

Crystal Structure of (Z)-3,4-Methylenedioxybenzaldehyde Oximum 4-Toluenesulfonate at 110 K

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(Z)-3,4-Methylenedioxybenzaldehyde oximum 4-toluenesulfonate, $C_{15}H_{15}NSO_6$, $M_r = 337.35$, monoclinic, $P2_1/n$, $a = 9.423(10)$, $b = 5.571(15)$, $c = 28.248(17)$ Å, $\beta = 90.96(7)^\circ$, $V = 1483$ Å³, $Z = 4$, $D_x(110\text{ K}) = 1.51\text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 1.39\text{ cm}^{-1}$, $F(000) = 704$.

The oximum ion. The benzene ring is nearly planar, the mean and maximum distances of the carbon atoms from a calculated best plane are 1.1 σ and 2.4 σ , respectively. The other non-hydrogen atoms of the oximum ion are distributed on the same side of the calculated ring plane with the exception of the methylene carbon atom C(8). Distances from the plane are C(7) $\pm 0.035(6)$, N(9) $\pm 0.107(5)$, O(10) $\pm 0.125(4)$, O(11) $\pm 0.094(4)$, O(12) $\pm 0.053(4)$ and C(8) $\mp 0.221(6)$ Å. The benzene ring and the attached oximum side chain are approximately coplanar, the dihedral angle being $2(4)^\circ$. Chelate formation, C(2)–H \cdots O(10) is observed as in all other aromatic Z-oximes and their derivatives,¹ the distance C(2) \cdots O(10) being $2.858(6)$ Å. The dimensions of the oximum moiety are within the accuracy of the structure determination identical with those found for (Z)-4-methoxybenzaldehyde hydrochloride.¹ The cations and anions form chains in the *b*-direction via hydrogen bonds, N(9)_{*x,y,z*} \cdots O(21)_{*x-1,y,z*} = $2.636(6)$ and O(10)_{*x,y,z*} \cdots O(20)_{*x-1,y+1,z*} = $2.536(5)$ Å.

The 4-toluenesulfonate ion. The benzene carbon atoms [C(11)–C(16)] are nearly coplanar, the mean and maximum deviations from planarity are 1.55 and 3.0 σ . The attached atoms deviate significantly from the plane, C(17) $\pm 0.074(7)$ and S(1) $\pm 0.079(2)$ Å, and the sulfonate oxygen atoms O(20) $\pm 0.889(4)$, O(21) $\pm 0.745(4)$, O(22) $\mp 1.251(4)$ Å. Excepting the CSO₃ moiety, the bond lengths and bond angles agree with the corresponding values found in a room-temperature structure determination of the monohydrate of 4-toluenesulfonic acid, C₇H₈SO₃ \cdot H₂O⁺. In that structure² the CSO₃ tetrahedron has nearly perfect C_{3v} symmetry, CSO-angles are $106.7 \pm 0.5^\circ$, and S–O distances 1.454 ± 0.004 Å; each of the three oxygen atoms accepts one hydrogen bond from the protonated water molecules. In the present structure, the CSO₃ tetrahedron is significantly distorted owing to only two of the oxygen atoms being hydrogen bonded; the bond S(1)–O(22) is ca. 0.030 Å shorter and the angle C(11)–S(1)–O(22) is ca. 4.4° larger than the corresponding dimensions involving the hydrogen-bonded atoms O(20) and O(21). Similar distortions, though less pronounced, of sulfonium tetrahedra are observed in several crystal structures of hydrated trifluoromethanesulfonates³ in which the oxygen atoms of an SO₃ moiety form a different number of hydrogen bonds with water.

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Table 1. Atomic coordinates and isotropic displacement parameters (\AA^2) with e.s.d.'s in parentheses.

Atom	x	y	z	$B_{\text{eq/iso}}$
C(1)	-0.0442(6)	0.447(1)	0.4257(2)	1.5(1) ^a
C(2)	0.0367(6)	0.650(1)	0.4141(2)	1.7(1) ^a
C(3)	0.1729(6)	0.681(1)	0.4327(2)	1.6(1) ^a
C(4)	0.2241(6)	0.502(1)	0.4620(2)	1.6(1) ^a
C(5)	0.1468(6)	0.301(1)	0.4730(2)	1.7(1) ^a
C(6)	0.0124(6)	0.262(1)	0.4553(2)	1.8(1) ^a
C(7)	-0.1873(6)	0.404(1)	0.4087(2)	2.0(1) ^a
C(8)	0.3653(6)	0.257(1)	0.5032(2)	2.4(1) ^a
N(9)	-0.2703(5)	0.5388(9)	0.3828(2)	2.3(1)
O(10)	-0.2250(4)	0.7543(8)	0.3658(2)	2.8(1)
O(11)	0.3509(4)	0.5019(7)	0.4864(1)	2.20(9)
O(12)	0.2233(4)	0.1578(7)	0.5042(1)	2.06(9)
S(1)	0.4632(2)	0.0892(3)	0.35999(6)	2.11(3)
O(20)	0.5675(4)	-0.0207(8)	0.3286(1)	2.56(9)
O(21)	0.4795(4)	0.3503(8)	0.3623(2)	3.3(1)
O(22)	0.4659(4)	-0.0221(8)	0.4059(1)	2.8(1)
C(11)	0.2964(6)	0.041(1)	0.3322(2)	1.9(1) ^a
C(12)	0.2708(6)	-0.167(1)	0.3065(2)	2.1(1) ^a
C(13)	0.1410(6)	-0.197(1)	0.2837(2)	2.3(1) ^a
C(14)	0.0351(6)	-0.023(1)	0.2860(2)	1.9(1) ^a
C(15)	0.0626(6)	0.181(1)	0.3129(2)	2.5(1) ^a
C(16)	0.1907(6)	0.213(1)	0.3365(2)	2.0(1) ^a
C(17)	-0.1028(7)	-0.052(1)	0.2593(2)	2.8(1) ^a

