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Synthesis and Supramolecular Structure of 6,6'-Diethoxy-2,2'-[1,1'-(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol

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The compound, 6,6'-diethoxy-2,2'-[1,1'-(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol, was synthesized by the reaction of 3-ethoxysalicylaldehyde with 1,6-*bis*(aminooxy)hexane in ethanol. The molecule lies across a crystallographic inversion centre (symmetry code: -x, -y, -z) and adopts an E configuration with respect to the azomethine C=N bond. Within the molecule, the two benzene rings are parallel to each other and with the distance of 3.976(4) Å. Intramolecular O-H···N hydrogen bonds are formed between the hydroxyl groups and the oxime nitrogen atoms. The distances between the hydroxyl groups and the oxime nitrogen atoms d(O2···N1) = 2.626(3) Å. Intermolecular C-H···O hydrogen bonds link the title molecules into an infinite 3D supramolecular network structure.

Key Words: Bisoxime compound, Synthesis, Supramolecular structure.

INTRODUCTION

Particular attention has recently been paid to the synthesis and crystal structure of bisoxime compounds and their analogues[1-3]. These compounds can easily form complexes with transition metal ions as versatile chelating ligands[4,5]. Some of them or their metal complexes are used in various organic reaction processes as catalysts, models of reaction centers of metalloenzymes and nonlinear optical materials. Because the oxime-type ligands are able to resist the metathesis of C=N bonds, we can use an O-alkyloxime unit (-CH=N-O-) instead of -CH=N- group in order to improve the stability of the ligands. Meanwhile, the large electronegativity of oxygen atoms can strongly affects the electronic properties of N_2O_2 coordination sphere, which can lead to different and novel properties and structures of the resulting complexes[6]. As an extension of our previous work, we report here the synthesis and crystal structure of a new salen-type bisoxime compound 6,6'-diethoxy-2,2'-[1,1'-(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol.

EXPERIMENTAL

3-Ethoxysalicylaldehyde was purchased from Alfa Aesar and used without further purification. 1,6-*Bis*(aminooxy) hexane was synthesized according to an analogous method reported earlier[7,8]. The other reagents and solvents were analytical grade reagents from Shanghai 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. 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.

Synthesis of 6,6'-diethoxy-2,2'-[1,1'-(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol: To a hot ethanol solution (10 mL) of 3-ethoxysalicylaldehyde (347.8 mg, 2.09 mmol) was added an ethanol solution (5 mL) of 1,6-*bis*(aminooxy) hexane (151.1 mg, 1.02 mmol). After the solution had been stirred at 328 K for 8 h, the reaction mixture was filtered, washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under vacuum to yield 259.3 mg of the title compound. Yield 57.2 %. m.p. 454-456 K. Anal. calcd. (%) for $C_{24}H_{32}N_2O_6$: C, 64.85; H, 7.26; N, 6.30. Found (%): C, 64.97; H, 7.05; N, 6.12. IR (KBr, ν_{max}, cm^{-1}): C=N, 1610 and Ar-O, 1255. Colourless block-like single crystals suitable for X-ray diffraction studies were obtained after several weeks by slow evaporation from a dichloromethane-methanol mixed solution of the title compound.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.38 mm × 0.15 mm × 0.11 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 title compound are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 878452.

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

Empirical formula	$C_{24}H_{32}N_2O_6$
Formula weight	444.52
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions, (Å, deg)	a = 4.8160(3), b = 18.6909(17), c = 13.2091(12), β = 102.4990(10)
Volume ($Å^3$)	1160.84(17)
Z	2
Density (calculated) (mg/m^3)	1.272
Absorption coefficient (mm^{-1})	0.091
$F_{(000)}$	476
Index ranges	$-5 \le h \le 5$, $-22 \le k \le 22$, $-15 \le l \le 8$
Reflections collected	5799
Independent reflections	2046 [$R_{(int)}$ = 0.0716]
Data/restraints/parameters	2046/0/146
Goodness of fit indicator	1.028
R [I > 2σ(I)]	R_1 = 0.0533, wR_2 = 0.1158
Largest diff. peak and hole (e $Å^{-3}$)	0.152 and -0.112

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 crystal structure of the title compound is built up by only the $C_{24}H_{32}N_2O_6$ molecules and all bond lengths and angles are in normal ranges[6,7]. The molecule lies across a crystallographic inversion centre (symmetry code: -x, -y, -z) and adopts an E configuration with respect to the azomethine C=N bond. Within the molecule, the two benzene rings are parallel to each other and with the distance of 3.976(4) Å.

