10, 2    L FOB FCA  -6  44  46   -4  75 -76              -1  76 -75              4 119 125
 -3  88 -61  -2  82  74   0  25  18   -8 115-112  -1  15 -21    L FOB FCA  -5  88  65   -3  55  54              -2  18  20
 -2  82  74  -1  68 -68   -2 226-234  -7 219-220   L FOB FCA   -9  49 -50  -4  58 -25   -2  27 -14
 -1  68 -68   0  17   5   -1  15 -21  -6  73  73  -9  49 -50   -8  25  46  -3  27 -14
  0  17   5   1  41  33   2  64  65   -5  30  17   I  11  -4
  1  41  33
```

XBL 6711-6071

39

Figure 1. - $(B_9C_2H_8Br_3)_2Co^-$ (hydrogens omitted).

XBL 6711-6069

Table III. Distances[a] in $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

ion no.:	1	2	3	4
atom		distances, Angstroms		
Co–C(2)	2.04(2)[b]	2.03(2)	1.98(2)	2.05(2)
Co–C(3)	1.99(2)	2.02(2)	2.00(2)	2.09(2)
		r.m.s. scatter[c] = .034		
Co–B(4)	2.09(3)	2.13(3)	2.14(3)	2.17(3)
Co–B(6)	2.05(2)	2.10(2)	2.12(3)	2.12(3)
		r.m.s. scatter = .037		
Co–B(5)	2.17(3)	2.17(2)	2.15(2)	2.16(3)
		r.m.s. scatter = .007		
Co–Br(5)	3.527(3)	3.530(3)	3.511(3)	3.527(3)
		r.m.s. scatter = .009		
Br(5)–Br(9)	3.716(5)	3.775(4)	3.709(4)	3.725(4)
Br(5)–Br(10)	3.689(4)	3.730(4)	3.756(4)	3.719(4)
		r.m.s. scatter = .027		
Br(9)–Br(10)	3.921(5)	3.869(5)	3.816(5)	3.876(4)
		r.m.s. scatter = .043		
B(5)–Br(5)	1.95(3)	2.00(2)	1.96(2)	1.94(3)
B(9)–Br(9)	1.96(3)	1.95(3)	1.98(3)	1.97(3)
B(10)–Br(10)	1.96(3)	1.98(3)	1.96(3)	1.96(2)
		r.m.s. scatter = .017		

Table III,   continued

C(2)-C(3)	1.68(3)	1.65(3)	1.63(3)	1.66(3)

r.m.s. scatter = .023

C(2)-B(6)	1.63(3)	1.75(3)	1.77(4)	1.78(3)
C(3)-B(4)	1.64(3)	1.68(3)	1.72(3)	1.84(3)
C(2)-B(11)	1.63(4)	1.75(4)	1.84(4)	1.72(3)
C(3)-B(8)	1.75(3)	1.69(4)	1.68(4)	1.64(3)
C(2)-B(7)	1.71(4)	1.71(4)	1.86(4)	1.71(4)
C(3)-B(7)	1.76(4)	1.73(4)	1.73(4)	1.69(4)

r.m.s. scatter = .064

B(4)-B(5)	1.91(4)	1.82(4)	1.88(3)	1.81(4)
B(4)-B(8)	1.79(4)	1.73(4)	1.76(4)	1.82(4)
B(4)-B(9)	1.84(4)	1.79(4)	1.88(3)	1.77(4)
B(5)-B(6)	1.69(3)	1.78(3)	1.80(4)	1.81(4)
B(5)-B(9)	1.81(4)	1.70(4)	1.82(3)	1.77(4)
B(5)-B(10)	1.74(4)	1.74(4)	1.77(3)	1.81(4)
B(6)-B(10)	1.74(4)	1.75(4)	1.81(4)	1.79(3)
B(6)-B(11)	1.74(4)	1.84(4)	1.90(4)	1.88(4)
B(7)-B(8)	1.88(4)	1.83(4)	1.63(5)	1.81(4)
B(7)-B(11)	1.79(5)	1.73(4)	1.82(5)	1.77(4)
B(7)-B(12)	1.91(5)	1.84(5)	1.74(4)	1.83(4)
B(8)-B(9)	1.75(4)	1.79(4)	1.74(4)	1.83(4)
B(8)-B(12)	1.89(4)	1.82(5)	1.67(4)	1.84(4)
B(9)-B(10)	1.76(4)	1.76(4)	1.71(4)	1.75(4)
B(9)-B(12)	1.75(5)	1.77(4)	1.62(4)	1.79(4)

Table III, continued

B(10)-B(11)	1.86(4)	1.76(4)	1.79(4)	1.76(4)
B(10)-B(12)	1.71(4)	1.74(4)	1.74(4)	1.78(4)
B(11)-B(12)	1.82(5)	1.79(4)	1.76(4)	1.79(4)

r.m.s. scatter = .060

N-Me(1)	1.49(5)	1.52(6)
N-Me(2)	1.46(4)	1.43(7)
N-Me(3)	1.49(3)	1.44(5)
N-Me(4)	1.57(4)	1.53(5)

r.m.s. scatter = .048

(a) None of these distances is corrected for thermal motion.

(b) The numbers in parentheses are the standard deviations in the least significant digit as calculated from the standard deviations of coordinates (Table I).

(c) Each of the "r.m.s. scatter" values given is the root-mean-square deviation from the average, $[\Sigma\Delta^2/(\underline{n}-1)]^{\frac{1}{2}}$, for the preceeding set of distances. These are given for comparison with the standard deviations calculated from the standard deviations of coordinates.

Table IV. Average Distances[a] in $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

number averaged	atoms	distance, Å
4	C–C	1.654 ± .017[b]
24	C–B	1.725 ± .013
72	B–B	1.786 ± .007
12	B–Br	1.963 ± .008
8	Co–C(2,3)	2.024 ± .013
8	Co–B(4,6)	2.115 ± .014
4	Co–B(5)	2.162 ± .014
4	Co–Br(5)	3.524 ± .005
8	Br(5)–Br(9,10)	3.727 ± .010
4	Br(9)–Br(10)	3.870 ± .025
8	N–Me	1.491 ± .018

(a) None of these distances is corrected for thermal motion.

(b) The error figures are the author's best estimate of the precision of these averages. They have been pessimistically chosen as the greater of $[(\Sigma\Delta^2)^{\frac{1}{2}}/(n-1)]$ or $[(\Sigma\sigma^2)^{\frac{1}{2}}/n]$, where Δ is the deviation from the average, σ is the standard deviation of a single distance as calculated

Table IV, continued

from the standard deviations of coordinates, and $\underline{n}$
is the number of distances averaged. The latter
expression was the larger for the C-C, B-Br, and
Co-B(5) distances.

eight B–C–C angles average 57° and $61\frac{1}{2}^O$. All four of these sets of angles show $2\frac{1}{2}^O$ root-mean-square deviations from the averages. The root-mean-square deviations are believed to be better measurements of the accuracy of these angles than the ~ 1.6^O values derived from the standard deviations of coordinates. The temperature factors in the dicarbollyl portion of the anions seem to indicate some rigid-body motion, but a rigid-body analysis was not done because of the absorption errors known to be in the data and because of the excessive effort it would require.

The packing of the approximately dumbbell-shaped anions and the tetramethylammonium ions is very similar to that of KHF_2[20] as indicated in Figure 2. The higher symmetry (tetragonal, I4/mcm) of the KHF_2 structure[20] is broken down to its $P2_1/c$ subgroup (on the doubled cell) by the anion's lack of cylindrical symmetry and the up and down (in $\underline{z}$) distribution of the bromine substituents. If we consider only the arrangement of plus and minus charges, this is approximately a CsCl-type structure.