^aAtoms are refined isotropically. $B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j$.

Experimental

The compound, prepared in diethyl ether from (*E*)-3,4-Methylenedioxybenzaldehyde oxime and 4-toluenesulfonic acid as described by Jerslev⁴ formed clusters of small needle-shaped crystals

which tended to split into fine threadlike crystals along the needle axis. Parallel extinction was observed. A crystal fragment ($0.025 \times 0.10 \times 0.75 \text{ mm}^3$) was used for the structure determination, performed with an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Mo

Table 2. Bond distances (\AA) with e.s.d.'s in parentheses.

Atoms	Bond	Atoms	Bond
C(1) C(2)	1.406(8)	N(9) O(10)	1.364(6)
C(1) C(6)	1.424(8)	S(1) O(20)	1.469(4)
C(1) C(7)	1.444(8)	S(1) O(21)	1.464(4)
C(2) C(3)	1.389(7)	S(1) O(22)	1.437(4)
C(3) C(4)	1.374(8)	S(1) C(11)	1.765(5)
C(4) C(5)	1.379(8)	C(11) C(12)	1.388(8)
C(4) O(11)	1.369(6)	C(11) C(16)	1.389(8)
C(5) C(6)	1.370(7)	C(12) C(13)	1.384(8)
C(5) O(12)	1.381(7)	C(13) C(14)	1.394(8)
C(7) N(9)	1.301(7)	C(14) C(15)	1.387(8)
C(8) O(11)	1.449(7)	C(14) C(17)	1.500(8)
C(8) O(12)	1.449(7)	C(15) C(16)	1.381(8)

Table 3. Bond angles ($^{\circ}$) with e.s.d's in parentheses.

Atoms			Angle	Atoms			Angle
C(2)	C(1)	C(6)	121.3(5)	O(20)	S(1)	O(21)	111.7(3)
C(2)	C(1)	C(7)	124.3(5)	O(20)	S(1)	O(22)	111.2(2)
C(6)	C(1)	C(7)	114.4(5)	O(20)	S(1)	C(11)	105.6(3)
C(1)	C(2)	C(3)	120.8(5)	O(21)	S(1)	O(22)	112.9(3)
C(2)	C(3)	C(4)	116.9(5)	O(21)	S(1)	C(11)	105.2(3)
C(3)	C(4)	C(5)	122.9(5)	O(22)	S(1)	C(11)	109.8(3)
C(3)	C(4)	O(11)	126.8(5)	S(1)	C(11)	C(12)	120.3(4)
C(5)	C(4)	O(11)	110.2(5)	S(1)	C(11)	C(16)	119.4(5)
C(4)	C(5)	C(6)	122.3(5)	C(12)	C(11)	C(16)	120.3(5)
C(4)	C(5)	O(12)	109.9(5)	C(11)	C(12)	C(13)	119.3(5)
C(6)	C(5)	O(12)	127.8(5)	C(12)	C(13)	C(14)	121.5(6)
C(1)	C(6)	C(5)	115.8(5)	C(13)	C(14)	C(15)	117.9(5)
C(1)	C(7)	N(9)	129.9(6)	C(13)	C(14)	C(17)	121.1(6)
O(11)	C(8)	O(12)	106.6(4)	C(15)	C(14)	C(17)	121.1(5)
C(7)	N(9)	O(10)	121.1(5)	C(14)	C(15)	C(16)	121.8(6)
C(4)	O(11)	C(8)	104.1(4)	C(11)	C(16)	C(15)	119.3(6)
C(5)	O(12)	C(8)	103.9(4)				

