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Synthesis and Crystal Structure of 5-Methoxy-4'-chloro-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol

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An asymmetrical Salamo-type compound 5-methoxy-4'-chloro-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol have been synthesized and characterized by single crystal X-ray crystallography. The crystal structure shows that the compound adopts an L-shaped configuration, in which the benzene rings are approximately perpendicular, making a dihedral angle of 84.09(3)º. And the molecule contains abundant intramolecular and intermolecular hydrogen bonding interactions. Thus, each molecule links six other molecules into an infinite 3D supramolecular structure by intermolecular hydrogen bonding interactions.

Keywords: Asymmetrical Salamo-type compound, Synthesis, Crystal structure.

INTRODUCTION

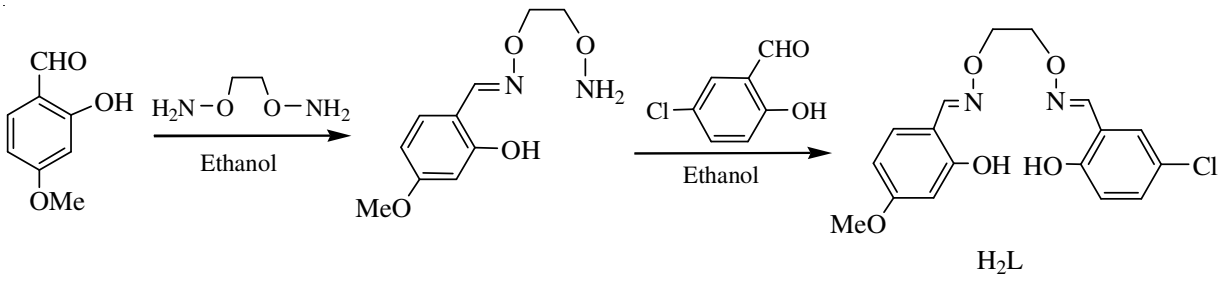
Salamo-type compounds and its analogues are extensively studied in the past few years. They can accommodate one or more metal ions to form diversiform complexes which have been attracted much interest for their applications as catalysts for organic reactions[1-4], models of reaction centers of metalloenzymes[5,6], nonlinear optical[7,8] and magnetic functional materials[9-13]. Particularly, asymmetrical Salamo-type compounds can create metal complexes in a more flexible fashion, which can lead to more desirable catalytic properties[14,15]. And recent studies have demonstrated that the asymmetrical Salamo-type compounds with two different substituents on the two benzene rings[16a,b], possess of potential applications[17]. Thus, we designed and synthesized an asymmetrical Salamo-type compound 5-methoxy-4'-chloro-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)] diphenol and characterized by single crystal X-ray crystallography.

EXPERIMENTAL

2-Hydroxy-4-methoxybenzaldehyde (≥ 99 %) and 2-hydroxy-5-chlorobenzaldehyde (≥ 99 %) were purchased from Alfa Aesar and used without further purification. 1,2-*Bis*(aminooxy)ethane was synthesized according to an analogous method reported earlier[18-20]. The others are the same as literature[16c].

General procedure: The major reaction steps involved in the synthesis of the title compound are given in **Scheme-I**. The title compound was synthesized according to an analogous method reported earlier[16,17]. Yield 87.0 %. m.p. 383-385 K. Anal. Calcd. for $C_{17}H_{17}N_2O_5Cl$ (%): C, 55.97; H, 4.70; N, 7.68. Found: C, 55.81; H, 4.86; N, 7.53.

A solution of the title compound (3.65 mg, 0.01 mmol) in ethanol (2 mL) was added dropwise to *n*-hexane (4 mL) at room temperature. The mixture was filtered and the filtrate was allowed to stand at room temperature for about 3 weeks. Then the solvent partially evaporated and several colourless



Scheme-I: Synthetic route to 5-methoxy-4'-chloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol

prismatical single crystals suitable for X-ray crystallographic analysis were obtained.

