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The Structure of 5-Methyl-3-sulphosalicylic Acid Dihydrate

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Abstract. $C_8H_8O_6S.2H_2O$, monoclinic, $P2_1/c$, a = 12·47 (2), b = 6·91 (1), c = 19·62 (2) Å, β = 134·5 (2)°, D_m = 1·48, D_x = 1·47 g cm^{-3}, Z = 4. The three-dimensional X-ray diffraction structure analysis revealed that the compound exists in an ionic state as $H_5O_2^+.SO_3^-CH_3.C_6H_2(COOH)OH$, aquaoxonium 5-methyl-3-sulphosalicylic acid. The pairs of molecules are linked together to form dimers by O—H···O hydrogen bonds. The structure is stabilized by the network of hydrogen bonds and weak van der Waals contacts.

Introduction. The three-dimensional X-ray diffraction data were collected by an equi-inclination Weissenberg photographic technique, using Cu $K\alpha$ radiation. Intensities of 951 non-zero independent reflections were estimated visually and the necessary corrections were applied; absorption correction was neglected (μ = 17·2 cm^{-1}; cross-section of the crystal = 0·3 × 0·2 mm). The structure was solved by the usual heavy-atom method and refined isotropically to an R value of 0·149, using the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). Scale and anisotropic temperature factors were then refined in alternate cycles along with the positional parameters of the non-hydrogen atoms (Lingafelter & Donohue, 1966). Four cycles of anisotropic refinement gave a final R value of 0·114 when the shifts in parameters were less than a tenth of their estimated standard deviations (e.s.d.'s). A difference Fourier map calculated at the end of the least-squares refinement did not suggest any definite positions of the hydrogen atoms. The final positional parameters are listed in Table 1.[*] The bond lengths (with e.s.d.'s) and angles are shown in Fig. 1. The average e.s.d. of the bond angles is of the order of 1·5°.

Table 1. *Atomic parameters* (×10^4) *of non-hydrogen atoms with their e.s.d.'s in parentheses*

	x	y	z
S	2083 (4)	2832 (6)	1799 (3)
C(1)	3098 (16)	−679 (22)	3862 (10)
C(2)	2950 (16)	−14 (22)	3141 (11)
C(3)	2242 (15)	20 (20)	2697 (10)
C(4)	1656 (15)	2911 (21)	3005 (10)
C(5)	1716 (17)	2172 (24)	3698 (12)
C(6)	2472 (15)	403 (24)	4154 (10)
C(7)	3899 (16)	−2611 (23)	4356 (10)
C(8)	1077 (18)	3332 (23)	4024 (13)
O(1)	3089 (13)	−3115 (15)	5047 (8)
O(2)	4404 (13)	−3551 (16)	4110 (8)
O(3)	3520 (13)	−956 (15)	2827 (8)
O(4)	1628 (14)	4920 (16)	1671 (8)
O(5)	3608 (10)	2695 (15)	2151 (7)
O(6)	991 (11)	1573 (16)	938 (8)
O(W1)	1769 (11)	7146 (16)	575 (8)
O(W2)	3638 (12)	−446 (16)	1432 (7)

Discussion. The structure analysis of 5-methyl-3-sulphosalicylic acid dihydrate (hereafter 5,3-MSSA) was undertaken as part of our programme to study the effect of substituted groups on the geometry and biological activity of the salicylic acid moiety. Structural data would also provide an explanation for the

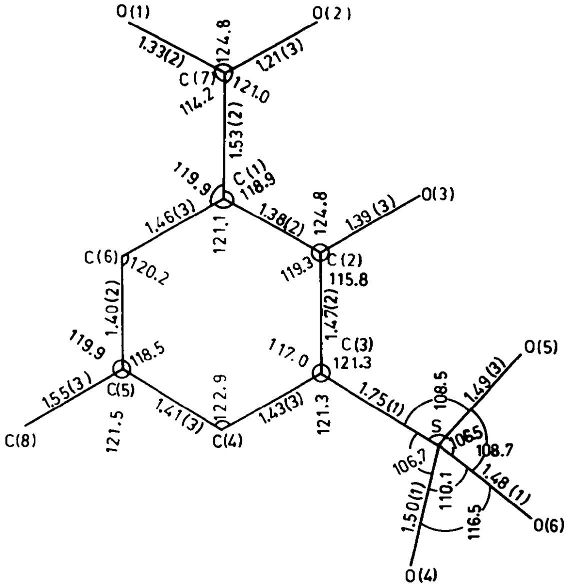

Fig. 1. Intramolecular bond lengths (Å) and angles (°).

