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 $(ArN_2)^+(X)^-$. 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, K₃B₃O₆. By W. SCHNEIDER* and G. B. CARPENTER,

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The results of a refinement of the structure of $K_3B_3O_6$ are described. The space group is R3c and the hexagonal axes are a=12.76 and c=7.34 Å. In the cyclic $B_3O_6^{3-}$ 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 Zachariasen (1937). The dimensions of the ion cannot be reconciled with the distances found in the isostructural Na₃B₃O₆ on the basis of a simple correlation between bond strength and bond length.

The cyclic metaborate ion $B_3O_6^{3-}$ was discovered by Zachariasen (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.

* 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 0kldata.

Subsequently Marezio, Plettinger & Zachariasen (1963b) redetermined the structure of the isostructural compound $Na_3B_3O_6$, 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 K₃B₃O₆

Standard deviations in the last digit are given in parentheses.

	x	β_{11}	$\beta_{22} = \beta_{12}$	β_{33}	$\beta_{13} = \beta_{23}$
К	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)

Needle-shaped crystals of $K_3B_3O_6$ were obtained by heating an equimolar mixture of K_2CO_3 and B_2O_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 Å; the estimated standard deviation in each is 0.01 Å. These values agree well with those of Zachariasen (1937). The space group is R3c with 18 KBO₂ units in the hexagonal cell; all atoms lie on twofold axes, positions 18(e) at x, 0, $\frac{1}{2}$, 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 Busing-Levy 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.

