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The Crystal Structure of Benzaldehyde-Potassium Bisulfite Addition Product (Potassium α-Hydroxybenzylsulfonate)

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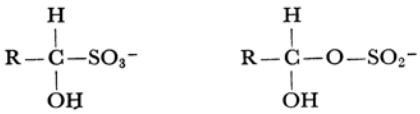
The addition compound of benzaldehyde and potassium bisulfite crystallizes in the monoclinic space group $P2_1/c$, with four formula units per unit cell with the dimensions: $a=16.37$, $b=6.07$, $c=9.12$ Å and $\beta=103.4°$. The structure was determined by the heavy atom method, and the structural parameters were refined by least-squares method with a block-diagonal approximation. The analysis showed that the addition product is potassium α-hydroxybenzylsulfonate, $C_6H_5CH(OH)SO_3^-\cdot K^+$. Three S-O bond distances range from 1.43 to 1.46 Å; the average of three O–S–O bond angle is 112.1°, while that of three O–S–C_α's is 106.7°. The bond distance of S–C_α, 1.831 Å, is significantly longer than those in other sulfonates so far reported. The potassium ion is surrounded by nine oxygen atoms; the K–O distances being from 2.73 to 3.27 Å.

The Strecker synthesis is one of the most important methods for the preparation of the α-amino acids. In one of its variations, the bisulfite addition product of an aldehyde plays an important role as an intermediate to an α-amino acid.[1] The addition product is generally more reactive than most of sulfonates commonly found. Although the structure (I) has been favored from chemical studies, no definite conclusion has yet been given which one of the presumed structures (I and II) is correct. If I is the case, the C–S bond seems to be too labile in comparison with other sulfonates.



(I) (II)

The determination of its structure, therefore, will be of importance from the organochemical viewpoints.

The present paper deals with the determination of the crystal structure of benzaldehyde-potassium bisulfite addition product, which was supplied by Professor Yoshiharu Izumi of this Institute.

Experimental

The crystal of benzaldehyde-potassium bisulfite addition product, $C_7H_7O_4SK$, was obtained by the recrystallization from a methanol-water solution. The unit cell dimensions were determined from the oscillation and the Weissenberg photographs around the principal axes. The density of the crystal was measured by the flotation method with a methylene iodide-carbon tetrachloride mixture.

A set of the three-dimensional intensity data was collected on the equi-inclination Weissenberg photographs, using the multiple-film technique with Ni-filtered Cu$K\alpha$ radiation. The crystals were rotated around the b axis ($k=0$ to 5) and the c axis ($l=0$ to 3). The intensities were estimated visually by comparison with a standard scale. They were corrected for Lorentz and polarization factors, and the spot-shape effects were also taken into account. The corrections for absorption and extinction were omitted.

Crystal Data

The crystal is a hygroscopic colorless lath elongated along the monoclinic unique axis. The cleavage parallel to the bc plane was found. The unit cell dimensions are:

$a=16.37\pm0.02$, $b=6.07\pm0.02$,
$c=9.12\pm0.02$ Å, $\beta=103.4\pm0.1°$.

The absent spectra were $0k0$ for k odd and $h0l$ for l odd, the space group being $P2_1/c$. The observed density, 1.697 g·cm^{-3}, suggested four formula units in a unit cell, the calculated density being 1.699 g·cm^{-3}.

Structure Determination

The crystal structure was solved by the heavy-atom method. The coordinates of the two heavier atoms, K and S, were deduced from the three-dimensional Patterson function. The electron density map based on these two atoms gave the

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1) For example, *Org. Syn.*, **27**, 20 (1947).

TABLE 1. THE FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS (Å)

Atom	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$
K	0.0609	0.002	0.2105	0.002	0.1143	0.002
S	0.1249	0.002	0.7064	0.002	0.2804	0.002
O(1)	0.0579	0.005	0.7076	0.007	0.1432	0.006
O(2)	0.1113	0.006	0.5371	0.006	0.3810	0.006
O(3)	0.1372	0.006	0.9228	0.006	0.3470	0.006
O(4)	0.2080	0.006	0.4542	0.006	0.1330	0.006
C(1)	0.2218	0.007	0.6440	0.008	0.2214	0.008
C(2)	0.2929	0.008	0.6107	0.009	0.3586	0.008
C(3)	0.3033	0.010	0.4101	0.012	0.4296	0.010
C(4)	0.3696	0.012	0.3789	0.012	0.5564	0.011
C(5)	0.4252	0.010	0.5489	0.014	0.6047	0.010
C(6)	0.4145	0.010	0.7491	0.013	0.5353	0.011
C(7)	0.3471	0.009	0.7840	0.011	0.4079	0.009