The pentagonal rings adjacent to cobalt are all planar to within the accuracy of this determination, but are tilted or slid over in such a way as to decrease the cobalt-carbon distance and increase the cobalt-boron distances (Table IV). The tilt and slide descriptions are equivalent and amount to ~ 3° and ~ .07 A, respectively. This is interpreted as the effect of the Br(5) of each dicarbollyl being crowded up against the hydrogens on the carbons of the other. This interpretation is supported by the short Br(5)-Br(9) and Br(5)-Br(10) distances (Table IV). If we assume that each hydrogen is 1.10 A from its carbon and in line with the carbon and the opposite icosahedral vertex, the bromine-hydrogen distance
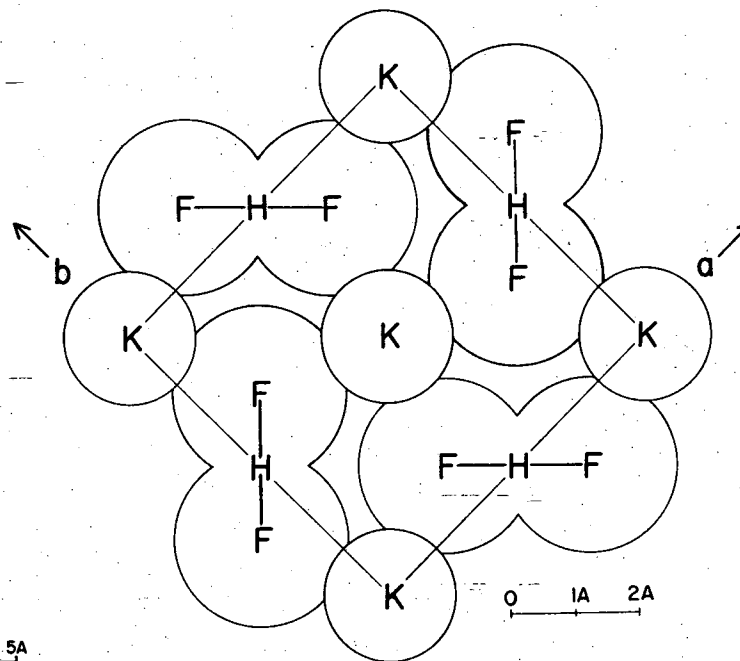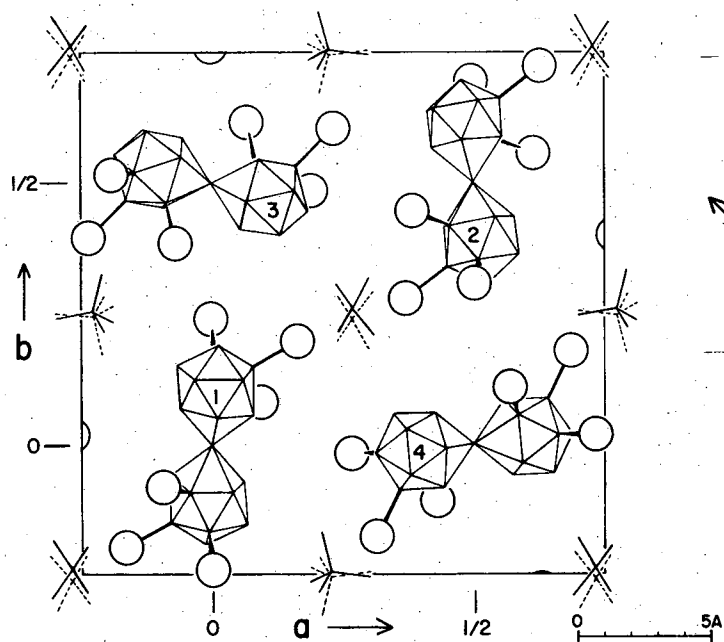
Figure 2. - The crystal structure of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$ compared with that of KHF_2. In both drwaings, the cations are at $\underline{z} = \pm \frac{1}{4}$ and the anions at $\underline{z} = 0$. The anions at $\underline{z} = \frac{1}{2}$ (not shown) are related to those shown by the $\underline{c}$ glide which runs horizontally across the center of each drawing.

is only 2.75 A, which is 0.40 A less than the sum of their van der Waals radii (1.95 ± 1.2 = 3.15 A).[21] A similar steric effect of about the same size, but in the opposite direction (carbons farther from metal than the borons) was found[22] in $B_9C_2H_9(CH_3)_2PdC_4(C_6H_5)_4$ in which the methyl groups are on the dicarbollyl carbons. These steric effects are not to be confused with the larger shift (about 0.6 A) observed by Wing[23] in the $Cu(B_9C_2H_{11})_2{}^{2-}$ anion where bonding effects are believed to be involved.

The electrophilic bromination sites found for this anion may be rationalized if we say that the charge distribution in the dicarbollyl portion is similar to that in 1,2 –dicarbaclovoduodecaborane ($B_{10}C_2H_{12}$), but modified by a polarization induced by the Co(III). Substitution sites[17-19] and dipole moments[24] found for $B_{10}C_2H_{12}$ derivatives and molecular orbital calculations[17,18] for the parent compound all lead to the conclusion that the borons farthest from carbon are the most susceptible to electrophilic attack and this susceptibility decreases as the carbons are approached. This analogy, considered alone, would indicate that our B(9) and B(10) are the most subject to electrophilic attack and B(5) and B(12) are second. Polarization by the cobalt would then determine the choice between B(5) and B(12), possibly causing B(5) to become more subject to electrophilic attack than the B(9)-B(10) pair.

References and Footnotes

(1) M. F. Hawthorne, D. C. Young, and P. A. Wegner. $\underline{J}$. $\underline{Am}$. $\underline{Chem}$. $\underline{Soc}$., $\underline{87}$, 1818 (1965).

(2) M. F. Hawthorne and T. D. Andrews, $\underline{ibid}$., $\underline{87}$, 2496 (1965).

(3) M. F. Hawthorne and R. L. Pilling, $\underline{ibid}$., $\underline{87}$, 3987 (1965).

(4) M. F. Hawthorne and T. D. Andrews, $\underline{Chem}$ $\underline{Commun}$., 443 (1965).

(5) L. F. Warren, Jr. and M. F. Hawthorne, $\underline{J}$. $\underline{Am}$. $\underline{Chem}$. $\underline{Soc}$., $\underline{89}$, 407 (1967).

(6) M. F. Hawthorne, $\underline{et}$ $\underline{al}$., $\underline{ibid}$., $\underline{90}$, 879 (1968).

(7) M. F. Hawthorne, private communication.

(8) A description of this work has been submitted to $\underline{Inorganic}$ $\underline{Chemistry}$ for publication.

(9) It may be argued that $\underline{F}^2$ should be the quantity averaged, but the "error" incurred is only 5.4% even if $\underline{F}_1 = 2\underline{F}_2$ ($\underline{I}_1 = 4\underline{I}_2$).

(10) J. Karle and I. L. Karle, $\underline{Acta}$ $\underline{Cryst}$., $\underline{21}$, 849 (1966).

(11) R. E. Long, $\underline{Ph}$. $\underline{D}$. $\underline{thesis}$, University of California, Los Angeles, 1965.

(12) "International Tables for X-ray Crystallography", vol. III, The Kynoch Press, Birmingham, England, 1962, pp. 204 - 207, 214.

(13) Late in the refinement, one cycle of full-matrix least-squares was run on all 361 parameters (12 fixed) and 3002 data to be sure that no errors were caused by the block-diagonal procedure. This one cycle required 74K storage and 43 minutes on a CDC 6600. These figures may be compared with the requirements for the final diagonal-matrix refinements of 28K storage and $2\frac{1}{4}$ minutes/cycle.

(14) A. Zalkin, D. H. Templeton, and T. E. Hopkins, $\underline{J}$. $\underline{Am}$. $\underline{Chem}$. $\underline{Soc}$., $\underline{87}$, 3988 (1965).

