

THE CRYSTAL AND MOLECULAR STRUCTURE OF *N, N'*-3, 6-DIOXA-1, 8-OCTANE BIS (SALICYLALDIMINE), C₂₀H₂₄N₂O₂₄*

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Abstract – The crystal structure of the compound C₂₀H₂₄N₂O₂₄ was determined by direct methods. The crystals are monoclinic, space group P2₁/n, and unit cell parameters are: a=10.2342 (9), b=4.8763 (5), c=19.3578 (11) Å, β=98.9632 (10)°, V=956.6 (5) Å³, Z=2, D_c=1.239 g cm⁻³, D_m=1.22 g cm⁻³. The final R-factors are converged to R=0.059 and R_w=0.056 for 553 independent observed reflections. The molecules are linked by van der Waals forces and an intramolecular hydrogen bond is present between O₂ and N₁ atoms. The ring system displays a deviation from planarity.

Keywords – Crystal structure, salen, schiff bases, salicylaldimine

1. INTRODUCTION

The ability of Schiff bases derived from salicylaldehyde as poly-dentate ligands to form very stable complexes with different cations is well known [1]. Their complexes have been known since the mid-nineteenth century [2], and before the general preparation of Schiff base ligands themselves [3]. Transition metal complexes of Schiff base ligands have contributed significantly to the development of transition metal chelate chemistry [4-7], and complexes of these ligands with some cations play a major role as speculative models in bio-inorganic chemistry, enzymatic studies [8] and selective membrane electrodes [9].

In this paper we report the molecular structure of a new Schiff base, *N, N'*-3, 6-dioxa-1, 8-octanebis (salicylaldimine) in order to investigate the nature of molecular conformation and chemical bondings.

2. EXPERIMENTAL

• Synthesis of Schiff Base 46:

2, 2- [3, 6-Dioxa-1, 8-octandiylbis (nitrilomethylidene)]-bis-phenol (46): A solution of 1, 8-diamino-3, 6-dioxaoctan (0.01 mol, 1.48 g) in methanol (15 ml) was added to a solution of salicylaldehyde (0.02 mol, 2.44 g), in methanol (10 ml). The reaction mixture was then refluxed with stirring for about 15 hours. The mixture was cooled and the solvent was evaporated to give a yellow oil, which

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was crystallized by petroleum ether (60-80 °C) to give 2, 2-[3, 6-dioxa-1, 8-octandiylbis (nitrilomethylidyne)] -bis-phenol 46 as yellow crystalline solid in 94 % yield (3.34 g). m. p. = 46 °C, $R_f = 0.56$ (n-Hexane-CH₃OH/94:4); ¹H NMR (CDCl₃, 250 MHz) δ 3.59 (s, 4H), 3.71 (s, 8H), 6.87 (dt, 2H, $J_1 = 7.5$ Hz, $J_2 = 1.0$ Hz), 6.93 (d, 2H, $J = 8.25$ Hz), 7.23 (d, 1H, $J = 1.5$ Hz), 7.26 (dd, 1H, $J_1 = 3.25$ Hz, $J_2 = 1.5$ Hz), 7.31 (dd, 2H, $J_1 = 7.25$ Hz, $J_2 = 1.63$ Hz), 8.32 (s, 2H), 13.39 (s, 2H); ¹³C (CDCl₃, 62.9 MHz) δ 59.01, 70.56, 96.12, 116.97, 118.65, 131.31, 132.17, 161.19, 166.36; IR (KBr), 650(m), 742(W), 765(vs), 850(s), 870(w), 925(m), 970(m), 1040(s), 1062(s), 1125(vs.), 1162(s), 1235(m), 1255 (w), 1280(s), 1325(m), 1342(m), 1408(w), 1450(s), 1470(m), 1500(m), 1510(s), 1587(m), 1615(m), 1645(vs.), 2890(s), 2920(s), 3020(m), 3450(br, s) cm^{-1} ; Ms, $m/z = 358$ ($M^+ + 2, 3.5$), 357 ($M^+ + 1, 12.6$), 356 ($M^+, 23.2$), 210(23.0), 192(18.9), 164(19.4), 150 (18.0), 149 (72.1), 148(41.3), 135(53.1), 121(44.3), 107 (base peak), 91 (25.4), 78 (24.3), 77(74.8), 65(33.7), 51 (38.5), 43(24.0), 41(19.1); UV (CHCl₃): λ_{max} (ϵ), 258 (33160), 313 (11787), 406 (680) nm.

