

**THE CRYSTAL AND MOLECULAR STRUCTURE OF
2-HYDROXYBENZYLALDEHYDE *O, O* (1,
4-DIOXOBUTANE-1, 4-DIYL)
OXIME, C₁₆H₁₃N₂O₆***

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Abstract – C₁₆H₁₃N₂O₆, M_r=239.30, Monoclinic, P2₁/n, a=7.6088(3), b=9.0108 (4), c=11.2161(6) Å, β=100.3633(4)°, V=759.90(6) Å³, Z=2, D_x=1.446g/cm³, D_m=1.450g/cm³, λ (MoKα)=0.71007 Å, T=293K, R=0.044, R_w=0.043 for 1295 observed reflections. The crystals were prepared by slow evaporation technique. A directed hydrogen bond is associated with the asymmetric part of the molecule between O₁---H₁ ... N₁ of 2.601 Å. The ring system is planar and the molecules are held together by vander Waals forces.

Keywords – Crystal structure, schiff bases, salenoxime

1. INTRODUCTION

Schiff bases are important classes of organic compounds and their chemistry has undergone remarkable development. There has been much interest in Schiff base ligands in recent years because of their ability to give selective and stable transition metal cation complexes [1]. Transition metal complexes of Schiff base ligands have contributed significantly to the development of transition metal chelate chemistry [2-5], and complexes of these ligands with some cations play a major role as speculative models in bio-inorganic chemistry, enzymatic studies [6] and selective membrane electrodes [7].

However, various modifications can be made to the basic Schiff base (salen) structure in an attempt to enhance the selectivity of these ligands and the stabilities of complexes formed. Among these modifications are the substitution of ligand donor atoms such as sulfur and oxygen and the inclusion of ester linkages.

In this paper, we report the molecular structure of a new compound [2-hydroxybenzaldehyde *O, O*-(1, 4-dioxobutane-1, 4-diyl) oxime], which is similar to salen, thus we prefer to call it salenoxime. The activity of this new compound has not been investigated, so the synthesis has not been described in the literature. Therefore, we have put our efforts into determining the molecular structure of the compound to investigate the nature of molecular conformation and chemical bondings, in order to find new applications for the compound which could be more effective than salen.

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2. EXPERIMENTS

To a solution of salicylaldehyde (2mmol) in dry EtOAc (15ml) in a 50ml round bottomed flask which had been cooled in an ice bath, oxalyl chloride (0.08 ml, 1mmol) was added with stirring. The reaction mixture was stirred vigorously for 2-3h to produce white precipitates. The resulting precipitates were filtered off and recrystallized from an appropriate solvent.

2-Hydroxybenzaldehyde *-O, O-(1,2-dioxetane-1,2-diy1)oxime* IR(KBr): 3301, 1778, 1606, 1566, 1271, 1128, 939, 869, 759 cm^{-1} ; ^1H NMR (CDCl_3 , 250 MHz) δ 7.03-7.13 (m, 4H), 7.31 (m, 2H), 7.48 (t, 2H), 8.68 (s, 2H). ^{13}C NMR (DMSO, 62.9 MHz) δ 115.52, 116.97, 119.90, 127.54, 134.44, 155.64, 158.00. MS, m/z (%) 328 (M^+ , 15.5)

Yellow single crystals suitable for crystal structure determinations, which were obtained by slow evaporation technique, from the concentrated solution of ethylacetate at room temperature for over five days. The D_m was measured by flotation.

a) Crystal data

$\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_6$

$M_r=239.29$

Monoclinic

$a=7.6088(3) \text{ \AA}$

$b=9.0108(4) \text{ \AA}$

$c=11.2161(6) \text{ \AA}$

$\beta=100.3633(4)^\circ$

$V=759.90(6) \text{ \AA}^3$

$P2_1/n$

$Z=2$

$D_c=1.446 \text{ gcm}^{-3}$, $D_m=1.450 \text{ gcm}^{-3}$

Yellow

MoK α radiation, $\lambda=0.71069 \text{ \AA}$

$T=293\text{K}$

$0.594 \times 0.338 \times 0.203\text{mm}$

b) Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

$2.1 \leq 2\theta \leq 26.3^\circ$

$-9 \leq h \leq 9$

$-11 \leq k \leq 0$

$0 \leq l \leq 13$

3 standard reflections were monitored every 200 reflections.

Intensity decay: none

1721 independent reflections measured.

1295 observed reflections with $F_o \geq 3 \sigma |F_o|$.

c) Refinements

Refinement on F

Absorption 1.1 mm^{-1}

Extinction factor $= 3.63547 \times 10^{-6}$

$R = (|F_o| - |F_c|) / |F_o| = 0.044$

$R_w = W (|F_o| - |F_c|) / W |F_o| = 0.043$

$W = 0.33494 / \sigma^2 |F_o|$

H-atoms positioned geometrically and not refined.

Atomic scattering factors are from the International Tables for X-ray Crystallography (1974, Vol. IV).

$\Delta P_{\text{max}} = 0.108 \text{ e } \text{Å}^{-3}$

Structure determination program: Molen/Sir

3. RESULTS AND DISCUSSION

The general conformation of the centrosymmetric molecule and atomic-numbering scheme is depicted in Fig. 1. Figure 2 shows the crystal packing along a-axis. Final positional parameters for all non-hydrogen atoms are given in Table 1. Molecular geometry data, including bond lengths and angles for non-hydrogen atoms, are shown in Tables 2 and 3, respectively. Table 4 gives some selected torsion angles.