References and Footnotes, continued

(15) A. Zalkin, D. H. Templeton, and T. E. Hopkins, _Inorg. Chem._, 5, 1189 (1966).

(16) A. Zalkin, D. H. Templeton, and T. E. Hopkins, _ibid._, 6, 1911 (1967).

(17) H. Beall and W. N. Lipscomb, _ibid._, 6, 874 (1967) and references therein.

(18) J. A. Potenza and W. N. Lipscomb, _ibid._, 5, 1471, 1478, 1483 (1966) and references therein.

(19) J. A. Potenza and W. N. Lipscomb, _ibid._, 3, 1673 (1964).

(20) R. W. G. Wyckoff, "Crystal Structures" vol. 2, Interscience Publishers, New York, 1964, pp. 277 ff.

(21) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, New York, 1960, p. 260.

(22) R. C. Petterson, A. Zalkin, and D. H. Templeton, unpublished results.

(23) R. M. Wing, _J. Am. Chem. Soc._, 89, 5599 (1967).

(24) R. Maruca, H. S. Schroeder, and A. W. Laubengayer, _Inorg. Chem._, 6, 572 (1967).

IV. The Crystal and Molecular Structure of <u>Tris</u>-difluorobora-borane —

Phosphorus Trifluoride, $B_4F_6PF_3$

A. Introduction

Timms has recently reported[1][*] the synthesis of a number of novel

boron fluoride compounds by reactions of the high temperature species,

boron monofluoride, on cold surfaces. Cocondensation of BF and PF_3

produces $B_4F_6PF_3$, a pyrophoric and water-sensitive substance which readily

sublimes (m. p. 55°, b. p. 74°) to form well-developed, colorless crystals

which are stable at room temperature. The present X-ray diffraction inves-

tigation[2] was undertaken to verify the proposed structure:

$$
\begin{array}{l}
F_2B{\diagdown} \\
F_2B\!\!-\!\!\!B\!\!-\!\!PF_3 \\
F_2B{\diagup}
\end{array}
$$
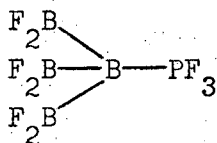
and to determine the bond distances and angles in this molecule.

B. Experimental

Samples of the compound, sealed into thin-walled glass capillaries,

were provided by Professor Timms. Crystals formed quite readily as the

compound was sublimed back and forth in the capillaries under the very

mild heating provided by a beam from a low voltage lamp. Persistence

seemed to be the only way to obtain a suitable crystal which did not have

others nearby. Complete data sets were taken on two different crystals.

The first crystal was a plate about .16 X .51 X 2.2 mm, where the

intermediate dimension is the inside diameter of its capillary. A crystal

---

* References and Footnotes for part IV are to be found on page 69.

this large was accepted because there was no assurance of ever obtaining

a better one, and because of the low absorption coefficient, μ, of 4.3 cm^{-1}

(μ^{-1} = 2.3 mm) for MoKα radiation. The crystal was mounted with its long

dimension, $\underline{b}$ axis, and capillary parallel to the instrument φ axis. Pre-

liminary oscillation and Weissenberg photographs gave the extinction rules,

Laue symmetry, and rough cell dimensions. More accurate cell dimensions

were derived from the Bragg angles of the $\underline{h}$00, 0$\underline{k}$0, and 00$\underline{l}$ 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 (λ(MoKα_1) = 0.70926 A) at the highest angles,

but the peaks were broad and the positions of reflections at low chi

angles could not be accounted for except by assuming a 2θ correction

as a function of phi. It is suspected that these difficulties were caused

by the large size of the crystal, which was certainly longer and probably

wider than the beam diameter, and by strains in the crystal (see below).

In spite of these troubles, a one-octant data set of 830 independent

intensities, exclusive of space-group absences, was taken, using the same

apparatus, by counting each reflection for 10 seconds with crystal and

counter stationary and an approximately 3.5° take-off angle to the X-ray

tube anode. Of these, 173 were recorded as zero. Measurements were also

taken at all the locations in the region of the data set which correspond

to space group absences. They were found to confirm the extinction rules

of 0$\underline{k}\underline{l}$, $\underline{k}$ + $\underline{l}$ $\neq$ 2$\underline{n}$ and $\underline{h}\underline{k}$0, $\underline{h}$ $\neq$ 2$\underline{n}$. Individual backgrounds were measured

for those reflections which were seriously affected by streaking from

other orders; otherwise, backgrounds were taken from a plot of back-

ground as a function of 2θ at various values of phi and chi. Three standard reflections which were measured at frequent intervals during the course of data taking showed only small, random fluctuations. Measurements included reflections up to $2\theta = 50°$ ($\sin\theta/\lambda = 0.595$). Standard deviations were assigned to the measurements of 5% of the intensity or a fixed minimum (8, 5, or 3 counts per second, for low, intermediate, and high 2θ), whichever was greater. The structure was initially solved using this data set, which was then definitely seen to be of unacceptable quality. A second set of samples was provided by Professor Timms, and a better crystal sought.

The second crystal had the shape of a cylinder ~.14 mm long and ~.15 mm in diameter (the inside diameter of its capillary). Nickel-filtered copper radiation was used in order to obtain as large a data set as possible from this smaller crystal. This crystal's smaller size made the larger absorption coefficient, μ, of 39 cm^{-1} ($\mu^{-1} = 0.26$ mm) for CuKα radiation acceptable. The maximum variation in transmission factors is estimated to be less than 20%. The crystal was mounted with its cylinder axis, $\underline{a}$ axis, and capillary parallel to the instrument φ axis. The cell dimensions were determined as before, and found to correctly predict the positions of off-axis reflections, in contrast to the trouble experienced with the first crystal. When a narrow receiving slit was being used to obtain accurate cell dimensions, the peaks were sharp and well-formed and the alpha doublet ($\lambda(\text{CuK}\alpha_1) = 1.5405$ A) was resolved in a majority of cases. After the slit was removed, the peaks at low chi angles showed a characteristic broad shape with an irregular top in both 2θ and omega scans. At high chi angles, a narrower, regular, peak shape

was maintained. This is again ascribed to distortions in the crystal,
since the troubles with the two crystals (this and the previous one)
seem to be correlated with the direction of the capillary axis and not
with the directions of the crystallographic axes. The strains might have
been the result of growth on a curved surface or of slight flexings of
the thin-walled capillaries as they were handled. However, it was found
that the calculated settings reproducibly gave the same part of the
irregular peaks (and the tops of the regular ones) and that point counts
taken at the calculated settings on a few peaks at chi = $0°$ and chi = $90°$
were in the same ratio as the integrated counts obtained by scanning
through those peaks (in 2θ). A second data set of 703 intensities,
including 100 recorded as zero, but not including space group absences,
was taken in the same way as before. Backgrounds were likewise obtained
as before, and again, frequently measured standard reflections showed no
systematic variations. The maximum value of 2θ was $120°$ ($\sin\theta/\lambda = 0.562$).
A standard deviation of 2.25 counts per second or 7.5% of the intensity,
whichever was greater, was assigned to each measurement. Both data sets
were corrected for Lorentz and polarization effects, but no corrections
were made for absorption or extinction.

