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Synthesis and Crystal Structure of 4,4'-Dichloro-6,6'-dibromo-2,2'-[(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol

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The compound 4,4'-dichloro-6,6'-dibromo-2,2'-[(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol with the molecular formula $C_{20}H_{20}N_2O_2Br_2Cl_2$, is central symmetric structure and two phenyl rings in each molecule are parallel to each other. Two intramolecular O2-H2···N1 hydrogen bonds involving the hydroxyl groups and oxime N atoms generate two S(6) ring motifs in each molecule. In the crystal structure, each molecule interlinks two neighboring molecules into a 1D infinite chain supramolecule through two intermolecular C8-H8···Cl1 hydrogen bonds.

Key Words: Salen-type bisoxime, Synthesis, Crystal structure.

INTRODUCTION

Salen and its analogues are most versatile chelate ligands in inorganic and organometallic chemistry. Their complexes can be used in many areas, such as medical imaging[1], inorganic biochemistry[2], optical materials[3] and catalysis[4]. In this paper, we report on the synthesis and crystal structure of a salen-type bisoxime compound, 4,4'-dichloro-6,6'-dibromo-2,2'-[(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol.

EXPERIMENTAL

3-Bromo-5-chloro-2-hydroxybenzaldehyde was purchased from Alfa Aesar and used without further purification. 1,6-*Bis*(aminooxy)hexane was synthesized according to an analogous method reported earlier[5]. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. X-ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

General procedure: 4,4'-Dichloro-6,6'-dibromo-2,2'-[(hexane-1,6-diyldioxy)- *bis*(nitrilomethylidyne)]diphenol was synthesized according to an analogous method reported earlier[6]. To an ethanol solution (8 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (158 mg, 0.67 mmol) was added an ethanol solution (3 mL) of 1,6-*bis*(aminooxy)hexane (49.0 mg, 0.33 mmol). The reaction mixture was stirred at 328 K for 4 h. The formed precipitate was separated by filtration and washed successively with ethanol/*n*-hexane(1:4) and *n*-hexane. The product was dried under vacuum to yield 145.1 mg of the title compound. Yield, 75.4 %. m.p. 493-494 K. Anal. calcd. (%) for $C_{20}H_{20}N_2O_2Br_2Cl_2$: C, 41.20; H, 3.46; N, 4.80. Found (%): C, 41.42; H, 3.54; N, 4.63.

The title compound was dissolved in chloroform/ethol (1:1) solution and allowed to stand at room temperature for about several weeks, colourless needle-like single crystals suitable for X-ray crystallographic analysis were obtained.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.53 mm × 0.40 mm × 0.15 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radition (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. Details of the data collection and refinements of the title compound are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC:712158.

RESULTS AND DISCUSSION

X-Ray crystallographic analysis revealed the crystal structure of the title compound. And the structure is shown in Fig. 1. Selected bond distances and angles are listed in Table-2.

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

Empirical formula	$C_{20}H_{20}N_2O_2Br_2Cl_2$
Formula weight	583.10
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P –1
Cell dimensions, (Å, deg)	a = 4.5419(10), b = 8.0851(14), c = 15.660(2), α = 76.9600(10), β = 84.470(2), γ = 86.470(2)
Volume ($Å^3$)	557.17(17)
Z	1
Density (calculated) (mg/m^3)	1.738
Absorption coefficient (mm^{-1})	3.907
$F_{(000)}$	290
Index ranges	$-5 \le h \le 5$, $-9 \le k \le 5$, $-18 \le l \le 18$
Reflections collected	2358/1946 [$R_{(int)}$ = 0.0477]
Independent reflections	1385
Data/restraints/parameters	1946/0/137
Goodness of fit indicator	1.063
R [I > 2σ(I)]	R_1 = 0.0356, wR_2 = 0.1026
Largest diff. peak and hole (e $Å^{-3}$)	0.672 and -0.865

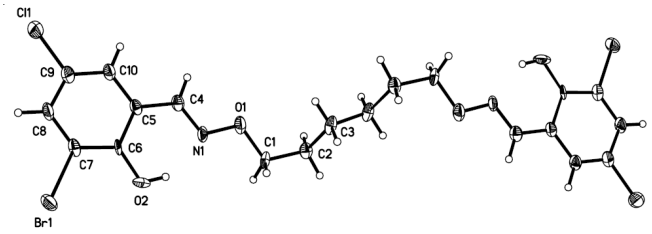

Fig. 1. Molecule structure of the title compound with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level

The title compound crystallizes in the triclinic system, space group P-1 and the unit cell contains only one crystallographically molecule. There is a trans configuration with respect to the methylidene unit. The two phenyl rings in each molecule are parallel to each other with a perpendicular interplanar spacing of *ca*. 2.647(3) Å.