TABLE 2. THE ANISOTROPIC TEMPERATURE FACTORS

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0.00220	0.01421	0.00822	−0.00048	−0.00089	−0.00161
S	0.00164	0.01393	0.00584	0.00089	0.00092	0.00103
O(1)	0.00191	0.02750	0.00863	0.00240	−0.00044	−0.00198
O(2)	0.00275	0.01690	0.01233	0.00173	0.00484	0.00860
O(3)	0.00393	0.01966	0.00741	0.00330	0.00171	−0.00243
O(4)	0.00342	0.02125	0.00765	0.00076	0.00324	−0.00313
C(1)	0.00182	0.01596	0.00703	−0.00054	0.00190	0.00012
C(2)	0.00231	0.02078	0.00672	0.00261	0.00279	0.00176
C(3)	0.00338	0.02874	0.01148	0.00410	0.00082	0.00763
C(4)	0.00494	0.03228	0.01405	0.00964	−0.00086	0.01123
C(5)	0.00319	0.05024	0.01149	0.00768	−0.00063	0.00219
C(6)	0.00314	0.04144	0.01483	−0.00441	−0.00005	−0.00743
C(7)	0.00294	0.02537	0.01160	−0.00118	0.00147	−0.00671

coordinates of all the non-hydrogen atoms. The structure factors calculated at this stage showed the discrepancy factor, R, of 0.36.

The coordinates and the temperature factors (anisotropic for K and S, and isotropic for C and O) of the atoms were subjected to the least-squares refinement with a block-diagonal approximation. After three cycles of refinement, the R factor decreased to 0.12. Then the carbon and the oxygen atoms were also assigned anisotropic temperature factors; after four cycles of refinement, the R decreased to 0.086; it was 0.12, if the non-observed reflections which were not used in the refinement were included. The three-dimensional (F_o-F_c) synthesis was made at this stage, but some of the hydrogen atoms could not be located; hence no hydrogen atoms were included in the refinement.

The final atomic coordinates and their estimated standard deviations are listed in Table 1. The anisotropic temperature factors in the form of

$$\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$$

are listed in Table 2. The observed and the calculated structure factors are shown in Table 3. The final three-dimensional electron-density distribution is shown in Fig. 1.

The atomic scattering factors used in the computations were taken from the International Tables for X-Ray Crystallography.[2] All the numerical computations were done on the IBM 7040 at the Teijin Co. Ltd., with the programs written by one of the present authors (T. A.).

Discussion

The analysis showed that the addition product is potassium α-hydroxybenzylsulfonate, $C_6H_5CH(OH)SO_3^-\cdot K^+$, which is shown by the formula I. The formula can explain some of the chemical properties.

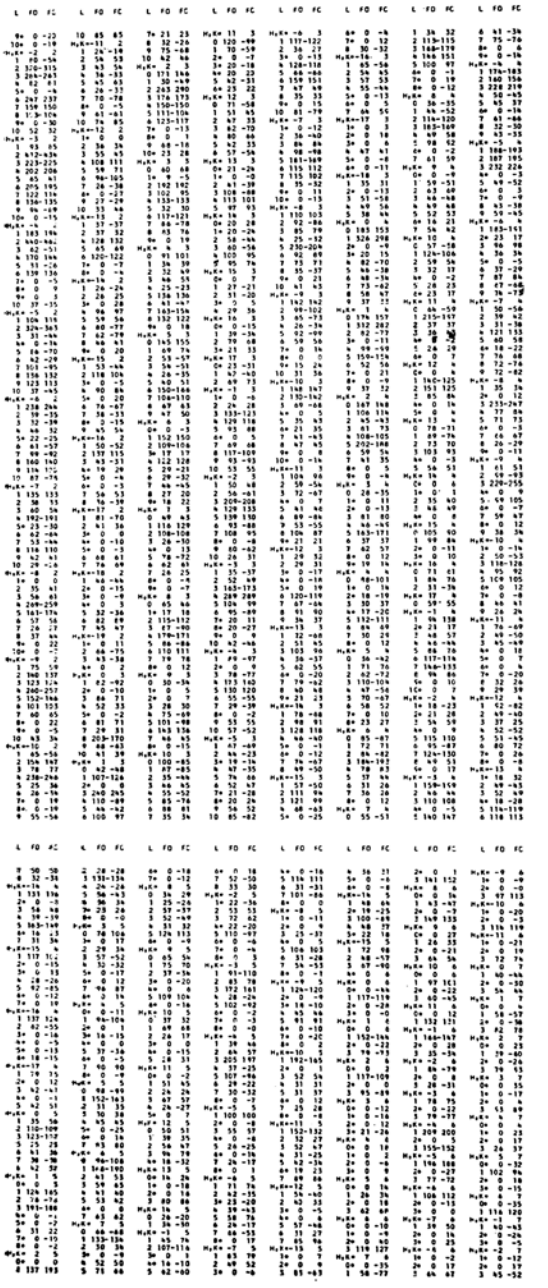
All the bond distances and angles shown in Fig. 2 are evaluated from the coordinates listed in Table 1. The estimated standard deviations of the bond distances and angles are: 0.007 Å for

2) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962).

S–O and S–C, 0.015 Å for C–C and C–O, 0.4° for the angles of O–S–O and O–S–C, 0.6° for S–C–C and S–C–O, and 1.0° for C–C–C and C–C–O.

The S–O bond lengths in the sulfonate group range from 1.429 to 1.460 Å, the average length being 1.446 Å. The bond angles of O–S–O are significantly larger than the regular tetrahedral angle, their average being 112.1°. The three

TABLE III. THE OBSERVED AND THE CALCULATED STRUCTURE FACTORS (×5)



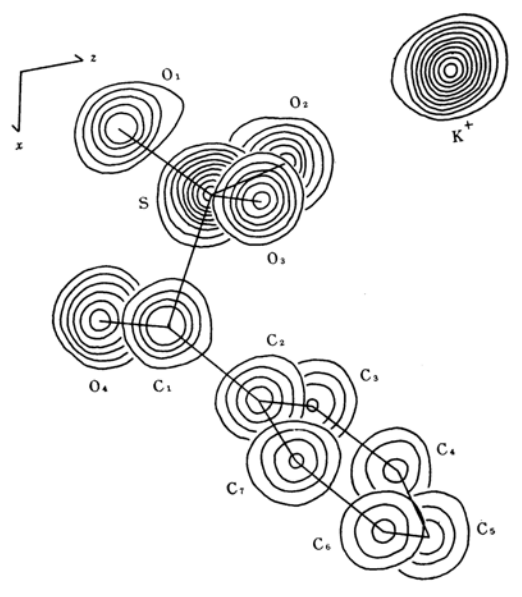


Fig. 1. A composite drawing of the final electron-density distribution viewed along the *b* axis. Contours are at intervals of 2 e.Å^{-3} beginning at the 2 e.Å^{-3} contour. For K and S, they are from the 2 e.Å^{-3} contour by intervals of 4 e.Å^{-3}.

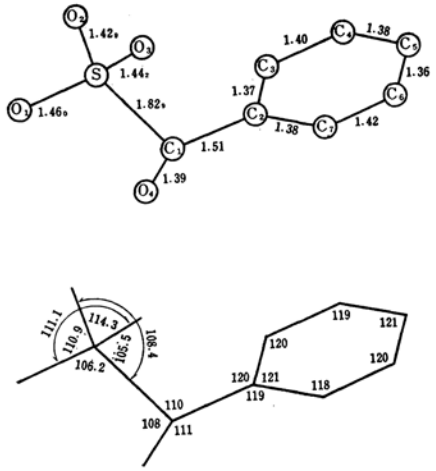


Fig. 2. Bond distances (Å) and angles (degrees).

bond angles of O–S–C(1) are significantly smaller than the tetrahedral angle; they are 106.7±1.4°. The configuration of this sulfonate group is similar to those reported so far. The S–C(1) bond distance of 1.829 Å is close to the sum (1.81 Å) of the single bond radii of S and C, but it is significantly longer than those found in other sulfonates, for example 1.780 Å in taurine[3] and 1.77 Å in a plant sulfolipid.[4] This fact seems to indicate that the bond nature of S–C in the present molecule differs from those in many sulfonates.