All computations were performed on a CDC 6600. Zalkin's unpublished
FORDAP and DISTAN programs were used for Fourier syntheses and distance-
and-angle calculations, while an unpublished Wilson-plot program by
Maddox and Maddox gave normalized structure factor magnitudes[3] which were
used in Long's sign-determining program[4] as described below. The unpublished
version of the Ganzel-Sparks-Trueblood least-squares program which was used,

minimizes the function $\Sigma w(|kF_o| - |F_c|)^2 / \Sigma w |kF_o|^2$, where F_o and F_c are

the observed and calculated structure factors, k is the scale factor, and

w is the weighting factor. For the early refinements, scattering factors

for neutral phosphorus, fluorine, and boron were taken from standard

tables.[5] The phosphorus scattering factors were corrected for the real

part of anomalous dispersion by +0.1 electrons for the molybdenum data

and +0.2 electrons for the copper data, and the imaginary part was

neglected. The final refinements were performed using the scattering

factors listed by Cromer and Waber[6] and both real and imaginary anomalous

dispersion corrections given by Cromer.[7,8] The anisotropic temperature

factors used have the form: $\exp(-0.25 \, \Sigma_i \Sigma_j h_i h_j b_i b_j B_{ij})$, $i,j = 1,2,3$,

where b_i is the ith reciprocal cell length.

C. Results

Four formula units of $(BF_2)_3 BPF_3$ are contained in the orthorhombic

unit cell, space group Pnma, with a = 13.893 ± .005 A, b = 10.578 ± .005 A,

and c = 6.075 ± .005 A. The calculated density is 1.82 g/cc. No direct

measurement of the density was attempted because of the highly reactive

nature of the compound. The Laue symmetry and observed extinction rules

correspond to space groups Pnma and Pn2$_1$a. Choosing the former space group

leads to a successful solution with six atoms on the mirror plane in the

fourfold special position set c: $\pm(x, \frac{1}{4}, z; \frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z)$ and four

more atoms in the general set of positions: $\pm(x, y, z; \frac{1}{2} - x, \frac{1}{2} + y,$

$\frac{1}{2} + z; x, \frac{1}{2} - y, z; \frac{1}{2} + x, y, \frac{1}{2} - z)$.

1. Determination of Structure

The Patterson function calculated from the first (Mo) data set was discouragingly featureless, consisting primarily of two positive regions at $y = 0$ and $\frac{1}{2}$, with a negative region between (i.e. it was dominated by very strong $0,k,0$ reflections). Several attempts at refining various trial structures guessed at from this Patterson function met with no success whatever. The author reasoned that the strong $0,k,0$ reflections would arise only if some large fraction of the atoms were concentrated at or near the same y coordinate, as would be the case if the molecule were bisected by the mirror plane in Pnma. With this in mind, the Wilson-plot program was used to calculate normalized structure factor magnitudes,[3] E_h, for use in the statistical method of sign determination (centrosymmetric case). Long's program[4] which iteratively applies the relation: $sE_h \sim s\Sigma_k E_k E_{h-k}$, where s is to be read "the sign of" was employed for this purpose. After enough signs were worked out by hand to yield a good starting set (of E's) for input, a run of Long's program using 99 E's $\geqq 1.5$ gave one set of signs which was more consistent than any other and which was arrived at in the fewest passes. A Fourier synthesis using the signed E's as coefficients gave ten largest peaks, six of them in the mirror plane, which formed the expected molecule. Least-squares refinement of isotropic phosphorus, fluorine, and boron atoms in the appropriate positions quickly reduced the R factor to 0.29, where $R = \Sigma \lvert \lvert kF_o \rvert - \lvert F_c \rvert \rvert / \Sigma \lvert kF_o \rvert$. It was immediately evident that the $0k0$ reflections had given intensities which were systematically too large by factors between 3.6 and 5.2. A refinement in which the $0k0$ reflections were

given zero weight did not reduce $\underline{R}$, but when they were omitted from the
calculation of $\underline{R}$, its value became 0.26. When all atoms were allowed
anisotropic temperature factors, $\underline{R}$ fell to 0.180 on all data and 0.145
if the 0$\underline{k}$0's were omitted. These values could not be improved upon and
a re-run of Long's program with the 0$\underline{k}$0 reflections omitted gave the same
structure a second time.

At this time the first (Mo) data set was discarded and the second
crystal and second (Cu) data set were obtained as described above. The
structure found from the first data set refined to $\underline{R}$ = 0.217 with iso-
tropic temperature factors. When all atoms were allowed anisotropic
temperature factors, the structure gave the final $\underline{R}$ value of 0.093 on
all 703 data and this can be reduced to 0.067 by omitting the contribu-
tions from the 100 reflections which were recorded as having zero
intensity. In the last cycle of the refinement, no parameter shifted by
as much as 1% of the standard deviation calculated for it from the least-
squares matrix. The standard deviation of an observation of unit weight,
defined as $[\Sigma\underline{w}(|\underline{kF_o}| - |\underline{F_c}|)^2/(\underline{u} - \underline{v})]^{\frac{1}{2}}$, where $\underline{u}$ is the number of data

and $\underline{v}$ is the number of independent parameters refined, was 1.33. Tests
of slightly non-centric structures in the other space group ($Pn2_1a$)
gave neither better agreement nor significant deviations from the higher
symmetry. The magnitudes of the three largest peaks on a final difference
Fourier were .50, .38, and .30 electrons/A^3. The final positional and
thermal parameters are presented in Table I, while Table II lists $|\underline{F_o}|$
and $\underline{F_c}$.

Table I. Final Positional and Thermal Parameters in $B_4F_6PF_3$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$[\overline{U^2}]^{\frac{1}{2}}$
P	.0998(1)[b]	¼[c]	.5699(4)	5.8(1)	6.0(1)	8.5(1)	0[c]	0.0(1)	0	(.33,.27,.27)[d]
F1(P)	.0497(3)	¼	.7931(10)	8.6(3)	15.8(5)	11.8(4)	0	4.8(3)	0	(.45,.44,.25)
F2(P)	.0524(2)	.1403(3)	.4588(7)	7.8(2)	9.2(2)	17.9(4)	−2.4(1)	−2.7(2)	−2.5(2)	(.49,.37,.25)
B(1)	.2311(5)	¼	.5805(10)	4.9(3)	3.2(3)	3.7(3)	0	0.4(3)	0	(.26,.22,.21)
B(2)	.2788(7)	¼	.3255(14)	7.3(5)	4.0(3)	5.3(5)	0	1.0(4)	0	(.31,.25,.23)
F1(2)	.2264(4)	¼	.1424(7)	15.0(4)	8.9(3)	3.6(2)	0	−1.3(2)	0	(.44,.33,.20)
F2(2)	.3694(3)	¼	.2902(8)	8.9(3)	9.7(3)	8.6(3)	0	4.2(2)	0	(.40,.35,.24)
B(3)	.2697(4)	.3788(5)	.7122(8)	7.8(3)	4.2(2)	4.4(2)	0.0(3)	−0.2(2)	0.3(2)	(.32,.24,.23)
F1(3)	.2131(2)	.4693(3)	.7870(5)	12.3(2)	4.9(1)	7.6(2)	1.4(1)	0.5(1)	−1.9(1)	(.40,.33,.21)
F2(3)	.3598(2)	.4004(3)	.7500(6)	9.3(2)	7.0(2)	11.3(2)	−1.8(2)	−3.1(2)	−1.7(2)	(.41,.34,.24)

(a) The units are $Å^2$.

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

(c) Values expressed without the use of a decimal point are fixed by symmetry.

(d) These are the principal root-mean-square amplitudes of vibration, in order of magnitude. For orientations, see Figures 1 and 2.

