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Synthesis and Crystal Structure of 4,4',6,6'-Tetrachloro-2,2'-[(1,4-butylene)dioxy*bis*(nitrilmethylidyne)]diphenol

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The compound 4,4',6,6'-tetrachloro-2,2'-[(1,4-butylene)dioxy*bis*(nitrilmethylidyne)]diphenol with the molecular formula $C_{18}H_{16}Cl_4N_2O_4$, was synthesized by the reaction of 3,5-dichloro-2-hydroxybenzaldehyde with 1,4-*bis*(aminooxy)butane in ethanol. The molecule is disposed about a crystallographic centre of symmetry and the molecule adopts an extended conformation where the two phenoldoxime moieties are apart from each other. There are strong O-H···N intramolecular hydrogen bond and weak C-H···O and C-H···Cl intermolecular hydrogen bonds and strong intermolecular π-π stacking interactions (the nearest benzene rings are parallel to that of another molecule, are *ca.* 2.512(2) Å), stabilizing the two dimensional structures of the present compound.

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

INTRODUCTION

Salen-type compounds have been intensively used as versatile chelating ligands in the formation of transition metal complexes[1]. Some of them or their metal complexes are used in various organic reaction processes as catalysts[2], models of reaction centers of metalloenzymes[3], have fascinating magnetic properties[4] and are non-linear optical materials[5]. They can also be used as biological models in understanding the structure of biomolecules and biological processes[6,7]. Most of their important features of these compounds are their preparative accessibility, diversity and structural variability, which make them more attractive. Some salen-type bisoxime derivatives, such as 2,2'-[(1,4-butylene)dioxy*bis*(nitrilomethylidyne)] dinaphthol[8], 4,4'-dibromo-2,2'-[ethylenedioxy*bis* (nitrilomethylidyne)]diphenol[9], 4,4'-dibromo-2,2'-[(1,3-propylene)dioxy*bis*(nitrilo-methylidyne)]diphenol[10], 2,2'-[(1,4-butylene)dioxy*bis*-(nitrilo-methylidyne)]diphenol[11], 4,4'-dichloro-2,2'-[(1,4-butylene)-dioxy*bis*(nitrilomethylidyne)]diphenol[12], 4,4',6,6'-tetra(*tert*-butyl)-2,2'-[(1,4-butylene)dioxy*bis*(nitrilomethylidyne)]-diphenol[13], 2,2'-[(1,4-butylene)dioxy*bis*(nitriloethylidyne)]-diphenol[14], 2,2'-[(propane-1,3-diyldioxy)*bis*-(nitrilomethylidyne)]diphenol[15] and 5,5'-*bis*(diethylamino)-2,2'-[ethylene-dioxy*bis*(nitrilomethylidyne)]diphenol[16] have been studied in recent years. In this paper, a new bisoxime compound, 4,4',6,6'-tetrachloro-2,2'-[(1,4-butylene)dioxy*bis*-(nitrilmethylidyne)]-diphenol was synthesized and characterized structurally.

EXPERIMENTAL

2-Hydroxybenzaldehyde was purchased from Alfa Aesar and used without further purification. 1,4-*bis*(Aminooxy)-butane was synthesized according to an analogous method reported earlier[3]. 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. IR spectra in the range 4000-400 cm^{-1} were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. The ^1H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using $CDCl_3$ as solvent. 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',6,6'-Tetrachloro-2,2'-[(1,4-butylene)dioxy*bis*-(nitrilmethylidyne)]diphenol: To an ethanol solution (6 mL) of 3,5-dichloro-2-hydroxybenzaldehyde (573.0 mg, 3.00 mmol) was added an ethanol (2 mL) solution of 1,4-*bis*(aminooxy)butane (180.1 mg, 1.50 mmol). The mixture solution was stirred at 328 K for 4 h. The precipitate was filtered and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under vacuum and to yield 480.30 mg of the title compound. Yield,

68.7 %. m.p. 475-476 K. Colourless needle-shaped single crystals suitable for X-ray diffraction studies were obtained after four weeks by slow evaporation from an tetrahydrofuran/ethyl acetate/ethanol (2:1:2) solution of 4,4'6,6'-tetrachloro-2,2'-[(1,4-butylene)dioxy*bis*(nitrilmethylidyne)]diphenol. Anal. calcd. (%) for: $C_{18}H_{16}Cl_4N_2O_4$: C, 46.45; H, 3.40; N, 5.87. Found (%): C, 46.38; H, 3.46; N, 6.01.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.45 mm × 0.40 mm × 0.17 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 293(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 title compound are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 684099.