The phenyl group is planar, and C(1) is roughly on the plane. The four atoms O(1), S, C(1) and C(2) make an extended zigzag form, and the plane of which is roughly perpendicular to the phenyl group (dihedral angle 82°). Thus the bond S–C(1) has a staggered form, and O(4) of the hydroxyl group is in trans to O(3) with respect to the S–C(1) bond.

All the intermolecular distances less than 4.0 Å are evaluated, and some of them are shown in Figs. 3 and 4. A potassium ion is coordinated by nine oxygen atoms, all but one of which are those of the sulfonate groups. The nine K–O distances range from 2.73 to 3.27 Å, their average being 2.965 Å. There are no other contacts shorter than 3.58 Å. The average distance, 2.965 Å, is consistent with 2.96 Å listed in the International Tables for X-Ray Crystallography[1] as the average of the K–O distances in the case of 9-fold coordination. The closest contact between the potassium ions is 3.60 Å, and that between the potassium ion and the sulfur atom is 3.40 Å.

There is one hydrogen bond which connects the hydroxyl group and the O(3) atom of the sulfonate group, their length being 2.70 Å and the angle C(1)–O(4)···O(3) being 107.6°. The hydrogen bond links the organic ions together, forming a chain parallel to the *c* axis. Thus the molecular contacts around $x=0$ are due to the hydrogen bond and the electrostatic (ionic) forces, while the molecular contacts *via* the phenyl groups

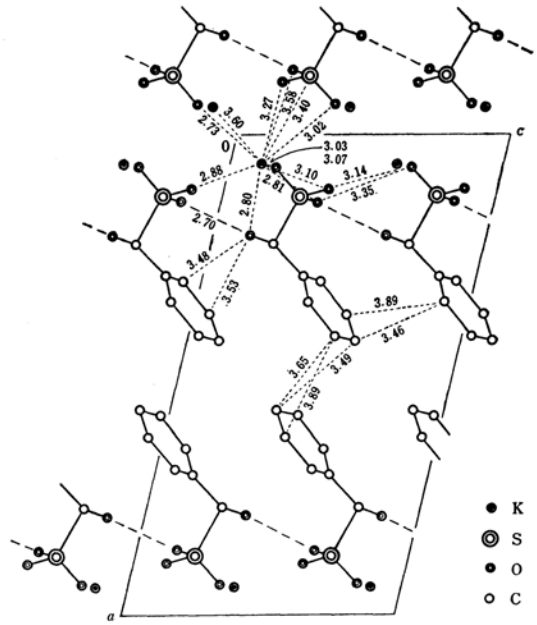


Fig. 3. The crystal structure viewed along the *b* axis. Broken lines show the hydrogen bonds. Some of the intermolecular approaches are shown by dotted lines.

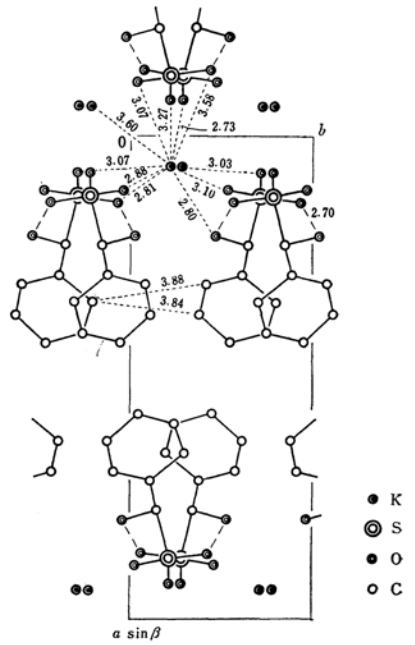


Fig. 4. The crystal structure viewed along the *c* axis.

3) Y. Okaya, *Acta Cryst.*, **21**, 726 (1966).
4) Y. Okaya, *ibid.*, **17**, 1276 (1964).

around $x=1/2$ are due mainly to the van der Waals forces. Such molecular packing can readily explain the existence of the cleavage parallel to the *bc* plane.

We wish to express our deep thanks to Professor Yoshiharu Izumi of this Institute for supplying the material and for his invaluable discussions. Thanks are also due to the staff of the computing center of the Teijin Co., Ltd., for the numerical computations on the IBM 7040.