There are two intramolecular O2-H2···N1 hydrogen bonds (Table-3) involving the hydroxyl groups and oxime N atoms generate two S(6) ring motifs in each molecule[7-10]. In the crystal structure, each molecule interlinks two neighboring molecules into a 1D infinite chain supramolecule through two intermolecular C8-H8···Cl1 hydrogen bonds. A view of the crystal packing for the title compound is given in Fig. 2.

TABLE-3
HYDROGEN BONDS [Å, º] FOR THE TITLE COMPOUND

D-H···A	d(D-H)	d(H···A)	∠DHA	d(D···A)
O2-H2···N1	0.82	1.94	146	2.662(3)
C8-H8···Cl1	0.93	2.84	165	3.746(3)

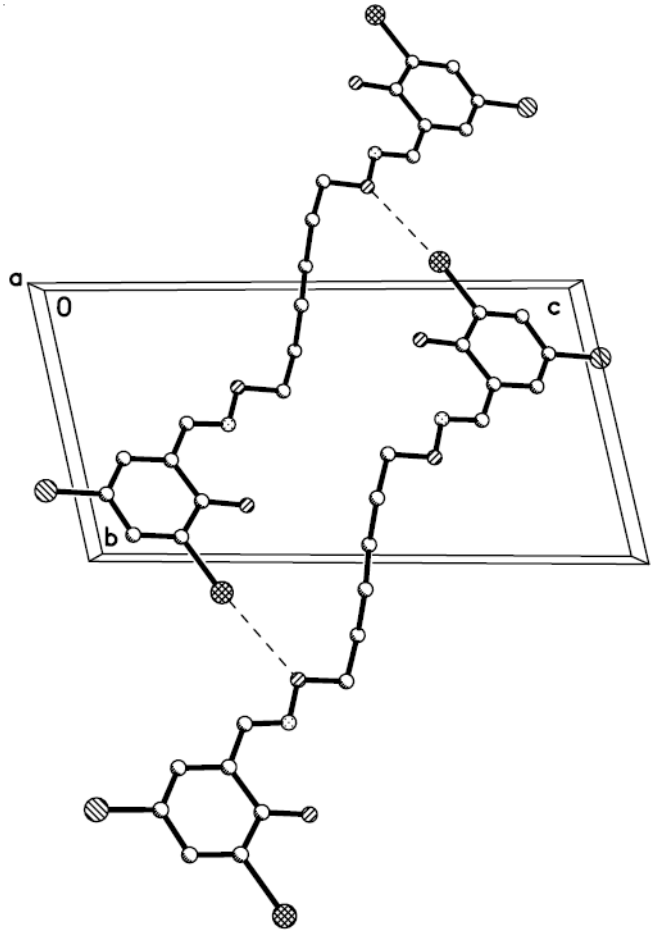

Fig. 2. A view of the crystal packing for the title compound

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º) FOR THE TITLE COMPOUND

Bond	Lengths	Bond	Lengths	Bond	Lengths
Br(1)-C(7)	1.914(17)	C(1)-C(2)	1.49(2)	C(6)-C(7)	1.39(2)
Cl(1)-C(9)	1.74(2)	C(2)-C(3)	1.55(3)	C(7)-C(8)	1.40(3)
N(1)-C(4)	1.30(2)	C(3)-C(3)	1.49(3)	C(8)-C(9)	1.36(3)
N(1)-O(1)	1.344(19)	C(4)-C(5)	1.42(2)	C(9)-C(10)	1.34(3)
O(1)-C(1)	1.43(2)	C(5)-C(10)	1.41(3)	–	–
O(2)-C(6)	1.34(2)	C(5)-C(6)	1.45(2)	–	–
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
C(4)-N(1)-O(1)	115.0(15)	C(10)-C(5)-C(6)	117.7(15)	C(8)-C(7)-Br(1)	118.9(12)
N(1)-O(1)-C(1)	111.1(13)	C(4)-C(5)-C(6)	122.5(17)	C(9)-C(8)-C(7)	116.1(16)
O(1)-C(1)-C(2)	112.5(16)	O(2)-C(6)-C(7)	121.7(15)	C(10)-C(9)-C(8)	123.9(19)
C(1)-C(2)-C(3)	112.1(15)	O(2)-C(6)-C(5)	121.8(15)	C(10)-C(9)-Cl(1)	120.0(15)
C(3)-C(3)-C(2)	109.7(18)	C(7)-C(6)-C(5)	116.5(16)	C(8)-C(9)-Cl(1)	116.1(15)
N(1)-C(4)-C(5)	121.9(16)	C(6)-C(7)-C(8)	124.4(16)	C(9)-C(10)-C(5)	121.4(17)
C(10)-C(5)-C(4)	119.8(15)	C(6)-C(7)-Br(1)	116.7(14)	–	–

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