Crystals of the C₂₀H₂₄N₂O₂₄ suitable for x-ray analysis were grown from a concentrated ether solution using a slow evaporation technique. The D_m was measured by flotation.

a) Crystal data:

C₂₀H₂₄N₂O₂₄
 $M_r = 356.42$
 Monoclinic
 $a = 10.2342$ (9) Å
 $b = 4.8763$ (5) Å
 $c = 19.3578$ (11) Å
 $\beta = 98.9632$ (10)°
 $V = 956.6$ (5) Å³
 P2₁/n
 $Z = 2$
 $D_c = 1.239$ g cm^{-3} , $D_m = 1.22$ g cm^{-3}
 $0.36 \times 0.30 \times 0.10$ mm³
 pale yellow
 MoK α radiation, $\lambda = 0.71069$ Å
 T = 293K

b) Data collection:

Enraf-Nonius CAD-4 diffractometer
 W/2 θ Scans
 $2.1^\circ \leq \theta \leq 26.32^\circ$
 $h = -11 \rightarrow 11$
 $k = -5 \rightarrow 0$
 $l = -21 \rightarrow 0$
 3 standard reflections monitored every 200 reflections.
 Intensity decay: none
 970 independent reflections measured.
 553 observed reflections, $I \geq 2\sigma(I)$.

c) Refinement:

Refinement on F

Absorption 0.08 mm^{-1}

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

H-atoms positioned geometrically and not refined.

 $R = (|F_o| - |F_c|) / |F_o| = 0.059$ $R_w = w (|F_o| - |F_c|) / w |F_o| = 0.056$ $W = 1.851 / \sigma^2 |F_o|$ $\Delta\rho_{\text{max}} = 0.103 \text{ e } \text{Å}^{-3}$

Structure determination program: Multan

3. RESULTS AND DISCUSSION

A plot of molecular conformation along with non-hydrogen atom labeling is given in Fig 1. Crystal packing diagram along b axis is given in Fig 2. Table 1 shows the final positional parameters for all non-hydrogen atoms. The bond lengths and bond angles for all non-H atoms are given in Table 2.