h it 1 Po it.Po

h k 1 Fo k-Po

b k 1 Po k.ec

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• 0	0 6 2081 -2226	5	59	229 254	8	4.	4 452 - 445	11	5 6	221 - 233
- 1	0 2 1260 -1193	6	0 0	148 - 156	8	4	7 545 604	12	0 0	269 244
i	0 4 675 649	6	1 2	505 549	8	5	0 442 - 432	12	06	165 - 187
- 1	0 8 168 161	- 6	1 2	843 828	8	2	3 722 - 704	12	1 2	520 522
1	1 0 208 - 138	5	1 5	72 - 88		2	6 303 24/	-12	1 4	221 111
1	1 3 1455 -1433	- 6	1 2	867 903	8	2	9 208 204	12	! ?	654 618
1	1 6 234 206	6	1 8	225 - 277	ä	2	2 222 400	-12		200 - 204
. 1	1 9 489 496	~ Ņ	1 8	311 - 331	8	3	7 441 - 427	15	5 ;	200 - 190
• 2	0 2 1938 -2512	2	5 1	1436 -1381	• 8	6	0 2025 2374	15	5 6	731 - 675
~ 2	0 4 1690 1694	- 2	5 1	490 - 453		ň	6 1480 -1491	12	íĭ	376 - 407
. 5	0 10 621 - 638	- 6	5 1	433 - 409	á	ĩ	2 461 - 448	12	5 é	476 482
- 5	1 1 381 - 351	ĕ	2 7	229 255	ś	7	4 256 - 219	-12	4 ž	574 557
2	1 4 558 - 505	- 6	2 7	462 432	- 9	1	2 301 - 309	-12	4 5	678 - 618
2	1 7 226 203	6	3 Ó	90 - 67	9	1	5 187 - 209	-12	4 8	334 - 336
2	2 0 589 517	6	33	255 - 308	- 9	1	5 247 278	12	5 1	376 393
2	2 6 382 - 346	6	4 2	584 622	2	1	8 159 114	-12	2 1	458 404
3	0 0 129 123	6	4 2	814 - 869	2	2	1 154 - 142	-12	8 4	120 150
2	0 6 107 - 68	2	4 8	229 - 222	- 2	5	4 991 004	11		225 - 216
2	1 2 1125 1171	2	2 1	130 - 157	_ 3	5	4 1172 1136	-13	÷ĭ	787 810
- 2	1 5 1144 1126	Å	2 7	346 - 380	- 3	3	0 146 136	13	1 3	369 372
- 1	1 5 309 - 280	š	6 6	950 -1047	á	ŝ	3 165 117	-13	1 4	432 - 401
- 1	1 8 487 - 468	ĕ	6 3	563 504	é	á.	2 283 - 267	13	1 6	267 207
- 5	1 8 225 - 202	6	66	634 669	- <u></u>	4	2 803 - 833	-13	17	536 - 602
- 5	2 1 1214 -1212	- Î	Ó Ż	1548 -1657	- 9	4	8 418 408	-13	22	323 266
5	2 4 83 - 75	7	0 4	1249 1289	9	5	4 592 602	13	2 5	406 - 418
3	2 7 346 377	- 7	0 8	775 834	9	6	3 132 201	13	3 1	237 - 228
• 3	3 0 1961 -2044	1	1 0	307 - 275	9	7	2 752 - 825	-12	2 2	527 559
2	3 3 724 - 650	- 7	1 1	182 - 158	× ×	×.	1 107 - 175	12	2 2	736 729
2	3 6 1011 965	4	1 2	574 → 540 309 ··· 366		2	2 612 670		: :	271 - 351
2	0 2 1042 -1071		1 2	108 252	-10	ň	1 528 525	-13	i õ	389 - 391
- 1	0 4 782 786	- 7	i ž	121 104	iŏ	ň	0 114 - 81	-13	4 î	135 - 100
- 1	0 8 411 384	ź	1 9	298 282	-10	1	1 302 - 272	13	4 3	555 591
4	0 10 284 - 301	Ĵ.	2 2	1311 -1376	10	1	3 748 - 739	-13	4 4.	257 251
4	1 0 423 - 383	7	28	666 709	-10	1	4 371 384	-13	62	315 311
•4	1 1 1732 1906	7	3 1	73 112	10	1	6 132 146	-13	6 5	380 419
4	1 3 1136 1133	- 1	3 2	347 342	-10	1	7 189 154	-14	0 2	736 - 665
- 4	1 4 854 - 815	1	2 2	12/ - 149	-10	2	2 163 133	-12	1 1	368 360
- 1	1 7 906 - 895		1 6	336 324	-10	ź	4 456 - 440	14	-i -i	272 - 317
- 1	1 9 402 - 382		1 6	263 - 201	-10	÷.	5 107 80	14	2 Ó	411 415
- 1	1 10 319 306	ż	55	230 253	10	3	7 626 - 657	-14	2 2	166 - 129
4	2 2 557 525	Ż	6 1	486 537	-10	- Ā	1 1066 -1159	-14	31	258 - 301
- 4	2 5 628 - 705	7	64	286 - 334	10	- 4	3 351 356	-14	37	178 241
- 4	2 8 178 - 124	7	6 7	196 - 196	-10	4	4 541 - 546	-14	5 2	755 - 683
- 4	3 1 1017 -1026	1	7 0	604 577	~10		7 746 702	-14	2 8	295 421
4	3 4 240 - 215	7	7 5	574 - 449	10	2	2 315 325	-14	2	456 - 420
- 1	5 7 294 258		0 4	177 117	10	3	3 247 - 204	-12	6 7	300 279
- 7	4 3 1160 1188	- 8	ŏā	75 100	11	6	2 914 - 911	15	ŏó	106 - 131
- 2	4 6 398 379	ă	i i	378 342	-11	ŏ	4 786 804	-15	1 2	279 299
- 1	4 9 480 - 485	ă	- i - i	197 173	11	1	1 272 - 294	~15	1 5	350 356
5	0 2 1347 -1488	8	1 7	207 - 170	11	1	4 242 - 245	-15	2 1	514 - 488
- 5	0 4 1108 1092	8	2 0	112 - 102	11	1	7 151 156	-15	2 4	366 - 307
5	0 8 634 596	- 8	2 2	722 676	- 11	2	0 113 120	-15	4 2	296 260
5	1 1 1205 1300	8	2 3	774 762	-!!	2	2 1086 -1021	-12	4 ?	404 - 425
2	1 7 705 - 674	- 8	5 2	174 176	-11	÷.	1 508 451	-12	2 1	381 - 350
2	2 0 780 730	_ 8	2 8	351 - 358		1	4 437 - 399	215	5 7	441 - 395
- 5	2 2 275 235	38	2 9	381 - 429	11	5	5 151 - 107	-15	1 2	333 365
- 5	2 5 549 - 496	- 8	3 1	1101 1042	-11	- 5	7 229 - 289	-16	3 2	143 164
5	2 6 526 - 507	8	3 2	432 434	11	á	1 537 - 549	-16	3 5	204 - 223
5	3 2 803 745	- 8	34	595 - 596	11	- 4	4 233 - 242	-16	4 1	229 - 214
5	3 5 706 760	8	3 5	414 353	11	4	7 324 331	-16	6 2	144 146
5	3 B 345 - 345	- B	3 7	580 - 599	11	5	0 336 322	-16	7 4	803 712
5	4 4 666 660	8	38	219 - 229	-11	ş	2 238 225	-17	21	252 274
2	2 2 250 - 558	8	4 1	119 - 837	-11	5	5 42/ 382	-17	2 2	293 268
	. 3.33							-10		240 - 204