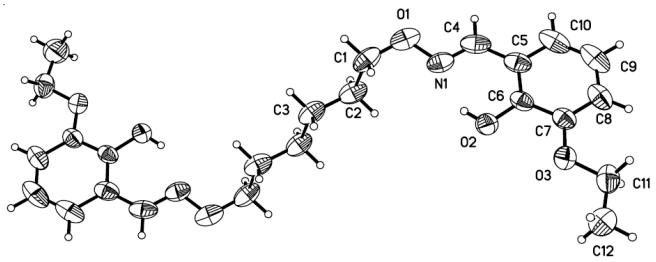

Fig. 1. Molecule structure of the title compound with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

In the crystal structure, intramolecular O-H···N hydrogen bonds (d(O2-H2) = 0.82 Å, d(H2···N1) = 1.91Å, d(O2···N1) = 2.626(3) Å, ∠O2-H2···N1 = 146º) are formed between the hydroxyl groups and the oxime nitrogen atoms[9-13]. Intermolecular C-H···O hydrogen bonds link the neighboring molecules into an infinite three-dimensional supramolecular network structure. The molecules of the title compound are linked by a pair of intermolecular C9-H11B···O2 hydrogen bond interactions into a 1D infinite zigzag chain along the a-axis (Fig. 2). Furthermore, this linkage is further stabilized by a pair intermolecular C9-H9···O2 hydrogen bond interactions to form an infinite 2D crapy layer parallel to the bc plane (Fig. 3). To sum up, with the help of intermolecular C-H···O hydrogen-bonding interactions, the crystal packing shows a self-assembling 3D supramolecular network structure[14-16].

