mal analysis and determination of hydrogen atom parameters, seemed unwarranted.

Bond lengths and angles calculated from the final atomic parameters are shown in Fig.1. A view of the crystal structure projected down the $b$ axis is shown in Fig. 2. Excluding the oxygen atoms, the molecule is planar within experimental error. The equation of the least-squares plane through the phenyl ring is $-0 \cdot 4583 x+5 \cdot 2702 y+7 \cdot 3449 z=$ $4 \cdot 1023$. The dimensions of the sulfonate group are similar to those found in a variety of related compounds.

The observed dimensions of the ring suggest that the molecule is quinoid in character. Of interest are the dimensions of the diazonium group as compared with those observed in structures of the type $\left(\mathrm{ArN}_{2}\right)^{+}(\mathrm{X})^{-}$. The $\mathrm{C}(4)-\mathrm{N}(1)$ distance of $1.39 \AA$ compares with the corresponding bond length of $1.385 \AA$ found in phenyldiazonium chloride (Rømming, 1963) and $1.41 \AA$ in phenyldiazonium tribromide (Anderson \& Rømming, 1962); it appears to be significantly shorter than the value of $1.45 \AA$ reported for the double salt of ferric chloride and $o$-methylphenyldiazonium chloride (Polynova, Bokii \& Porai-Koshits, 1965). The $N(1)-N(2)$ bond length of $1 \cdot 14 \AA$ is marginally longer than the values of $1 \cdot 097,1 \cdot 11$ and $1 \cdot 11 \AA$ respectively re-
ported for these salts. The diazonium group is linear within experimental error.

The molecular packing is quite reasonable with no intermolecular distances shorter than the sum of the normally accepted van der Waals radii. The shortest intermolecular approaches are found at the polar ends of the molecule. These are $2.92 \AA$ between $\mathrm{N}(2)$ and $\mathrm{O}(3)(-1+x, y, z) ; 2.92$ $\AA$ between $\mathrm{N}(2)$ and $\mathrm{O}(1)(1-x, 1-y, \bar{z})$; and $2.79 \AA$ between $\mathrm{N}(1)$ and $\mathrm{O}(1)(1-x, 1-y, \bar{z})$.

This work was supported by the Robert A. Welch Foundation of Houston, Texas.

## References

Anderson, O. \& Rømming, C. (1962). Acta,Chem. Scand. 16, 1882.
Busing, W. R., Martin, K. O. \& Levy, H. A. (1962). ORFLS, A Fortran Crystallographic Least Squares Program. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
Polynova, T. N., Bokil, N. G. \& Porai-Koshits, M. A. (1965). Zh. Strukt. Khim. 6, 878.

Rømming, C. (1963). Acta Chem. Scand. 17, 1444.

Acta Cryst. (1970). B26, 1189
Bond lengths and thermal parameters of potassium metaborate, $\mathbf{K}_{3} \mathbf{B}_{3} \mathbf{O}_{6}$. By W.Schneider* and G. B. Carpenter, Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912, U.S.A.
(Received 29 October 1969)

The results of a refinement of the structure of $\mathrm{K}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$ are described. The space group is $R \overline{3} c$ and the hexagonal axes are $a=12.76$ and $c=7.34 \AA$. In the cyclic $\mathrm{B}_{3} \mathrm{O}_{6}{ }^{3-}$ ion the endocyclic $\mathrm{B}-\mathrm{O}$ distances are $1.398 \AA$ and the exocyclic B-O distances are $1.331 \AA$. The results agree closely with the original results of Zachariasen (1937). The dimensions of the ion cannot be reconciled with the distances found in the isostructural $\mathrm{Na}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$ on the basis of a simple correlation betweern bond strength and bond length.

The cyclic metaborate ion $\mathrm{B}_{3} \mathrm{O}_{6}{ }^{3-}$ was discovered by Za chariasen (1937) in potassium metaborate. This ion consists of a planar six-membered ring of alternating boron and oxygen atoms with $\mathrm{B}-\mathrm{O}=1 \cdot 38 \AA$, and three other oxygen atoms bonded to the boron atoms at $\mathrm{B}-\mathrm{O}=1.33 \AA$. The same ion was found also in sodium metaborate (Fang, 1938).

A later nuclear magnetic resonance study (Bray, Edwards, O'Keefe, Ross \& Tatsuzaki, 1961) of potassium metaborate suggested that boron might not have the trigonal coordination reported from the original diffraction work.