Table II. Observed and Calculated Structure Factors (× 9.0) for $B_4F_6PF_3$

```
K  FOB  FCA        4  430-419        1   15  -6       11   0 -13
H,L= 0, 0          5  190-194        2  196 198       H,L= 5, 2
 2  762-952        6  161 137        3   79  80        0   17  14
 4  484 484        7  103 -98        4   23 -34        1   58  62
 6  545-552        8   93 -87        5   17  19        2  101  94
 8  450 460        9  186-180        6   65  62        3    0   5
10  148-147       10   25  20        7   30  33        4   37 -35
H,L= 0, 1         11   46  48        8   50 -49        5  110 103
 1  383 411       H,L= 2, 1         9   22  19        6   76  84
 3  764 858        0  128 133       H,L= 3, 5         7   17  18
 5  190 177        1  136 137        0   90 -90        8   30 -50
 7    0 -11        2  403-416        1   67 -52        9   34  42
 9   60  70        3  779-778        2    0   1       10    0  -3
11   90  92        4  748 757        3   49  32       H,L= 5, 3
H,L= 0, 2          5  107 104        4   39 -34        0   85 -80
 0  777-866        6   24 -15        5    0  34        1  134 137
 2  351-330        7  175-173        6   17  22        2   63 -64
 4  115-118        8   23  34        7   50  48        3   67 -64
 6   89  93        9   67 -59       H,L= 3, 6         4    0 -16
 8    0 -32       10   83 -98        0    0 -23        5   79  77
10   54 -64       11   79 -79        1    0   1        6   38 -30
H,L= 0, 3         H,L= 2, 2         2    0   9        7    0  20
 1   78 -83        0  747 751        3   16 -26        8    0  -2
 3  543-528        1  564-589        4   54 -64        9   16  12
 5  152 156        2  272 264        5    0  -5       H,L= 5, 4
 7   98 -98        3   44 -50       H,L= 4, 0         0   16  10
 9    0  21        4   66 -65        0   30  20        1   71  66
H,L= 0, 4          5   27 -16        1  783-799        2    0  -8
 0  160 164        6   33  44        2  178 188        3  117-126
 2  230 213        7  302 283        3   79  81        4  118-109
 4  147-129        8  104 103        4  117 100        5   35  42
 6   46  51        9   30 -20        5  199 191        6   25  24
 8   24  20       10    0 -14        6  264 281        7   61 -65
H,L= 0, 5         11   26  26        7  289 287        8   16  11
 1  164 183       H,L= 2, 3         8    0   5        H,L= 5, 5
 3   78 -85        0  151 136        9   30 -17        0   17  16
 5   97 104        1   37  27       10   17 -30        1   17  -4
 7   63 -80        2   74 -76       11   41  41        2   65  56
H,L= 0, 6          3  168 150       H,L= 4, 1         3   46  42
 0   30 -34        4   66 -64        0   76  79        4   17 -12
 2    0  -4        5   86  77        1   74 -75        5   51 -48
 4   16  -8        6  169-172        2  373-372        6   16  18
H,L= 1, 1          7   30  14        3   91 -74        7   21 -21
 0  626-639        8   52  61        4   87 -80       H,L= 5, 6
 1  405 390        9   24  33        5   30  26        0   16   4
 2  305 286       10    0  -2        6  192-199        1   28  40
 3  194-173       H,L= 2, 4         7  145 147        2    0  -8
 4  110 127        0   21  10       H,L= 4, 2         3   15  -6
 5   12  11        1  122 120        0   21  10        4   33  39
 6   31  18        2  183-191        1   30  38       H,L= 6, 0
 7  172-171        3    0  -1        8   30  38        0  543-517
 8  129-128        4   52  57        9   80  71        1  592-574
 9   76  70        5   24  19       10   34  41        2  401 377
10   65  60        6   70 -67       11   41  45        3  216-216
11   46 -49        7   60 -70       H,L= 4, 3         4  222-234
H,L= 1, 2          8    0  -1        0    0  22        5   54 -56
 0  121-114        9    0 -11        1  187-200        6   99  98
 1  115-105       H,L= 2, 5         2   28  22        7   44 -50
 2  379 370        0    0  39        3  220 234        8  193-197
 3  292 277        1  114 -90        4  229 228        9   30 -40
 4   99-106        2   55 -65        5  120-120       10   70  72
 5  184-182        3   39  30        6    0  -7       H,L= 6, 1
 6  151 153        4   84  98        7    0   4        0  263 261
 7  107 123        5   35 -36        8   17  19        1   52 -49
 8   99 -99        6   17 -14        9   71 -70        2  325 335
 9   25 -44        7   28  31       10   15 -20        3  164 166
10   17   9       H,L= 2, 6        H,L= 4, 4         4   14  12
11   15  25        0    0  -8        0   52 -65        5   33 -36
H,L= 1, 3          1   17  15        1   86 -87        6   27  -6
 0  367-369        2   29  27        2   77  81        7   17  18
 1  112 105        3   44 -34        3    0  10        8   30 -18
 2  153 151        4   16 -11        4    0 -18        9   16  14
 3   13  -9        5   30  18        5   17   5       H,L= 6, 2
 4   76 -73       H,L= 3, 1         6   82  80        0  191-194
 5  146 140        0  290-275        7   55  57        1  197 205
 6   81  74        1  585 579        8    0   2        2   87  99
 7   64  72        2   42 -43        9   15  16        3   73 -68
 8   55 -42        3   71 -74       H,L= 4, 5         4   39 -40
 9   34  30        4  143 136        0   30 -22        5  260 260
10   23  26        5  103  98        1   30  32        6  142 139
H,L= 1, 4          6   74 -76        2    0  -2        7   24  -8
 0  194-191        7   90 -85        3   55 -46        8   25 -13
 1   56 -65        8    0  17        4   25 -26        9   29  16
 2   43  52        9   97  86        5    0  18       10   27  22
 3   54  51       10    0  10        6   23 -26       H,L= 6, 3
 4  217-223       11   16 -20        7    0  -8        0  274-278
 5  106 -95       H,L= 3, 2        H,L= 4, 6         1   78 -76
 6   80  71        0  176 164        0   33  28        2    0 -22
 7   30  29        1  298 301        1   17  20        3   62  81
 8   17 -25        2  269-243        2   33 -19        4   40 -46
 9   16 -19        3  283-284        3   16  -6        5  123-129
H,L= 1, 5          4  112-113        4    0  10        6   25   6
 0   93  96        5   40  47        5   52 -55        7   46  53
 1    0  19        6   43  41        6    0   1        8   30 -21
 2   64 -53        7  105-109       H,L= 5, 1         9   16  -9
 3   25   3        8   49  30        0   16  10       H,L= 6, 4
 4   78  56        9   35  36        1   71  66        0   98 102
 5   67 -65       10   24  19        2    0  -8        1   55 -51
 6   38 -35       11   26 -30        3  117-126        2   33 -19
 7   40 -48       H,L= 3, 3         4  118-109        3   16  -6
 8    0  14        0  156 163        5   35  42        4   67  62
H,L= 1, 6          1   26  35        6   25  24        5   52 -55
 0   42  37        2   19 -24        7   61 -65        6    0   1
 1    0  -5        3   14   9        8   16  11       H,L= 6, 5
 2    0 -11        4  156 152        9   41 -48        0   17  26
 3    0  22        5  128-134       10    0 -13        1   58 -66
 4   62  73        6   76 -74                          2   25  18
 5    0  -6        7   99 -85                          3   69  71
H,L= 2, 0          8    0   5                          4    0  10