X-Ray structure determination: The X-Ray structure determination of the title compound is the same as reported earlier[16]. Details of the data collection and refinements of the title compound are listed in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPOUND

Empirical formula	$C_{17}H_{17}N_2O_5Cl$
Formula weight	364.78
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	Pc
Cell dimensions, (Å, deg)	a = 10.4013(13), b = 4.5863(5), c = 18.125(2), β = 100.887(2)
Volume (Å^3)	849.09(17)
Z	2
Density (calculated) (mg/m^3)	1.427
Absorption coefficient (mm^{-1})	0.256
$F_{(000)}$	380
Crystal size	0.32 × 0.08 × 0.05
Index ranges	-12 ≤ h ≤ 11, -3 ≤ k ≤ 5, -21 ≤ l ≤ 21
Reflections collected	3948/2369 [R(int) = 0.0986]
Independent reflections	510
Data/restraints/parameters	2369/2/227
Goodness of fit indicator	1.043
R [I > 2σ(I)]	R_1 = 0.0675, wR_2 = 0.1019
Largest diff. peak and hole (e Å^{-3})	0.286 and -0.283

RESULTS AND DISCUSSION

Crystal structure of the title compound: X-ray crystallographic analysis reveals the crystal structure of the title compound, in which all bond lengths and angles are in normal ranges. ORTEP-style drawing of the present compound is shown in Fig. 1. Selected bond lengths and angles are listed in Table-2. The molecule crystallizes in the monoclinic system, space group Pc, with two crystallographically independent molecules in the unit cell. The title compound adopts an L-shaped configuration, in which the benzene units are approximately perpendicular, making a dihedral angle of 84.09(3)° and dihedral angles of the two oxime groups with the adjacent benzene rings are 3.6(4)° and 2.93(3)°, respectively.

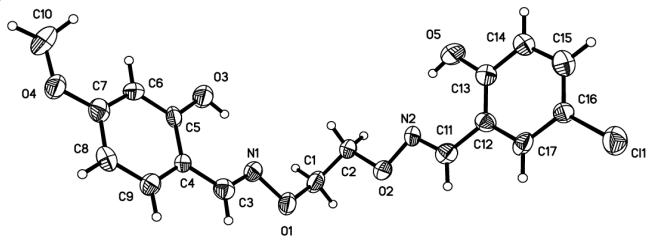


Fig. 1. ORTEP-style drawing of the title compound (Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level)

Intermolecular interactions of the title compound: The molecule contains abundant intramolecular and intermolecular hydrogen bonding interactions. The extended hydrogen bonding network is formed by O-H···N and C-H···O hydrogen bonds. Hydrogen bond data are summarized in Table-3.

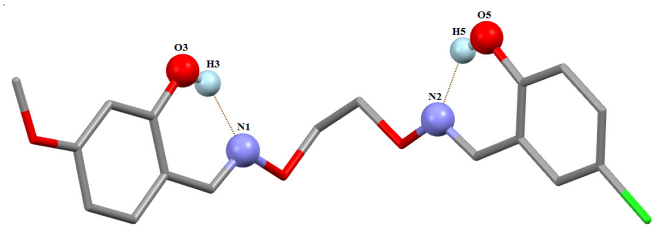


Fig. 2. View of the intramolecular hydrogen bonding interactions of the title compound

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE TITLE COMPOUND

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cl1-C16	1.714(9)	O4-C10	1.400(13)	C8-C9	1.403(16)
N1-C3	1.257(13)	O5-C13	1.371(12)	C11-C12	1.479(15)
N1-O1	1.419(10)	C1-C2	1.450(14)	C12-C13	1.338(15)
N2-C11	1.281(12)	C3-C4	1.434(14)	C12-C17	1.379(13)
N2-O2	1.398(11)	C4-C5	1.383(12)	C13-C14	1.390(16)
O1-C1	1.460(13)	C4-C9	1.387(15)	C14-C15	1.392(15)
O2-C2	1.439(10)	C5-C6	1.376(14)	C15-C16	1.340(13)
O3-C5	1.355(13)	C6-C7	1.356(15)	C16-C17	1.419(15)
O4-C7	1.357(13)	C7-C8	1.398(15)		
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
C3-N1-O1	111.3(8)	O3-C5-C6	118.1(9)	C13-C12-C11	121.8(10)
C11-N2-O2	111.2(8)	O3-C5-C4	121.0(10)	C17-C12-C11	116.9(9)
N1-O1-C1	108.3(7)	C6-C5-C4	120.9(10)	C12-C13-O5	124.2(11)
N2-O2-C2	108.5(7)	C7-C6-C5	121.5(10)	C12-C13-C14	120.5(10)
C7-O4-C10	117.2(9)	C6-C7-O4	125.7(10)	O5-C13-C14	115.3(10)
C2-C1-O1	113.5(10)	C6-C7-C8	119.4(11)	C13-C14-C15	119.5(10)
O2-C2-C1	109.1(8)	O4-C7-C8	114.9(11)	C16-C15-C14	119.7(11)
N1-C3-C4	122.4(10)	C7-C8-C9	119.0(11)	C15-C16-C17	121.0(10)
C5-C4-C9	118.1(10)	C4-C9-C8	121.0(10)	C15-C16-Cl1	121.2(9)
C5-C4-C3	122.4(10)	N2-C11-C12	120.2(9)	C17-C16-Cl1	117.8(7)
C9-C4-C3	119.5(9)	C13-C12-C17	121.4(10)	C12-C17-C16	117.9(10)