* Present address: Gesellschaft für Kernforschung, Institut für Material- und Festkörperforschung, 75 Karlsruhe, Weberstr. 5, Germany.

At that time the present authors undertook a re-examination of the potassium compound in order to resolve the discrepancy. We found that Zachariasen's model was in fact quite accurate, giving an $R$ value of $12 \%$ with our $0 k l$ data.

Subsequently Marezio, Plettinger \& Zachariasen (1963b) redetermined the structure of the isostructural compound $\mathrm{Na}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$, and found $\mathrm{B}-\mathrm{O}=1.433$ in the ring and $\mathrm{B}-\mathrm{O}=$ $1-280 \AA$ outside the ring. This is the extreme difference found for bonds to trigonal boron. The corresponding two points are the ones that lie farthest off the calculated bond order - bond length curve of Coulson \& Dingle (1968). Since we did not find such a large difference in B-O distances in the potassium compound, it seems worthwhile now to report our results.

Table 1. Parameters for $\mathrm{K}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$
Standard deviations in the last digit are given in parentheses.

|  | $x$ | $\beta_{11}$ | $\beta_{22}=\beta_{12}$ | $\beta_{33}$ | $\beta_{13}=\beta_{23}$ |
| :--- | :---: | :---: | :---: | :---: | ---: |
|  | $x$ | $0.5613(1)$ | $0.0025(1)$ | $0.0021(1)$ | $0.0051(2)$ |
| $\mathbf{K}$ | $0.8889(6)$ | $0.0024(3)$ | $0.0034(5)$ | $0.0040(9)$ | $-0.0006(1)$ |
| $\mathbf{B}$ | $0.0008(4)$ |  |  |  |  |
| $\mathbf{O}(1)$ | $0.7843(3)$ | $0.0024(2)$ | $0.0025(3)$ | $0.0064(7)$ | $-0.0007(3)$ |
| $\mathrm{O}(2)$ | $0.1084(4)$ | $0.0018(2)$ | $0.0015(3)$ | $0.0113(8)$ | $-0.0002(4)$ |

Needle-shaped crystals of $\mathrm{K}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$ were obtained by heating an equimolar mixture of $\mathrm{K}_{2} \mathrm{CO}_{3}$ and $\mathrm{B}_{2} \mathrm{O}_{3}$, according to the method of Atterberg (1906). Lattice constants for the hexagonal cell, from rotation and precession photographs, were $a=12.76$ and $c=7.34 \AA$; the estimated standard deviation in each is $0.01 \AA$. These values agree well with those of Zachariasen (1937). The space group is $R \overline{3} c$ with $18 \mathrm{KBO}_{2}$ units in the hexagonal cell; all atoms lie on twofold axes, positions $18(e)$ at $x, 0,4$, etc.

Intensities were measured photometrically on precession photographs of the zones [100] and [210] of the same crystal. No corrections for absorption or extinction were applied. There were 277 independent reflections of measurable intensity.

The structure was refined, starting with Zachariasen's (1937) parameters, by difference synthesis and finally by full-matrix least-squares refinement on $F$ with the BusingLevy program. The final discrepancy index, for observed reflections only, was 0.071 . This was lowered to 0.061 when

Table 2. Observed and calculated structure factors Starred reflections were omitted from the refinement.
the six strongest reflections, which appeared to suffer from extinction, were omitted. The final parameters are given in Table 1, and the observed and calculated structure factors in Table 2.

Important interatomic distances and angles are presented in Table 3. The boron-oxygen distances are within $0.02 \AA$ of those reported by Zachariasen (1937), and are similar to those found for trigonally bonded boron in other metaborates and metaboric acid where chains, rather than rings, occur. For the bonds to shared oxygen atoms and to the unshared oxygen atom respectively, the values reported are 1.385 (10) and 1.401 (9), 1.326 (10) $\AA$ in calcium metaborate (Marezio, Plettinger \& Zachariasen, 1963a); 1.389 (6) and 1.400 (6), 1.330 (6) $\AA$ in lithium metaborate (Zachariasen, 1964); and 1 -371 (7) and 1 -386(7), 1 -345(7) $\AA$ in monoclinic metaboric acid (Zachariasen, 1963). However, the distances found here do not show the extreme difference reported for the sodium analog, $\mathrm{Na}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$.

