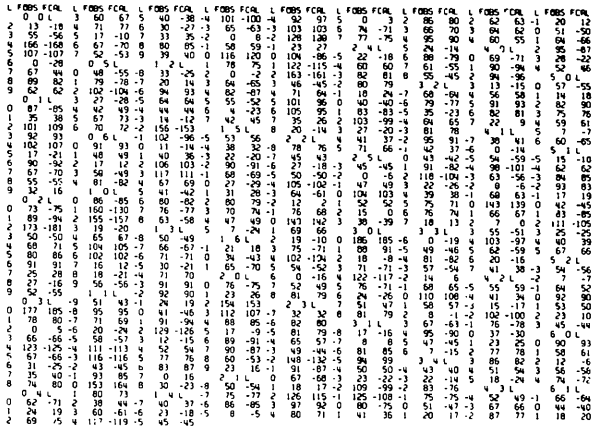
Table 2. *Interatomic distances for* $KNaThF_6$

| | | | |
|---|---|---|---|
| 3[Th–F(1)]* | 2·28 (2) Å | 3[K–F(1)] | 2·68 (2) Å |
| 3[Th–F(2)] | 2·40 (2) | 3[K–F(1)] | 2·79 (2) |
| 3[Th–F(2)] | 2·42 (2) | 3[K–F(2)] | 2·87 (2) |
| 3[Na–F(1)] | 2·26 (2) | 3[Na–F(2)] | 2·54 (2) |
| F(1)–F(2) | 2·72 (2) | 2[F(1)–F(1)] | 2·86 (3) |
| F(1)–F(2) | 2·84 (2) | F(1)–F(2) | 2·97 (2) |

* The coefficient in front of the bond denotes the number of equal bonds in the structure.

Table 3. *Observed and calculated factors for* $KNaThF_6$



Cromer & Waber (1965) and the values of $\Delta f' = -3{\cdot}95$ and $\Delta f'' = 10{\cdot}29$ electrons were used for the anomalous dispersion of Ag $K\alpha$ radiation by thorium (Cromer, 1965). The standard deviation of an observation of unit weight, $[\sum w(F_o - F_c)^2/(n_o - n_v)]^{1/2} = 1{\cdot}377$ where $n_o$ is the number of reflections and $n_v$ the number of parameters. The agreement index $R = \sum ||F_o^2| - |F_c^2|| / \sum |F_o^2|$ is 0·095 for 365 independent reflections.

The refined parameters are listed in Table 1, the interatomic distances in Table 2 and the structure factor data in Table 3. Fig. 1 is a stereoscopic pair of drawings showing one asymmetrical unit of $KNaThF_6$, and Fig. 2 shows a complete unit cell. The Na polyhedron is an irregular octahedron which appears to be squashed along one of the triad axes. The Th and K polyhedra are the trigonal prisms with pyramids on each prism face typical of 9 coordination.

The Th and K polyhedra alternate with one another along the *c* axis and share the bases of the trigonal prisms. The K polyhedra share edges with K and Th polyhedra in adjacent columns within the unit cell. The Na octahedra tie the unit cells together perpendicular to the *c* axis by sharing edges with the Th and K polyhedra.

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## The crystal structure of *p*-sulfobenzenediazonium inner salt.

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The crystal structure of *p*-sulfobenzenediazonium inner salt, $C_6H_4N_2O_3S$, has been determined. Observed unit-cell parameters are $a = 8{\cdot}10$ (1), $b = 9{\cdot}94$ (1), $c = 9{\cdot}46$ (1) Å and $\beta = 97{\cdot}4$ (2)°. The space group is $P2_1/n$. Three-dimensional visual data were collected with Cu $K\alpha$ radiation. The trial structure was obtained by Patterson methods and refined to a final $R$ of 13%.

The crystal structure of *p*-sulfobenzenediazonium inner salt, $^{\ominus}O_3S$–$C_6H_4$–$N_2^{\oplus}$, has been determined. Needle-like crystals of the compound about 0·2 to 0·3 mm in diameter and suitable for X-ray analysis were grown from an aqueous solution and mounted on a glass fibre. Weissenberg photographs (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å) indicated the space group to be $P2_1/n$–$C_{2h}^5$ ($h0l$ absent when $h+l = 2n+1$; $0k0$ absent when $k = 2n+1$). Unit-cell dimensions are $a = 8{\cdot}10$ (1), $b = 9{\cdot}94$ (1), $c = 9{\cdot}46$ (1) Å and $\beta = 97{\cdot}4$ (2)°. The observed density, measured by flotation, is 1·69 g.cm$^{-3}$; the density calculated from the X-ray data is 1·63 g.cm$^{-3}$ assuming four molecules per unit cell. Multiple-film equi-inclination Weissenberg photographs were taken about the *a* axis ($h = 0$–6). Intensities were measured visually. The Lorentz–polarization factor was applied and the data were correlated by using a series of oscillation photographs in the usual way. No corrections were made for extinction or absorption. A total of 521 reflections in the region of reciprocal space explored had detectable intensities.

Patterson projections and the sharpened Patterson–Harker section $P(u\frac{1}{2}w)$ were synthesized and served to establish trial positional parameters for the sulfur atom. A fourfold sharpened superposition function based on the sulfur atom trial parameters was constructed. Although ra-

ther poorly resolved, this function yielded a discernible image of the molecule from which positional parameters for the remaining atoms could be assigned. A three-dimensional electron density map phased on these parameters clearly defined the atomic locations and yielded a trial structure essentially the same as that obtained from the superposition function. At this point a set of scaled structure factors was calculated for all 521 reflections. The reliability index was 0·44.