TABLE-3
DATA FOR HYDROGEN-BONDING INTERACTIONS (Å, º)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠ D-H···A	Symmetry code
O3-H3···N1	0.82	1.87	2.598(6)	147	x, y, z
O5-H5···N2	0.82	1.90	2.610(7)	144	x, y, z
C9-H9···O5	0.93	2.47	3.397(7)	178	1+x, y, z
C11-H11···O3	0.93	2.52	3.404(7)	159	x, 2-y, 1/2+z
C15-H15···O4	0.93	2.47	3.368(9)	162	-1+x, -y, 1/2+z

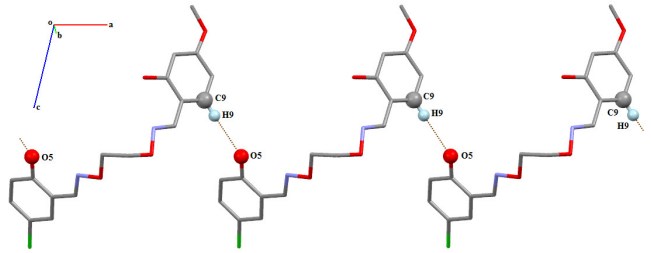


Fig. 3. View of the 1D chain motif of the title compound along the a axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

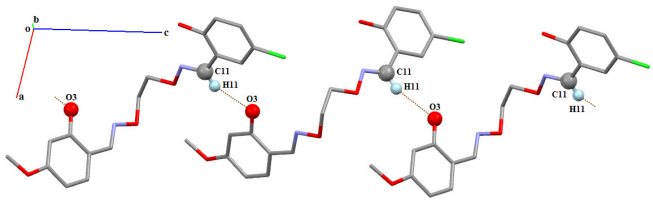


Fig. 4. View of the 1D chain motif of the title compound along the c axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

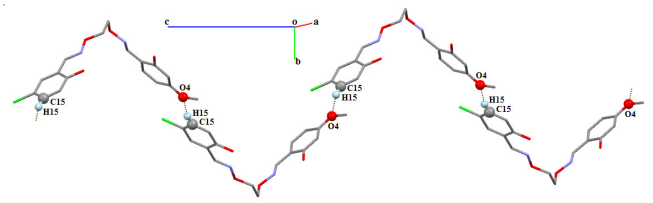


Fig. 5. View of the 1D chain motif of the title compound (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

The molecule has two pairs of strong intramolecular O3-H3···N1 and O5-H5···N2 hydrogen bonding interactions (Fig. 2). Furthermore, each -C9H9 group of the benzene ring is hydrogen-bonded to phenoxy oxygen (O5) atom of the other benzene ring into an infinite 1D chain along the a axis (Fig. 3). Meanwhile, this linkage is stabilized by two pairs of intermolecular C11-H11···O3 hydrogen bonding interactions between the -C11H11 unit of the oxime group and phenoxy oxygen (O3) atom of the benzene ring, forming another infinite 1D chain along the c axis, as illustrated in Fig. 4. In addition to, the molecule is linked by two pairs of intermolecular C15-H15···O4 hydrogen bond, resulting in the third infinite 1D Z-shaped chain (Fig. 5). Thus, each molecule links six other molecules to form an infinite 3D network supramolecular structure through intermolecular hydrogen bonding interactions.

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