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 Å 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) Å in calcium metaborate (Marezio, Plettinger & Zachariasen, 1963a); 1.389 (6) and 1.400 (6), 1.330 (6) Å in lithium metaborate (Zachariasen, 1964); and 1.371(7) and 1.386(7), 1.345(7) Å in monoclinic metaboric acid (Zachariasen, 1963). However, the distances found here do not show the extreme difference reported for the sodium analog, $Na_3B_3O_6$.

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 O(1) is bonded, is directed toward the nearest potassium atom. The long axis of the ellipsoid of the ring atom O(2) is nearly perpendicular to the ring.

Since the isostructural K₃B₃O₆ and Na₃B₃O₆ 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 B-O(1) and 0.92 for B-O(2). If we then attribute a strength of $\frac{1}{7}$ to each of the seven short $K \cdots O$ distances about each potassium atom, the sum of bond strengths is 1.81 about 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 $K \cdots O$ 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 $K \cdots O$ bond strengths to attain the ideal valence of 2 for every oxygen atom, we find bond strengths 0.18 for $K \cdots O(1)$ and 0.08 for $K \cdots O(2)$. This is in contradiction to the experimental result that the $K \cdots O(2)$ distance is the shorter.

Our results for $K_3B_3O_6$ agree better with the π -bond order curve (Coulson & Dingle, 1968) than do those for $Na_3B_3O_6$.

Table 3. Interatomic distances and angles in K₃B₃O₆

Standard deviations in the last digits are given in parentheses.

K-O(1)	2·849 (6) Å	O(2)-BO(2)	117·3 (8)°
K = O(1) (2×)	2.801 (2)	O(1) - B - O(2)	121.3 (4)
$K = O(1) (2 \times)$	2.835 (3)	B O(2)B	122.6 (8)
$K = O(2) (2 \times)$	2.775 (5)		
BO(1)	1.331 (10)		
$B - O(2) (2 \times)$	1.398 (5)		
$O(1) - O(2) (2 \times)$	2.381 (5)		
O(2) - O(2)	2.389 (9)		

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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	а	b*	с	σ
K	R_1	0·086 (8) Å	90°	46°	136°	3°
	R_2	0.123 (4)	0	90	90	
	R_3	0.134 (4)	90	44	46	
В	R_1	0.071 (40)	90	50	40	9
	R_2	0.129 (19)	0	90	90	
	R_3	0.144 (23)	90	40	130	
O(1)	R_1	0.092 (20)	90	53	37	6
	R_2	0.121 (12)	0	90	90	
	R_3	0.161 (13)	90	37	127	
O(2)	R_1	0.096 (15)	0	90	90	15
	R_2	0.107 (12)	90	7	97	
	R_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 $B_3O_6^{3-}$ 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 π -electron system. Pauling (1945) had originally suggested that the fourth orbital of boron was used in double bond formation here. The bond 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 B_2O_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 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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