Refinement was carried out using the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The quantity minimized was $\sum w\left(F_o-\frac{1}{k}F_c\right)^2$. The $R$ index was lowered to a final value of 0·13 using individual isotropic temperature factors. The weighting scheme used was

$$\sqrt{w}=1|F| \text{ for } |F|>4|F|_{\min},$$

$$\sqrt{w}=\frac{1}{4|F|_{\min}} \text{ for } |F|\leq 4|F|_{\min}.$$

All unobserved reflections were assigned zero weight. Hydrogen atom parameters were not included in the refinement. Final atomic parameters and estimated standard deviations are listed in Table 1. A list of observed and calculated structure factors is available from the authors on request. The rather large thermal parameters are probably a reflection of the fact that this compound is highly sensitive to X-radiation. During data collection several crystals had to be employed and all were observed to rapidly discolor in the X-ray beam. Because of these experimental difficulties, further refinement of the data, including anisotropic ther-

Table 1. *Final atomic parameters*

E.s.d.'s are given in parentheses.

| | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| S | 0·7664 (10) | 0·7850 (6) | 0·0496 (6) | 5·63 (11) |
| O(1) | 0·8264 (30) | 0·6978 (17) | −0·0586 (20) | 9·35 (45) |
| O(2) | 0·7278 (27) | 0·9223 (17) | −0·0073 (17) | 8·28 (41) |
| O(3) | 0·8742 (27) | 0·7818 (16) | 0·1827 (18) | 8·08 (38) |
| C(1) | 0·5776 (35) | 0·7163 (21) | 0·0856 (22) | 5·68 (46) |
| C(2) | 0·4235 (35) | 0·7745 (21) | 0·0300 (22) | 5·37 (44) |
| C(3) | 0·2706 (37) | 0·7290 (21) | 0·0576 (24) | 5·90 (46) |
| C(4) | 0·2787 (39) | 0·6096 (23) | 0·1467 (24) | 6·29 (50) |
| C(5) | 0·4332 (36) | 0·5445 (20) | 0·2074 (23) | 5·66 (48) |
| C(6) | 0·5788 (38) | 0·5993 (22) | 0·1767 (24) | 6·00 (48) |
| N(1) | 0·1321 (34) | 0·5537 (19) | 0·1810 (21) | 6·97 (45) |
| N(2) | 0·0122 (36) | 0·5099 (22) | 0·2119 (23) | 8·68 (54) |

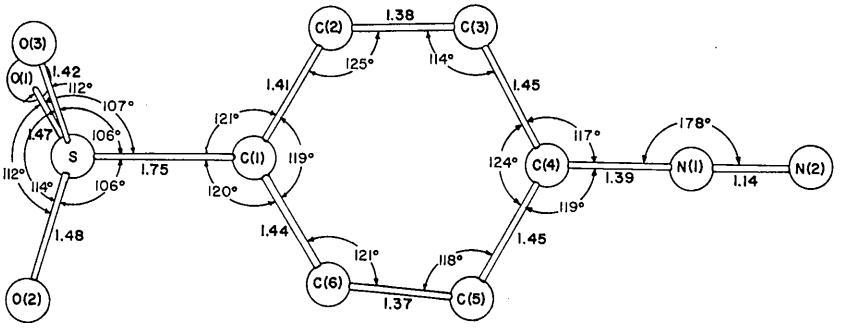


Fig. 1. Bond lengths and angles in the molecule.

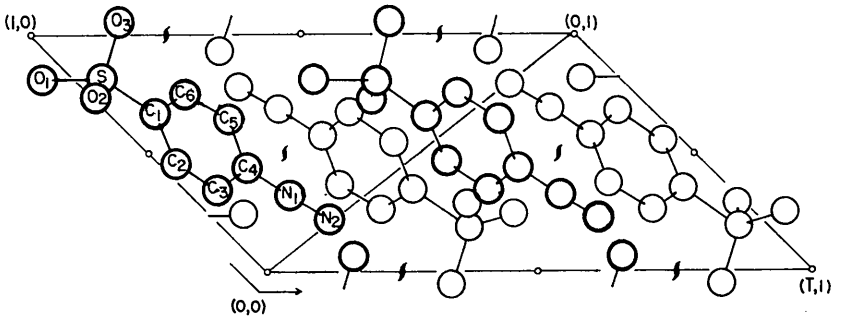


Fig. 2. Projection of the structure down the *b* axis.

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 $-0{\cdot}4583x+5{\cdot}2702y+7{\cdot}3449z=4{\cdot}1023$. 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 $(ArN_2)^+(X)^-$. 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 reported 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, $K_3B_3O_6$.

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The results of a refinement of the structure of $K_3B_3O_6$ are described. The space group is $R\bar{3}c$ and the hexagonal axes are $a=12{\cdot}76$ and $c=7{\cdot}34$ 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 $Na_3B_3O_6$ 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. 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*kl* data.

Subsequently Marezio, Plettinger & Zachariasen (1963*b*) 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.

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Table 1. *Parameters for* $K_3B_3O_6$

Standard deviations in the last digit are given in parentheses.

| | $x$ | $\beta_{11}$ | $\beta_{22}=\beta_{12}$ | $\beta_{33}$ | $\beta_{13}=\beta_{23}$ |
|---|---|---|---|---|---|
| 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) |