The thermal motion ellipsoid of each atom is described in Table 4 by the root-mean-square displacements along the principal axes $R_{1}, R_{2}$ and $R_{3}$ and by the angles that these axes make with the $a, b^{*}$ and $c$ axes of the crystal. Symmetry requires that one principal axis be parallel to $a$. The shapes and orientations of the thermal ellipsoids appear to be reasonable. The shortest axis for the potassium atom is directed generally toward the nearest oxygen atoms. The shortest axis of the $O(1)$ ellipsoid, which is similar to the ellipsoid of the boron atom to which $\mathrm{O}(1)$ is bonded, is directed toward the nearest potassium atom. The long axis of the ellipsoid of the ring atom $\mathrm{O}(2)$ is nearly perpendicular to the ring.

Since the isostructural $\mathrm{K}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$ and $\mathrm{Na}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$ exhibit different degrees of difference between the two types of boron-oxygen bonds, it is not possible to reconcile both structures with Pauling's principle of valence balancing when the same bond strength - bond length curve is used for both. If Zachariasen's (1963) correlation is used, we deduce bond strengths of 1.10 for $\mathrm{B}-\mathrm{O}(1)$ and 0.92 for $\mathrm{B}-\mathrm{O}(2)$. If we then attribute a strength of 4 to each of the seven short $\mathrm{K} \cdots \mathrm{O}$ distances about each potassium atom, the sum of bond strengths is 1.81 about $\mathrm{O}(1)$ and 2.14 about $O(2)$. Although this equal partitioning of the potassium valence cannot be far wrong in view of the similarity of the $\mathrm{K} \cdots \mathrm{O}$ distances, the valence sums about the oxygen atoms are too far from the normal value 2 to represent a satisfactory interpretation. If, on the other hand, we adjust the $\mathrm{K} \cdots \mathrm{O}$ bond strengths to attain the ideal valence of 2 for every oxygen atom, we find bond strengths 0.18 for $\mathrm{K} \cdots \mathrm{O}(1)$ and 0.08 for $\mathrm{K} \cdots \mathrm{O}(2)$. This is in contradiction to the experimental result that the $\mathrm{K} \cdots \mathrm{O}(2)$ distance is the shorter.

Our results for $\mathrm{K}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$ agree better with the $\pi$-bond order curve (Coulson \& Dingle, 1968) than do those for $\mathrm{Na}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$.

Table 3. Interatomic distances and angles in $\mathrm{K}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$
Standard deviations in the last digits are given in parentheses.

| $\mathrm{K}-\mathrm{O}(1)$ |  | 2.849 (6) $\AA$ | $\mathrm{O}(2)-\mathrm{B}-\mathrm{O}(2)$ | 117.3 (8) ${ }^{\circ}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{K}-\mathrm{O}(1)$ | ( $2 \times$ ) | 2.801 (2) | $\mathrm{O}(1)-\mathrm{B}-\mathrm{O}(2)$ | 121.3 (4) |
| $\mathrm{K}-\mathrm{O}(1)$ | (2x) | 2.835 (3) | $\mathrm{B}-\mathrm{O}(2)-\mathrm{B}$ | $122 \cdot 6$ (8) |
| $\mathrm{K}-\mathrm{O}(2)$ | ( $2 \times$ ) | 2.775 (5) |  |  |
| $\mathrm{B}-\mathrm{O}(1)$ |  | 1.331 (10) |  |  |
| $\mathrm{B}-\mathrm{O}(2)$ | (2x) | 1.398 (5) |  |  |
| $\mathrm{O}(1)-\mathrm{O}(2)$ | (2x) | $2 \cdot 381$ (5) |  |  |
| $\mathrm{O}(2)-\mathrm{O}(2)$ |  | 2.389 (9) |  |  |

Table 4. Principal axes of the thermal motion ellipsoids for the atoms of $\mathrm{K}_{3} \mathrm{~B}_{3} \mathrm{O}_{6}$
For each principal axis of each atom the columns give the r.m.s. displacement (with standard deviation in parentheses) and the angles that the axis makes with the $a, b^{*}$ and $c$ axes of the crystal. The last column gives the standard deviation in the angles that are not determined by symmetry.