 0  662-653        9    0  13                          5   37 -35
 1  356-339       10   31 -30
 2  408-406       H,L= 3, 4
 3  475 489        0   82 -77


  6   0   5        4   43 -41        4   97 -96
H,L= 6, 6         5   17  15        5   46  52
 0   16   6        6    0  -2        6    0  63
 1   16  -1        7   15  19        7    0 -23
 2   22 -13       H,L= 8, 5         8   15 -14
 3    0   5        0   38 -38       H,L= 11, 2
H,L= 7, 1         1   38  37        0   62 -58
 0  104  97        2   17  11        1   46 -40
 1  148-139        3    0  -2        2   39  31
 2   60 -56        4   16 -28        3    0  -7
 3  224 218        5    0  -1        4   17  15
 4   64 -59       H,L= 9, 1         5    0  -3
 5  232-231        0   65  66        6    0  11
 6   16 -23        1   26 -28        7    0  -6
 7  127 126        2  110 111       H,L= 11, 3
 8   43  42        3   57  58        0   78  83
 9   38 -40        4  182-182        1   30 -29
10   16 -14        5   54 -52        2   17 -16
H,L= 7, 2         6   85  80        3    0   7
 0  245 255        7    0  48        4   17  -3
 1    0  -7        8   24 -17        5   16  -5
 2  147-159        9   16 -15        6    0 -12
 3  148-161       H,L= 9, 2        H,L= 11, 4
 4   56  60        0   16  -3        0   29 -29
 5   97  97        1  209-211        1   33 -22
 6   93 -90        2   48 -57        2   16  18
 7   60 -64        3  220 220        3   36  44
 8   62  56        4   38  44        4   26 -22
 9    0  -1        5   93 -91       H,L= 12, 0
10   21 -33        6   17  -4        0  105-104
H,L= 7, 3         7   17  68        1   72 -75
 0  213 214        8   23  13        2   25  11
 1  101  94        9   41 -48        3   43  32
 2   35 -38       H,L= 9, 3        4   25  18
 3   59  58        0  104-111        5   60 -56
 4   34  35        1   29 -27        6   23 -21
 5   34 -31        2   24  25        7   51  51
 6   46 -39        3    0   7       H,L= 12, 1
 7   17 -27        4   49 -48        0   70  69
 8   55  50        5   49 -48        1    0   9
 9   15   2        6   48  47        2   17   6
H,L= 7, 4         7   23  11        3   50 -47
 0   80  72        8   30 -28        4   52 -61
 1   68  71       H,L= 9, 4        5    0  10
 2  114-113        0   39  27        6    0 -21
 3    0  -5        1   49 -47        7    0 -11
 4  111 116        2    0   3       H,L= 12, 2
 5   46  41        3   39 -40        0   58  55
 6   29 -34        4    0   8        1   17  25
 7    0  -9        5   16  -5        2   25 -26
 8   36  34        6   16 -12        3   76  71
H,L= 7, 5         H,L= 9, 5        4   42  50
 0   83 -76        0   86  76        5   33 -25
 1    0 -19        1   28  29        6   31 -30
 2    0   3        2   23 -14       H,L= 12, 3
 3   34 -27        3    0  -1        0   30  28
 4   17  -8        4   15  11        1   42  38
 5    0  11       H,L= 10, 0        2   59 -51
 6   15   8        0   27-102        3   17 -14
H,L= 7, 6         1   95  83        4   51  49
 0   15  18        2   42 -36        5    0  10
 1   30 -30        3   68  66       H,L= 12, 4
 2    0   6        4  196 203        0   22 -29
H,L= 8, 0         5   65 -51        1   27 -33
 0   85  86        6   43 -44        2    0   8
 1  184 176        7   77 -80        3    0  -2
 2  104-105        8    0  11       H,L= 13, 1
 3   88 -85        9   15  -4        0   17  21
 4   90  90       H,L= 10, 1        1   46  37
 5  299 310        0   28  34        2   17 -12
 6  146-134        1   16  -4        3   71 -71
 7   63 -70        2   36 -30        4    0  -5
 8   70 -65        3   60 -65        5   56  56
 9   53  47        4  128 129        6   15  16
10    0   9        5   25  29       H,L= 13, 2
H,L= 8, 1         6   17   1        0   73 -80
 0  181-184        7    0  36        1    0   1
 1   14   9        8    0   2        2   63  63
 2  117-119       H,L= 10, 2        3    0   5
 3  181 183        0   90  93        4   42 -40
 4   84 -97        1   96 -90        5   15  -5
 5  129-128        2   99 -99       H,L= 13, 3
 6   38  45        3   24   6        0   16  11
 7   55 -58        4   65  65        1    0   4
 8    0  -8        5   17  17        2    0  -6
 9    0   1        6   91 -92        3   22 -13
10   15  23        7   58  54        4   15  -7
H,L= 8, 2         8   31  22       H,L= 14, 0
 0  145-153       H,L= 10, 3        0   24  -7
 1   47  58        0   30  29        1   24 -16
 2   15 -12        1  111 104        2   55  55
 3  198-199        2    0   3        3   57  64
 4  169 159        3   25 -23        4   42 -36
 5   56  45        4   63 -72        5   47 -51
 6   17  11        5   17  15       H,L= 14, 1
 7   99 -95        6   16 -20        0    0   2
 8   45 -48        7   48 -47        1   29 -25
 9   31  30       H,L= 10, 4        2    0 -12
H,L= 8, 3         0   69 -55        3   43  47
 0  104-107        1   24  22        4   22  11
 1   75  72        2   30  25        5   14 -14
 2  225 231        3    0  12       H,L= 14, 2
 3  113-102        4    0  10        0   53 -55
 4   83 -91        5    0  -1        1   23 -22
 5   63  61       H,L= 10, 5        2   22  17
 6   70  69        0    0   9        3   22  26
 7   17  10        1   31  28       H,L= 14, 3
 8   59 -57        2   15 -14        0   48  50
H,L= 8, 4         H,L= 11, 1       H,L= 15, 1
 0   17  18        0   38 -35        0   43  48
 1   44 -37        1   68  63        1   15 -10
 2   25   3        2   59  50        2   47 -50
 3   39  38        3   86 -85
```

XBL 687-1323

2. Discussion

The $B_4F_6PF_3$ molecule is shown in Figure 1. The duplicate atom labels are caused by the crystallographic mirror plane which bisects the molecule and contains F1(P), P, B(1), B(2), F1(2) and F2(2). The atoms F2(P), P, B(1), and B(3) all lie in another plane to within the accuracy of this determination; F1(3) and F2(3) deviate from it by only a small ($\sim3^{o}$) rotation of the BF_2 group about the B-B bond. This second plane makes an angle of $120^{o} \pm 1^{o}$ with the mirror plane so that the molecule has approximately 3m (C_{3v}) point symmetry, only one mirror of which is required by crystal symmetry. The fluorines on phosphorus are in a staggered configuration with respect to the BF_2 groups on B(1), and the angles at B(1) are tetrahedral to within the experimental accuracy.

Distances and angles found in this structure are presented and compared with those found for related compounds in Table III. These inter-atomic distances must be corrected for the effect of thermal motion in order to arrive at quantities which are comparable to the results of studies by other methods (e.g., spectroscopic and electron-diffraction methods). This is particularly true in view of the large thermal para-meters found here. Large thermal parameters are consistent with the observations that this is a low-melting, readily sublimable crystal. The accuracy of thermal corrections is poor, however, because of the ambi-guity as to the correct model on which to base their calculation. The minimum and "riding-model" corrections[9] in Table III are included to indicate the approximate magnitude of the calculated corrections.