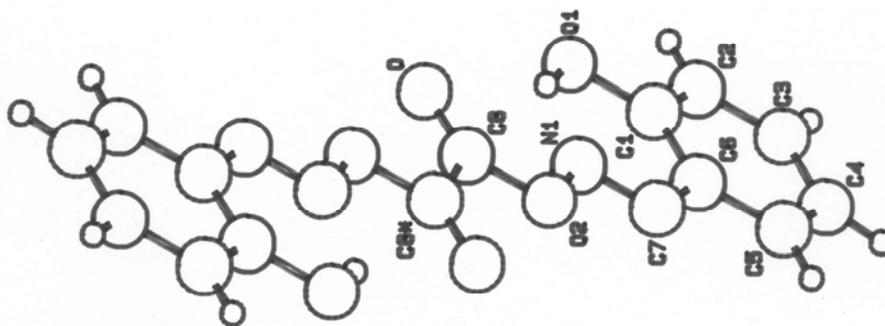


Table 1. Positional parameters and their estimated standard deviations

Atom	x	y	z	B(A ²)
O2	0.6120(2)	0.3361(2)	0.5484(1)	3.97(4)
C8	0.5220(3)	0.4306(3)	0.4669(2)	3.60(5)
N1	0.5465(3)	0.1995(2)	0.4921(20)	3.71(4)
C6	0.7768(3)	-0.0356(3)	0.5287(2)	3.10(5)
C5	0.8689(4)	-0.1356(3)	0.6120(2)	4.08(6)
C1	0.7321(3)	-0.0807(3)	0.4068(2)	3.44(5)
O	0.4829(3)	0.4108(2)	0.3610(2)	5.45(5)
O1	0.6385(3)	0.0060(2)	0.3192(2)	4.96(4)
C2	0.7815(4)	-0.2194(3)	0.3736(2)	4.28(5)
C7	0.7312(3)	0.1101(3)	0.5698(2)	3.43(5)
C3	0.8728(4)	-0.3151(3)	0.4577(2)	4.49(6)
C4	0.9157(4)	-0.2738(3)	0.5781(2)	4.59(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
 $(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(\cos\gamma) * B(1,2) + ac(\cos\beta) * B(1,3) + bc(\cos\alpha) * B(2,3)]$

Table 2. Bond lengths in angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O2	C8	1.343(3)	C6	C7	1.454(3)
O2	N1	1.429(3)	C5	C4	1.368(4)
C8	O	1.185(3)	C1	O1	1.353(3)
N1	C7	1.274(3)	C1	C2	1.376(4)
C6	C5	1.393(3)	C2	C3	1.371(4)
C6	C1	1.408(3)	C3	C4	1.383(4)

Numbers in parentheses are estimated standard deviations in the least significant digits

Table 3. Bond angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C8	O2	N1	110.9(2)	C6	C1	O1	122.8(2)
O2	C8	O	126.3(2)	C6	C1	C2	119.7(2)
O2	N1	C7	110.7(2)	O1	C1	C2	117.5(2)
C5	C6	C1	118.0(2)	C1	C2	C3	121.0(2)
C5	C6	C7	119.4(2)	N1	C7	C6	118.3(2)
C1	C6	C7	122.6(2)	C2	C3	C4	120.3(2)
C6	C5	C4	121.8(2)	C5	C4	C3	119.3(2)
C8	O2	N1	110.9(2)				

Numbers in parentheses are estimated standard deviation in the least significant digits

Table 4. Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle 4	Angle
N1	O2	C8	O	-3.96 (0.35)
C8	O2	N1	C7	-179.70 (0.21)
O2	N1	C7	C6	179.56 (0.20)
C1	C6	C5	C4	0.19 (0.38)
C7	C6	C5	C4	-179.69 (0.24)
C5	C6	C1	O1	177.99 (0.23)
C5	C6	C1	C2	-0.75 (0.35)
C7	C6	C1	O1	-2.13 (0.36)
C7	C6	C1	C2	179.13 (0.23)
C5	C6	C7	N1	-179.75 (0.22)

Table 4. (Continued)

Atom 1	Atom 2	Atom 3	Angle 4	Angle
C1	C6	C7	N1	0.37 (0.35)
C6	C5	C4	C3	0.69 (0.42)
C6	C1	C2	C3	0.43 (0.39)
O1	C1	C2	C3	-178.37 (0.24)
C1	C2	C3	C4	0.47 (0.42)
C2	C3	C4	C5	-1.03 (0.43)

The crystal structure of the title compound indicates the presence of a crystallography inversion centre between C₈*—C₈ bond (Fig. 1), and consequently, the molecule as a whole lie on special positions with two formula units per unit cell. The same inversion centre was also reported earlier for similar structures [8]. The geometry of the ring system (average bond lengths of 1.383(3) Å and bond angles of 120.0 (2)°) is regular with slight distortions of bond lengths (C₅-C₆, C₁-C₆) and angles around C₁ and C₆, which is similar to those reported earlier [8-9]. The other bond length and angles are in accord with the expected values reported elsewhere [8-10].

The conformation of O=C₈-O₂-N₁ chain is synperiplanar with the torsion angles of -3.96(4)°. Values of near 180° are found for the most torsion angles.

Intermolecular contacts correspond to normal vander Waals attractions, while there is an intramolecular hydrogen bond distance of 2.601 Å between O₁-H₁...N₁ atoms. No other atoms are involved in hydrogen bonding. The linked hydrogen bonded atoms indicate that a significant part of the hydrogen bonding involves the π-orbital electrons of C₈---O bond.

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