

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 $-0.4583x + 5.2702y + 7.3449z = 4.1023$. 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 $(\text{ArN}_2)^+(\text{X})^-$. The C(4)–N(1) distance of 1.39 Å compares with the corresponding bond length of 1.385 Å found in phenyldiazonium chloride (Rømming, 1963) and 1.41 Å in phenyldiazonium tribromide (Anderson & Rømming, 1962); it appears to be significantly shorter than the value of 1.45 Å 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 1.14 Å is marginally longer than the values of 1.097, 1.11 and 1.11 Å 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 Å between N(2) and O(3) $(-1+x, y, z)$; 2.92 Å between N(2) and O(1) $(1-x, 1-y, \bar{z})$; and 2.79 Å between N(1) and O(1) $(1-x, 1-y, \bar{z})$.

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Bond lengths and thermal parameters of potassium metaborate, $\text{K}_3\text{B}_3\text{O}_6$. By W. SCHNEIDER* and G. B. CARPENTER, *Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912, U.S.A.*

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The results of a refinement of the structure of $\text{K}_3\text{B}_3\text{O}_6$ are described. The space group is $R\bar{3}c$ and the hexagonal axes are $a=12.76$ and $c=7.34$ Å. In the cyclic $\text{B}_3\text{O}_6^{3-}$ ion the endocyclic B–O distances are 1.398 Å and the exocyclic B–O distances are 1.331 Å. The results agree closely with the original results of Zachariassen (1937). The dimensions of the ion cannot be reconciled with the distances found in the isostructural $\text{Na}_3\text{B}_3\text{O}_6$ on the basis of a simple correlation between bond strength and bond length.

The cyclic metaborate ion $\text{B}_3\text{O}_6^{3-}$ was discovered by Zachariassen (1937) in potassium metaborate. This ion consists of a planar six-membered ring of alternating boron and oxygen atoms with B–O = 1.38 Å, and three other oxygen atoms bonded to the boron atoms at B–O = 1.33 Å. 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.

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

Subsequently Marezio, Plettinger & Zachariassen (1963*b*) redetermined the structure of the isostructural compound $\text{Na}_3\text{B}_3\text{O}_6$, and found B–O = 1.433 in the ring and B–O = 1.280 Å 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 $\text{K}_3\text{B}_3\text{O}_6$*

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

Standard deviations in the last digit are given in parentheses.

Table 4. *Principal axes of the thermal motion ellipsoids for the atoms of K₃B₃O₆*

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	<i>a</i>	<i>b</i> *	<i>c</i>	σ
K	<i>R</i> ₁	0.086 (8) Å	90°	46°	136°	3°
	<i>R</i> ₂	0.123 (4)	0	90	90	
	<i>R</i> ₃	0.134 (4)	90	44	46	
B	<i>R</i> ₁	0.071 (40)	90	50	40	9
	<i>R</i> ₂	0.129 (19)	0	90	90	
	<i>R</i> ₃	0.144 (23)	90	40	130	
O(1)	<i>R</i> ₁	0.092 (20)	90	53	37	6
	<i>R</i> ₂	0.121 (12)	0	90	90	
	<i>R</i> ₃	0.161 (13)	90	37	127	
O(2)	<i>R</i> ₁	0.096 (15)	0	90	90	15
	<i>R</i> ₂	0.107 (12)	90	7	97	
	<i>R</i> ₃	0.169 (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 B₃O₆³⁻ 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 π -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 B₂O₃ 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* α radiation, are *a* = 13.21 and *c* = 7.78 Å for RbBO₂, and *a* = 13.68 and *c* = 8.36 Å for CsBO₂ (all dimensions with estimated standard deviations of 0.01 Å). 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.

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