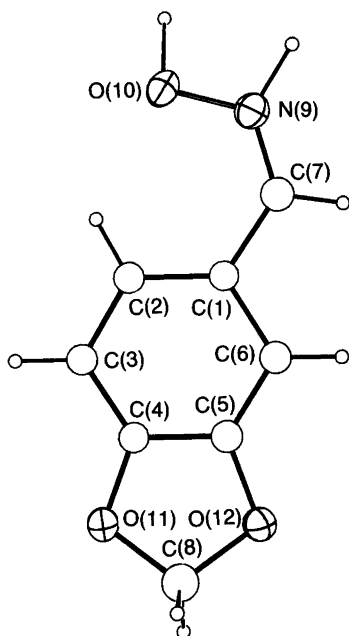


Fig. 1. ORTEP drawing¹⁰ of the (Z)-3,4-methylenedioxybenzaldehyde oximium ion indicating the numbering of the atoms. Ellipsoids and spheres representing non-hydrogen atoms enclose 50% probability, hydrogen atoms are represented by spheres of arbitrary radius.

K_{α} radiation, and an Enraf–Nonius gas flow, low-temperature device. The temperature (ca. 110 K) was monitored with a thermocouple placed a few centimeters above the crystal in the exhaust pipe, the variations of the temperature being to within 1 K. Cell constants were determined using 12 reflections ($12.6 < \theta < 20.4^{\circ}$). Based on an analysis of reflection profiles the ω scan mode was selected for data collection, $\Delta\omega = 2.5 + 0.34 \tan\theta$. The maximum scan time was 240 s and scan speeds were in the range 0.9 – $5.5^{\circ} \text{ min}^{-1}$. Intensities of three standard reflections (1 0 –3, 2 1 –9, 1 1 –2) measured every 10000 s showed no systematic variations. 1782 independent reflections in the range $1 < \theta < 22^{\circ}$ ($0 \leq h \leq 9$, $0 \leq k \leq 5$, $-28 \leq l \leq 28$) were used. The data was corrected for Lorentz and polarization effects. The variance $\sigma^2(|F|^2)$ was estimated from counting statistics plus the term $(0.07|F|^2)^2$. 966 observed reflections ($|F|^2 > \sigma|F|^2$) were used in structure refinement. The structure was solved by direct methods using MULTAN⁵ and refined by full-matrix least-squares calculations minimizing $\Sigma w(|F|_o - |F|_c)^2$. All hydrogen atoms were located in a difference density map and introduced in idealized positions with a thermal parameter $B = 3.0 \text{ \AA}^2$. 133 parameters refined were the scale factor, positional parameters for all non-hydrogen atoms, anisotropic thermal parameters for

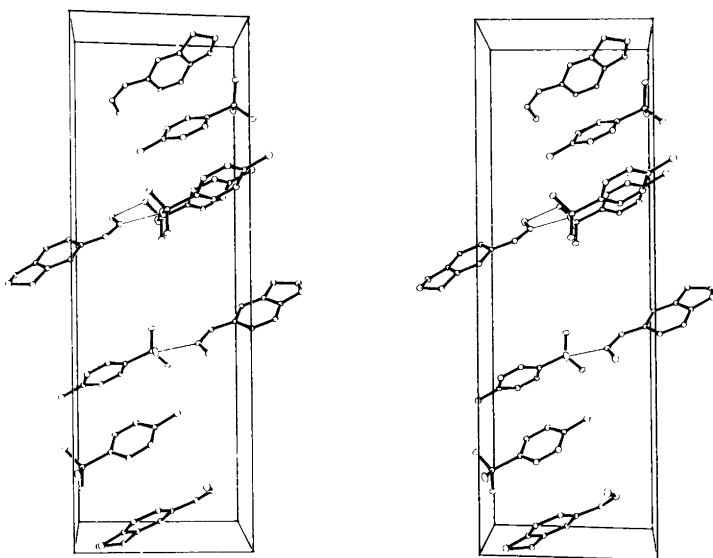


Fig. 2. Stereoview along the b axis, of the packing and the hydrogen bonding in the crystal.

the S, O and N atoms, and isotropic thermal parameters for the remaining non-hydrogen atoms. The final R -values were $R = 0.053$ and $R_w = 0.057$. The maximum shifts in the final cycle were 0.02σ . The maximum and minimum densities in the final Fourier map was $+0.40$ and $-0.40 e \text{ \AA}^{-3}$. The calculations were performed on a MicroVAX II computer using the Enraf-Nonius SDP programs.⁶ Atomic scattering factors by Cromer and Mann⁷ for S, N, O and C, by Stewart *et al.*⁸ for H and the anomalous scattering of S by Cromer and Liberman⁹ were used as contained in the program. The final atomic parameters are listed in Table 1, bond distances are given in Table 2 and bond angles in Table 3. Fig. 1 shows an ORTEP¹⁰ drawing of the oximium ion with the atomic numbering indicated, and Fig. 2 shows hydrogen bonds and the packing of the ions in the crystal. A list of observed and calculated $|F|$ -values is available from the author.^a

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