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

Empirical formula	$C_{18}H_{16}N_2O_4Cl_4$
Formula weight	466.13
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Cell dimensions	a = 4.2525(5) Å, b = 7.9844(10) Å, c = 14.3333(19) Å, α =74.5330(10)º, β = 84.330(6)º, γ = 80.533(2)º
Volume	461.88(10) $Å^3$
Z	1
Density (calculated)	1.676 mg/m^3
Absorption coefficient	0.671 mm^{-1}
$F_{(000)}$	238
Index ranges	$-5 \le h \le 4$, $-9 \le k \le 4$, $-16 \le l \le 16$
Reflections collected/unique	1819/1555 [$R_{(int)}$ = 0.0387]
Independent reflections	1395
Data/restraints/parameters	1555/0/128
Goodness of fit indicator	1.046
R [$I > 2\sigma(I)$]	R_1 = 0.0664, wR_2 = 0.1252
Largest diff. peak and hole	0.427 and -0.419 e. Å

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. The single crystal structure of the title compound is built up by only the $C_{18}H_{16}Cl_4N_2O_4$ moleculars (Fig. 1), in which all bond lengths are in normal ranges. The X-ray crystallography reveals the title compound crystallizes in the triclinic system, space group P-1 with a = 4.2525(5) Å, b = 7.9844(10) Å, c = 14.3333(19) Å, α = 74.5330(10)º, β = 84.330(2)º, γ = 80.533(2)º and Z = 1. The molecule is disposed about a crystallographic centre of symmetry and the molecule adopts an extended conformation where the two phenoldoxime moieties are apart from each other. The distance (1.365(2) Å) of two parallel benzene rings in the title compound is shorter than

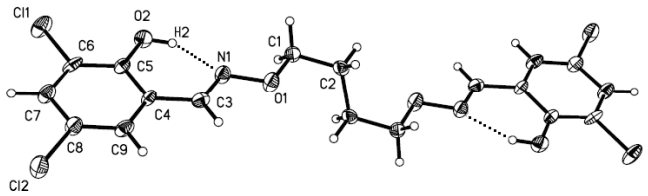

Fig. 1. Molecule structure of the title compound with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

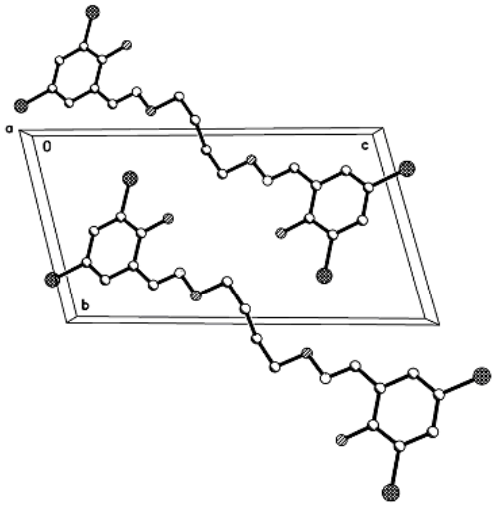

Fig. 2. Molecular packing arrangement in the unit cell

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cl(1)-C(6)	1.702(8)	O(2)-C(5)	1.315(9)	C(4)-C(5)	1.397(10)
Cl(2)-C(8)	1.714(9)	C(1)-C(2)	1.443(11)	C(5)-C(6)	1.349(12)
N(1)-C(3)	1.251(10)	C(2)-C(2)	1.532(16)	C(6)-C(7)	1.340(12)
N(1)-O(1)	1.365(9)	C(3)-C(4)	1.407(11)	C(7)-C(8)	1.378(12)
O(1)-C(1)	1.402(9)	C(4)-C(9)	1.367(11)	C(8)-C(9)	1.326(12)
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
C(3)-N(1)-O(1)	110.8(7)	C(5)-C(4)-C(3)	122.1(7)	C(5)-C(6)-Cl(1)	118.8(6)
N(1)-O(1)-C(1)	109.6(6)	O(2)-C(5)-C(6)	119.6(7)	C(6)-C(7)-C(8)	118.2(8)
O(1)-C(1)-C(2)	105.9(6)	O(2)-C(5)-C(4)	121.7(7)	C(9)-C(8)-C(7)	122.4(8)
C(1)-C(2)-C(2)	115.6(10)	C(6)-C(5)-C(4)	118.6(7)	C(9)-C(8)-Cl(2)	119.6(7)
N(1)-C(3)-C(4)	120.5(7)	C(7)-C(6)-C(5)	121.9(8)	C(7)-C(8)-Cl(2)	118.0(7)
C(9)-C(4)-C(5)	119.8(7)	C(7)-C(6)-Cl(1)	119.3(7)	C(8)-C(9)-C(4)	119.1(8)
C(9)-C(4)-C(3)	118.1(7)	–	–	–	–

the distance (2.028(3) Å) of parallel benzene ring planes in 4,4'-dichloro-2,2'-[(1,4-butylene)dioxy*bis* (nitrilomethylidyne)]-diphenol[12]. The oxime, chloro groups and phenolic alcohols have anticonformation, which is similar to what is observed in our previously reported salen-type bisoxime of 2,2'-[(1,4-butylene)dioxy*bis*(nitriloethylidyne)] diphenol[14]. There are strong O-H···N intramolecular hydrogen bond between N1 atom and O2 atom of hydroxyl. Three C atoms, one N atom, one O atom and one H atom generate a six-membered ring through hydrogen bonds (d(O2-H2) = 0.82 Å, d(H2···N1) = 1.83 Å, d(O2···N1) = 2.555(3) Å, ∠O2-H2···N1 = 146º), which with weak C-H···O and C-H···Cl intermolecular hydrogen bonds and strong intermolecular pai-pai stacking interactions (the nearest benzane rings are parallel to that of another molecule, are *ca.* 2.512(2) Å), stabilizing the two dimensional structures of the title compound[17].

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