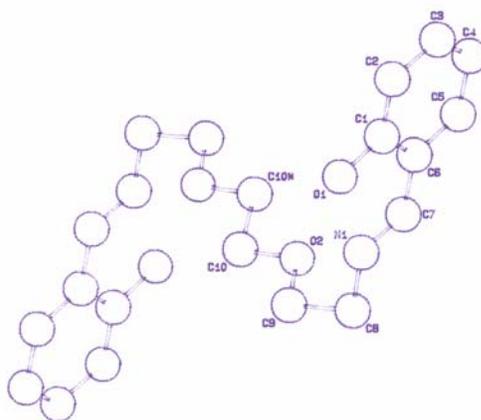


Fig. 1. Molecular configuration with atomic numbering scheme

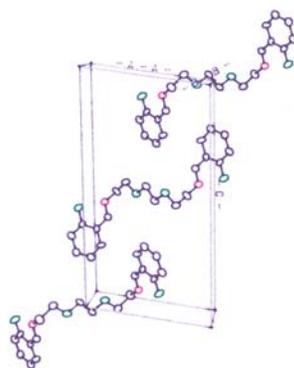


Fig. 2. Crystal packing viewed down b-axis

Table 1. Positional parameters and their Estimated Standard Deviations

Atom	\bar{x}	\bar{y}	\bar{z}	B (A ²)
N1	0.6024(3)	0.344(2)	0.9169(4)	6.9(3)
C7	0.623(1)	0.311(2)	0.8541(5)	5.9(3)
O2	0.8690(7)	0.239 (2)	0.9777(4)	7.1(2)
C6	0.5448(9)	0.105(2)	0.8089(4)	5.1(3)
C5	0.586(1)	0.074(2)	0.7430(5)	6.4(3)
O1	0.4122(7)	-0.012(2)	0.8912(3)	8.3(2)
C2	0.374(1)	-0.253(2)	0.7782(6)	8.0(3)
C8	0.684(1)	0.548(3)	0.9598(6)	7.9(4)
C1	0.4397(8)	-0.066(3)	0.8253(5)	6.5(3)
C3	0.417(1)	-0.273(2)	0.7114(5)	6.9(3)
C4	0.523(1)	-0.113(3)	0.6950(6)	7.5(4)
C10	0.962(1)	0.078(2)	1.0255(5)	7.2(4)
C9	0.774(1)	0.382(3)	1.0150(5)	7.6(4)

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 Distances (in Angstroms) and Bond Angles (in degrees)

Atom_1	Atom_2	Distance	Atom_1	Atom_2	Distance		
N1	C7	1.27(1)	C5	C4	1.39 (2)		
N1	C8	1.47(2)	O1	C1	1.37(1)		
C7	C6	1.49(1)	C2	C1	1.39(2)		
O2	C10	1.46(1)	C2	C3	1.43(2)		
O2	C9	1.47(1)	C8	C9	1.53(2)		
C6	C5	1.41(1)	C3	C4	1.41(2)		
C6	C1	1.43(1)					
C7	N1	C8	117.6(9)	N1	C8	C9	105.7(9)
N1	C7	C6	119.8(9)	C6	C1	O1	111.0(9)
C10	O2	C9	111.6(7)	C6	C1	C2	122.8(9)
C7	C6	C5	113.5(9)	O1	C1	C2	126.2(9)
C7	C6	C1	128.3(8)	C2	C3	C4	121(1)
C5	C6	C1	118.2(9)	C5	C4	C3	121(1)
C6	C5	C4	120. (1)	O2	C9	C8	106.2(8)
C1	C2	C3	117. (1)				

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

The geometry of the molecular structure indicates that the molecule as a whole has an inversion center (c) between C₁₀-C₁₀* bond, and therefore lie on special positions with two formula units per unit cell (Fig 1). The ring system has average bond lengths and bond angles of 1.41(2) Å^o and 120(1)^o. The C₁-C₂-C₃ and C₁-C₆-C₅ bond angles are smaller than the average value. The C₆-C₇ bond length of 1.49 (1) Å^o can be considered as single C_(sp²)-C_(sp²) bond distance. A calculated least square plane through ring system displayed a deviation from planarity, and was found to adopt a puckered conformation: The maximum out- of- plane deviations are -0.59, -0.5, 0.54 and 0.68Å for C₁, C₆, C₃ and C₄, respectively.

In this molecule, C-O bond lengths are of two different types. O₂-C₁₀ and O₂-C₉ bond lengths are comparable [1.46(1) and 1.47(1) Å^o, respectively], while O₁-C₁ is significantly shorter [1.37(1) Å^o]. The latter is similar to those of some double bond characters reported by Tenon et. al [10], and Ondracek et al [11]. The N-C bond lengths around N are very dissimilar [1.29(1) Å^o and 1.49(2) Å^o]. The N₁-C₇ is typical of a double bond and N₁-C₈ is single. These values are in agreement with those reported elsewhere [11-13]. Therefore the chain is likely to correspond to C₆-C₇=N₁-C₈-C₉-O₂-C₁₀, and approximately adopts the extended conformation. All other bond lengths and angles are within the expected ranges.

The compound is stabilized by an intramolecular hydrogen bond distance of 2.601 Å between O₁ and N₁ atoms. All intermolecular contacts correspond to normal van der Waals interactions.

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