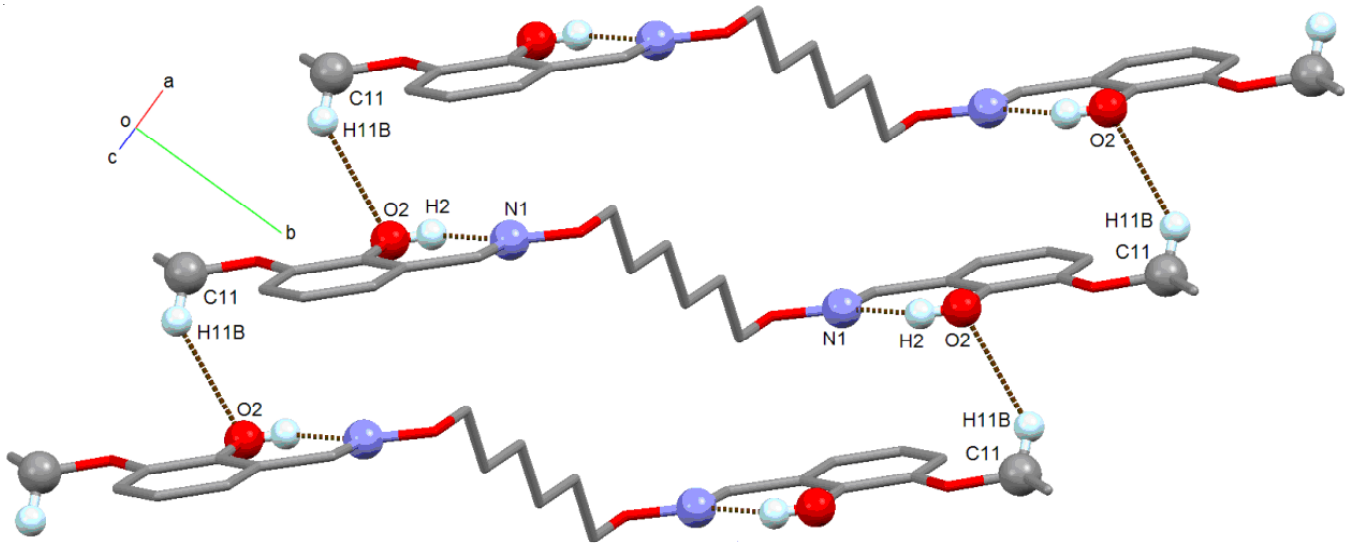

Fig. 2. Part of the supramolecular structure containing intramolecular O2-H2···N1 and intermolecular C11-H11B···O2 hydrogen bonds along a axis for the title compound

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
N(1)-C(4)	1.284(4)	C(1)-C(2)	1.512(4)	C(6)-C(7)	1.405(4)
N(1)-O(1)	1.399(3)	C(2)-C(3)	1.514(4)	C(7)-C(8)	1.354(4)
O(1)-C(1)	1.428(3)	C(3)-C(3)$^{\#1}$	1.528(5)	C(8)-C(9)	1.373(4)
O(2)-C(6)	1.360(3)	C(4)-C(5)	1.461(4)	C(9)-C(10)	1.372(5)
O(3)-C(7)	1.356(3)	C(5)-C(6)	1.373(4)	C(11)-C(12)	1.465(4)
O(3)-C(11)	1.424(3)	C(5)-C(10)	1.398(4)	–	–
Bond	Angles	Bond	Angles	Bond	Angles
C(4)-N(1)-O(1)	111.2(3)	C(6)-C(5)-C(10)	119.7(4)	C(8)-C(7)-C(6)	119.6(3)
N(1)-O(1)-C(1)	108.8(3)	C(6)-C(5)-C(4)	121.9(3)	O(3)-C(7)-C(6)	114.8(3)
C(7)-O(3)-C(11)	117.5(3)	C(10)-C(5)-C(4)	118.4(4)	C(7)-C(8)-C(9)	120.7(4)
O(1)-C(1)-C(2)	114.0(3)	O(2)-C(6)-C(5)	123.1(3)	C(10)-C(9)-C(8)	120.9(4)
C(1)-C(2)-C(3)	113.3(3)	O(2)-C(6)-C(7)	116.9(3)	C(9)-C(10)-C(5)	119.3(4)
C(2)-C(3)-C(3)$^{\#1}$	113.4(3)	C(5)-C(6)-C(7)	120.0(3)	O(3)-C(11)-C(12)	109.2(3)
N(1)-C(4)-C(5)	121.3(3)	C(8)-C(7)-O(3)	125.7(4)	–	–

Symmetry transformations used to generate equivalent atoms: $^{\#1}$-x+2, -y+2, -z+1.

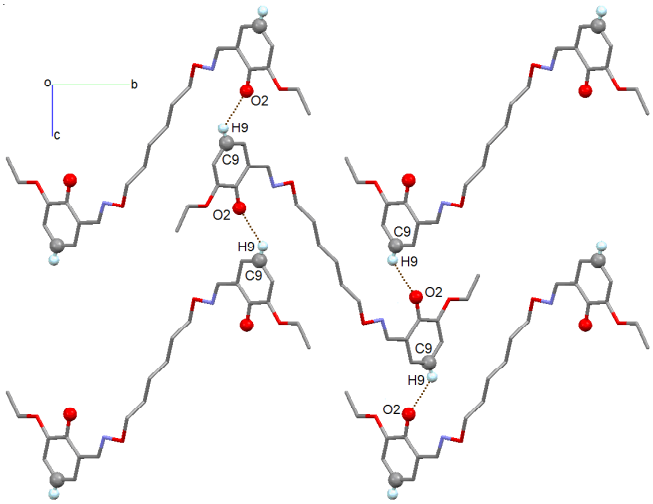

Fig. 3. Part of the supramolecular structure containing intermolecular C9-H9···O2 hydrogen bonds along bc plane for the title compound

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