The author can find no chemical or molecular-packing-forces
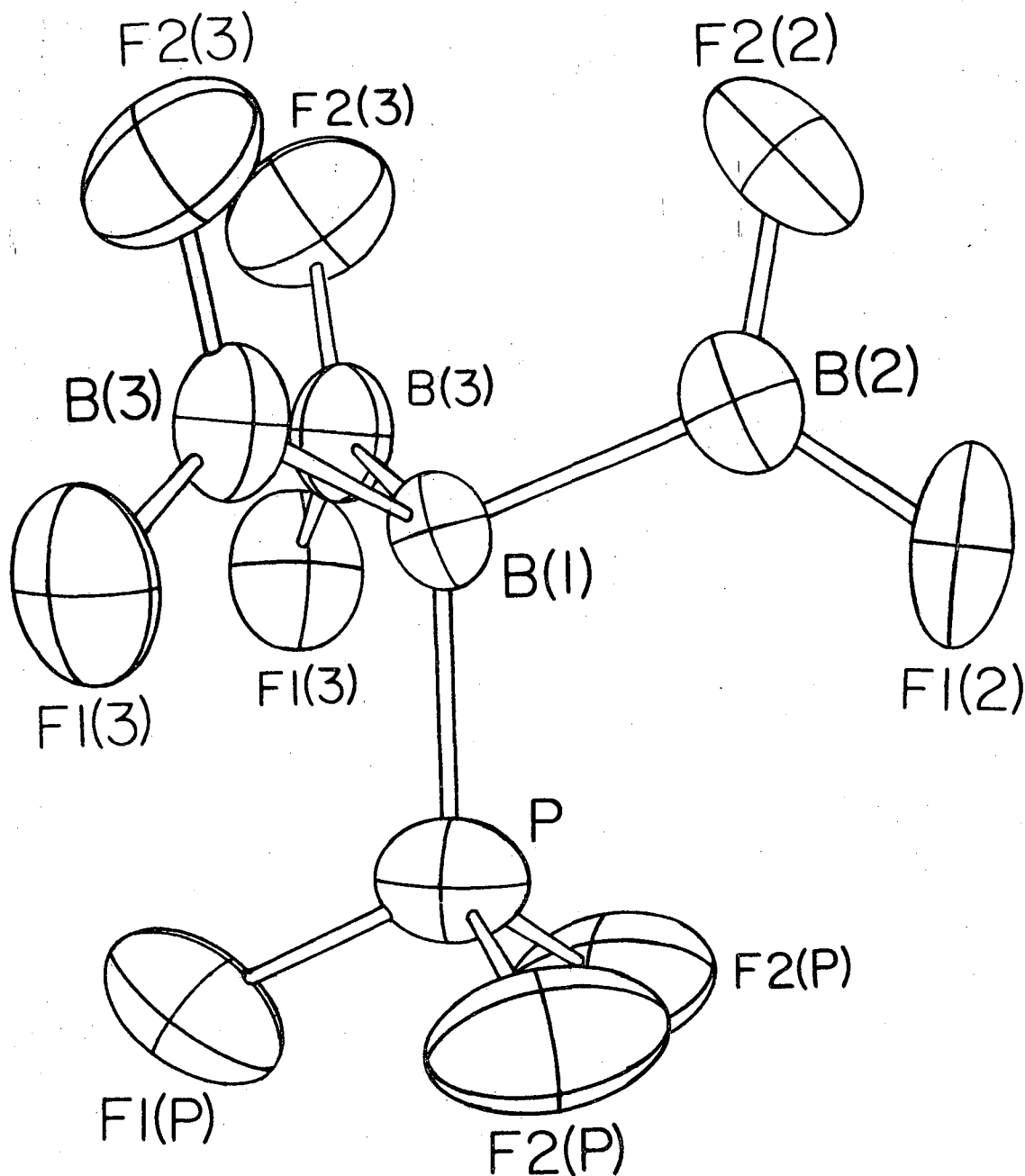
Figure 1. - The $B_4F_6PF_3$ molecule. The molecule is bisected by a crystallographic mirror plane which contains F1(P), P, B(1), B(2), F1(2), and F2(2). The thermal elipsoids have been reduced to 30% probability contours for the sake of clarity.

Table III. Distances and Angles in $B_4F_6PF_3$ and Comparison Compounds

atoms	distance, A	comparison distance	comparison compound
B(2)-F1(2)	1.330(10)[a]		
B(2)-F2(2)	1.276(10)		
B(3)-F1(3)	1.319(6)		
B(3)-F2(3)	1.293(7)	1.30	BF_3[d]
average	1.305 ± .015[b]	1.32 ± .035	B_2F_4[e]
(thermal correction = .009, .051)[c]			
B(1)-B(2)	1.685(10)		
B(1)-B(3)	1.668(7)		
average	1.677 ± .015	1.67 ± .045	B_2F_4
(thermal correction = .001, .013)			
B(1)-P	1.825(7)		
	1.825 ± .015	1.836 ± .012	H_3BPF_3[f]
(thermal correction = .005, .026)			
P-F1(P)	1.525(6)		
P-F2(P)	1.496(4)	1.535 ± .02	PF_3[g]
average	1.511 ± .015	1.538 ± .008	H_3BPF_3
(thermal correction = .013, .066)			
	intra-molecular, non-bonded		
B(2)-B(3)	2.719(9)		

Table III, continued

B(3)-B(3)	2.725(11)		
F1(2)-F2(2)	2.180(7)		
F1(3)-F2(3)	2.176(4)	2.23 ± .024	B_2F_4
F1(P)-F2(P)	2.339(7)		
F2(P)-F2(P)	2.321(7)		
F2(2)-F2(3)	3.217(5)		
F2(3)-F2(3)	3.181(7)		
F1(2)-F2(P)	3.299(6)		
F1(3)-F1(P)	3.246(4)		
F1(3)-F2(P)	3.210(5)		

inter-molecular F-F contacts

F2(P)-F2(3)	3.088(5)	[3.09$_5$]	B_2F_4
F1(P)-F2(3)	3.092(5)	[3.11]	
F1(2)-F1(3)	3.174(4)	[3.12$_5$]	
F2(P)-F2(2)	3.178(6)	[3.22]	
F2(2)-F1(3)	3.183(3)	[3.27]	
F1(2)-F1(3)	3.209(4)	[3.28]	
F2(P)-F2(3)	3.236(5)	[3.28]	
F1(P)-F1(2)	3.244(7)	[3.30]	
F1(3)-F1(3)	3.271(2)	[3.34]	
F1(3)-F2(3)	3.292(5)	[3.37]	

Table III, continued

F2(P)-F2(P)	3.343(7)	[3.45]	
F1(2)-F2(3)	3.413(5)		
all others	> 3.5		

bond angles

F1(2)-B(2)-F2(2)	113.6(7)		
F1(3)-B(3)-F2(3)	112.8(5)		
average	113.2° ± 1°	[115°]	B_2F_4
B(1)-B(2)-F1(2)	123.6(7)		
B(1)-B(2)-F2(2)	122.8(7)		
B(1)-B(3)-F1(3)	124.5(5)		
B(1)-B(3)-F2(3)	122.7(5)		
average	123.4° ± 1°	[122.5°]	B_2F_4
B(2)-B(1)-B(3)	108.3(4)		
B(3)-B(1)-B(3)	109.5(5)		
B(2)-B(1)-P	111.1(5)		
B(3)-B(1)-P	109.8(3)		
average	109.7° ± 1°	109.5°	(tetrahedral)
B(1)-P-F1(P)	115.2(3)		
B(1)-P-F2(P)	117.2(2)		
average	116.2° ± 1°		

Table III, continued

F1(P)-P-F2(P)	101.5(2)		
F2(P)-P-F2(P)	101.8(3)	$100^{\circ} \pm 2^{\circ}$	PF_3
average	$101.7^{\circ} \pm 1^{\circ}$	$99.8^{\circ} \pm 1^{\circ}$	H_3BPF_3

(a) The number in parentheses is the standard deviation in the least
significant digit as calculated from the standard deviations of
coordinates.

(b) The standard deviations of .015 A and 1° listed for average values
are based upon comparisons of distances expected to be the same
and the author's past experience. They are believed to be better
representations of the accuracy of these results than those
calculated from the standard deviations of coordinates.

(c) The two corrections for thermal motion given are a minimum
correction and a "riding-model" correction, respectively. Both are
much less than the maximum possible correction. (see text and
reference 9).

(d) "Tables of Interatomic Distances and Configuration in Molecules
and Ions", Special Publication No.11, The Chemical Society,
Burlington House, London, W.1, 1958, page M18.