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33583 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

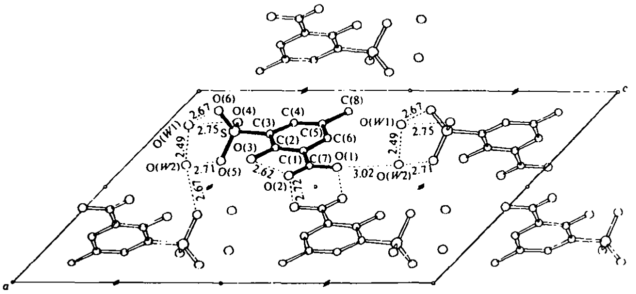

Fig. 2. Molecular packing viewed along *b*. The molecule corresponding to the coordinates in Table 1 is shown by solid lines, and important hydrogen bonds are shown by broken lines.

differences in chemical and physical properties of such compounds.

The average deviation (±0·02 Å) of atoms from the least-squares plane of the benzenoid ring suggests that the ring is planar. In the carboxylic acid group the difference in C—O lengths (Δr = 0·12 Å) and in C—C—O angles ($\Delta\theta$ = 6·8°) shows that there is no orientational disorder, in accordance with the study of carboxylic acids by Leiserowitz (1976). A linear correlation exists between the Δr and $\Delta\theta$ values of carboxylic acids. Dieterich, Paul & Curtin (1974) showed that there is a continuum of these values (Δr, $\Delta\theta$) from ordered (with large values of Δr, $\Delta\theta$) to disordered structures. Currie, Speakman & Curry (1967) reported that Δr ranges widely from 0·04 to 0·12 Å. The atom O(3) of the phenolic group is hydrogen bonded (2·62 Å) with O(2). This type of intramolecular hydrogen bonding is common in salicylic acid as well as in substituted salicylic acids (Sundaralingam & Jensen, 1965; Mootz & Fayos, 1970; Vyas, Sakore & Biswas, 1978). The intramolecular hydrogen bond (2·89 Å) between O(3) and O(5) of the phenolic and sulphonate groups, respectively, may be responsible for the higher value of the phenolic dissociation constant (p*K* = 13·98; Chattopadhya & Singh, 1972).

The similarity of the three S—O bond lengths [1·50 (1), 1·49 (3) and 1·48 (1) Å] suggests that there is no hydrogen atom attached to any of the oxygen atoms (Taesler & Olovsson, 1968). Further, the difference of 4·7° between C—S—O (average 107·1) and O—S—O (average 111·8°) angles is comparable with similar structures containing a sulphonate group (Greenberg & Okaya, 1969). The short contact (2·49 Å) between O(*W*1) and O(*W*2) suggests that the acid proton is attached to the two water molecules, yielding an aquaoxonium ion ($H_5O_2^+$). Most sulphonic acids are found to exist in the ionic state in crystal structures and yield different protonated water species (Arora & Sundaralingam, 1971; Mootz & Fayos, 1970; Lundgren & Lundin, 1972; Lundgren, 1972; Attig & Mootz, 1976). In the crystal structure of 4-methyl-5-sulphosalicylic acid tetrahydrate, the carboxyl group is also ionized along with the sulpho group, yielding two protonated water species: H_3O^+, oxonium, and $H_7O_3^+$, diaquaoxonium (Vyas, Sakore & Biswas, 1978).

A projection of the 5,3-MSSA structure as viewed along the *b* axis is shown in Fig. 2, in which hydrogen bonds are shown by broken lines. All oxygen atoms of the sulphonate group take part in intermolecular hydrogen bonding. The anionic molecules of 5,3-MSSA are interlinked by two hydrogen bonds (O—H···O, 2·72 Å) forming dimers through the carboxylic acid groups. This type of dimerization, although observed in several similar structures, is absent in 4-methyl-5-sulphosalicylic acid tetrahydrate (Vyas, Sakore & Biswas, 1978).

The anionic dimers are further linked through a network of hydrogen bonds involving the cationic water species which play an important role in stabilizing the structure of 5,3-MSSA.

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