|  | Principal axis | Displacement | $a$ | $b^{*}$ | c | $\sigma$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| K | $R_{1}$ | 0.086 (8) $\AA$ | $90^{\circ}$ | $46^{\circ}$ | $136^{\circ}$ | $3^{\circ}$ |
|  | $R_{2}$ | $0 \cdot 123$ (4) | 0 | 90 | 90 |  |
|  | $R_{3}$ | $0 \cdot 134$ (4) | 90 | 44 | 46 |  |
| B | $R_{1}$ | 0.071 (40) | 90 | 50 | 40 | 9 |
|  | $R_{2}$ | $0 \cdot 129$ (19) | 0 | 90 | 90 |  |
|  | $R_{3}$ | $0 \cdot 144$ (23) | 90 | 40 | 130 |  |
| $\mathrm{O}(1)$ | $R_{1}$ | 0.092 (20) | 90 | 53 | 37 | 6 |
|  | $R_{2}$ | $0 \cdot 121$ (12) | 0 | 90 | 90 |  |
|  | $R_{3}$ | $0 \cdot 161$ (13) | 90 | 37 | 127 |  |
| $\mathrm{O}(2)$ | $R_{1}$ | 0.096 (15) | 0 | 90 | 90 | 15 |
|  | $R_{2}$ | $0 \cdot 107$ (12) | 90 | 7 | 97 |  |
|  | $R_{3}$ | $0 \cdot 169$ (9) | 90 | 83 | 7 |  |

Confirmatory evidence for variability of metaborate ring dimensions has come from infrared studies. Hisatsune \& Suarez (1964) reported that the strongest bands of the $\mathrm{B}_{3} \mathrm{O}_{6}{ }^{3-}$ ion occur at lower frequencies in a potassium chloride matrix than in one of sodium chloride. Similarly, Goubeau \& Hummel (1959) found the strongest bands to occur at higher frequencies in sodium metaborate than in metaboric acid. They interpreted this as a general tightening of the bonding in the metaborate ion in the salt, arising from increasing participation of a $\pi$-electron system. Pauling (1945) had originally suggested that the fourth orbital of boron was used in double bond formation here. The bond tightening appears to increase from sodium to potassium metaborate, in agreement with the decrease in average boron-oxygen bond length.
In an attempt to investigate whether the boron-oxygen bond length increases further on proceeding to rubidium and cesium metaborates, these compounds have been prepared by one of us (W.S.) by fusion of the alkali carbonates with $\mathrm{B}_{2} \mathrm{O}_{3}$ in platinum crucibles. In both cases the products were obtained in the form of clear hexagonal needles up to 1 cm in length. Lattice constants, determined from the precession photographs prepared with Mo $K \alpha$ radiation, are $a=13.21$ and $c=7.78 \AA$ for $\mathrm{RbBO}_{2}$, and $a=13.68$ and $c=8.36 \AA$ for $\mathrm{CsBO}_{2}$ (all dimensions with estimated standard deviations of $0.01 \AA$.) Both compounds are isostructural with the sodium and potassium compounds. Unfortunately it has not been possible to obtain good infrared
spectra of these compounds to see if further decreases of important frequencies occur.

We do not propose to do further work on these compounds.

We are grateful for the support of the Office of Naval Research for the initial work on potassium metaborate.

## References

Atterberg, A. (1906). Z. anorg. Chem. 48, 368.
Bray, P. J., Edwards, J. O., O’Keefe, J. G., Ross, V. F. \& Tatsuzaki, I. (1961). J. Chem. Phys. 35, 435.
Coulson, C. A. \& Dingle, T. W. (1968). Acta Cryst. B24, 153.

Fang, S.-M. (1938). Z. Kristallogr. 99, 1.
Goubeau, J. \& Hummel, D. (1959). Z. phys. Chem. 20, 15.
Hisatsune, I. C. \& Suarez, N. D. (1964). Inorg. Chem. 3, 168.

Marezio, M., Plettinger, H. A. \& Zachariasen, W. H. (1963a). Acta Cryst. 16, 390.
Marezio, M., Plettinger, H. A. \& Zachariasen, W. H. (1963b). Acta Cryst. 16, 594.
Pauling, L. (1945). The Nature of the Chemical Bond. Ithaca: Cornell Univ. Press.
Zachariasen, W. H. (1937). J. Chem. Phys. 5, 919.
Zachariasen, W. H. (1963). Acta Cryst. 16, 385.
Zachariasen, W. H. (1964). Acta Cryst. 17, 749.