(e) L. Trefonas and W. N. Lipscomb, *J. Chem. Phys.*, 28, 54 (1958).
Numbers in square brackets are the author's calculation from cell
dimensions and positional parameters given. (X-ray crystallographic
study)

(f) R. L. Kuczkowski and D. R. Lide, Jr., *ibid.*, 46, 357 (1967).
(microwave study)

Table III, continued

(g) Q. Williams, J. Sheridan, and W. Gordy, _ibid._, 20 164 (1952).

(microwave and electron diffraction study)

explanation for the apparent difference ($\sim$ .04 A) between the axially

and equatorially directed B-F distances. Since this difference could

have arisen from a small ($\sim$ .02 A $\leqq$ 2σ) shift of the two borons, the

author is not willing to assert that it is real in the absence of

supporting evidence. The up-and-down orientations of the BF_2 groups

was unexpected because the F-F distances between different groups would

be greater if the BF_2 groups were in a propeller-like configuration. The

observation that each fluorine has at least two inter-molecular F-F

contacts shorter than any intra-molecular one (except between two

fluorines bonded to the same atom) shows that the fluorine contacts within

the molecule are not short enough to control the configuration. The BF_2

orientations are evidently governed by the meshing together of fluorines

on adjacent molecules (see Figure 2). The existence of inter-molecular

F-F contacts shorter than the intra-molecular ones also indicates that

the B-P distance is not controlled by F-F interactions. This, and the

fact that the B-P distance found here is not significantly different from

that found for H_3BPF_3, indicates that BF_2 will not only formally replace

hydrogen,[1] but is quite similar to hydrogen in its electronic effects

on the rest of the molecule.
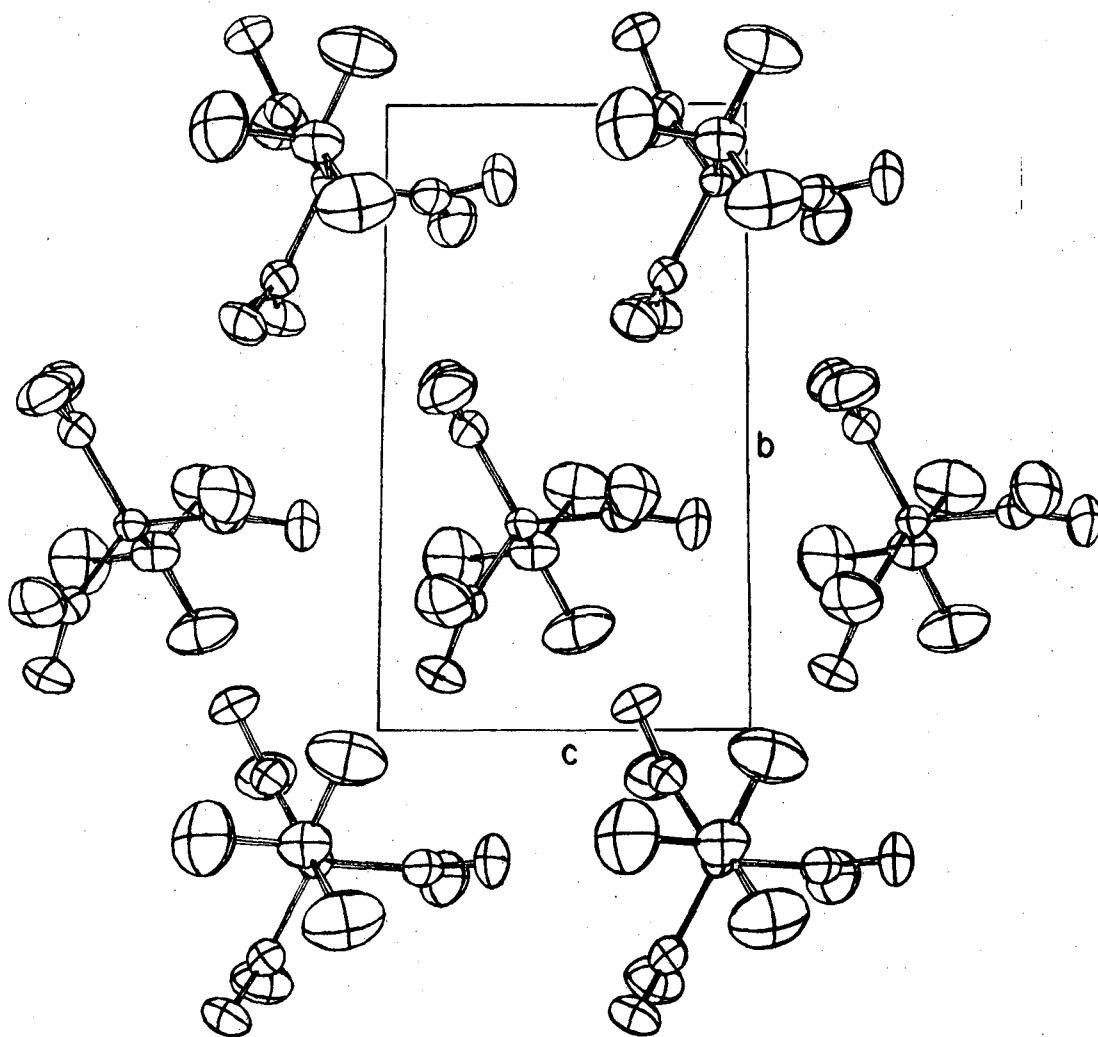
Figure 2. - Molecular Packing in $B_4F_6PF_3$. This is one layer, approximately $\frac{1}{2}$ _a_ thick, seen in perspective. The other layers are related to the one shown by the _a_ glide perpendicular to _c_.

References and Footnotes

(1) P. L. Timms, J. Am. Chem. Soc., 89, 1629 (1967).

(2) A description of this work is to be submitted to Inorganic Chemistry for publication.

(3) J. Karle and I. L. Karle, Acta Cryst., 21, 849 (1966).

(4) R. E. Long, Ph. D. thesis, University of California, Los Angeles, 1965.

(5) "International Tables for X-ray Crystallography", vol. III, The Kynoch Press, Birmingham, England, 1962, pp. 202-3, 214-5.

(6) D. T. Cromer and J. T. Waber, Acta Cryst., 18, 104 (1965).

(7) D. T. Cromer, ibid., 18,17 (1965).

(8) No significant changes in either the structural parameters or the quality of agreement were found as a result of the change in scattering factors.

(9) W. R. Busing and H. A. Levy, Acta Cryst., 17, 142 (1964).

Acknowledgments

I thank Professor David H. Templeton for his continued interest, guidance, and instruction during the course of this work. I also thank Dr. Allan Zalkin for the use of his computer programs and his constant effort in maintaining and improving them. Mrs. Helena Ruben is thanked for her too-often unrecognized attention to the details of supply and maintainence necessary to the performance of this work. Dr. Michael G. B. Drew is thanked for his aid in the application of statistical methods of phase determination. All of the above, as well as Dr. Ted E. Hopkins, Dr. Roger C. Petterson, Mr. David J. St. Clair, and Mr. Mark S. Fischer are thanked for their warm friendship and many stimulating, instructive conversations.

I thank Professor M. F. Hawthorne for supplying crystals of $Rb_2B_{20}H_{18}$ and $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$, and for helpful discussions regarding these substances. I thank Professor P. L. Timms for providing samples of $B_4F_6PF_3$ and for providing them in such a convenient form. Both Professor Timms and Mr. Ralph Kirk are thanked for discussions regarding the $B_4F_6PF_3$ results.

Particular thanks go to my wife, Barbara, for typing numerous drafts and the final copy of this report.

I thank the National Science Foundation for a graduate fellowship (1964-1967) and the U. S. Atomic Energy Commission, under whose auspices this work was performed.