



Synthesis and Supramolecular Structure of 3,3'-Dibromo-1,1'-[butane-1,4-diylldioxybis(nitrilomethylidene)]dibenzene

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(Received: 3 April 2012;

Accepted: 21 December 2012)

AJC-12594

The compound, 3,3'-dibromo-1,1'-[butane-1,4-diylldioxybis(nitrilo-methylidene)]dibenzene with the molecular formula $C_{18}H_{18}N_2O_2Br_2$, was synthesized by the reaction of 3-bromobenzaldehyde with 1,4-bis(aminoxy)butane in ethanol. The molecule lies across a crystallographic inversion centre (symmetry code: $-x, -y, -z$) and adopts an extended form. Within the molecule, the two aromatic rings are aligned with the angle of $5.57(3)^\circ$, but extend in opposite directions from the tetramethylene bridge. In the crystal structure, weak intermolecular C-H...O hydrogen bonds and C-H... π stacking interactions link the title molecules into an infinite 3D supramolecular network structure.

Key Words: Bisoxime compound, Synthesis, Supramolecular structure.

INTRODUCTION

Salen-type compounds are one of most prevalent mixed-donor ligands in the field of coordination chemistry¹⁻³. They play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and supramolecular architectures. In the past few years, salen-type compounds have been used widely as ligands in the formation of transition metal complexes^{4,5}. Many salen-type complexes have been structurally characterized, but only a relatively small number of free salen-type bisoxime compounds have been characterized. As an extension of our work⁶⁻⁸, we report here the synthesis and crystal structure of a new salen-type bisoxime compound 3,3'-dibromo-1,1'-[butane-1,4-diylldioxybis(nitrilomethylidene)]dibenzene.

EXPERIMENTAL

3-Bromobenzaldehyde was purchased from Alfa Aesar and used without further purification. 1,4-Bis(aminoxy)butane was synthesized according to an analogous method reported earlier⁶. 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 APEX 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: 3,3'-Dibromo-1,1'-[butane-1,4-diylldioxybis(nitrilomethylidene)]dibenzene was synthesized according to an analogous method reported earlier^{7,8}. To an ethanolic solution (2 mL) of 3-bromobenzaldehyde (407.7 mg, 2.13 mmol) was added an ethanolic solution (3 mL) of 1,4-bis(aminoxy)butane (128.1 mg, 1.07 mmol). The mixture solution was stirred at 328 K for 4 h. When cooled to room temperature, the precipitate was filtered and washed successively with ethanol and ethanol-hexane (1:4), respectively. The product was dried under vacuum to yield 94.8 mg of the title compound. Yield, 19.6 %. m.p. 323.5-325.5 K. Anal. calcd. (%) for $C_{18}H_{18}N_2O_2Br_2$: C, 47.60; H, 3.99; N, 6.17. Found (%): C, 47.42; H, 3.83; N, 6.00. IR (KBr, ν_{max} , cm^{-1}): C=N, 1625 and C-O, 1176. 1H NMR (400 MHz, $CDCl_3$): 2.05 (t, $J = 4.0$ Hz, 4H, CH_2), 4.22 (t, $J = 4.0$ Hz, 4H, CH_2 -O), 6.86 (d, $J = 4.0$ Hz, 2H, PhH), 6.95 (s, 2H, PhH), 7.22 (s, 2H, PhH), 7.36 (d, $J = 4.0$ Hz, 2H, PhH), 8.03 (s, 2H, N=CH). Colourless needle-shaped single crystals suitable for X-ray diffraction studies were obtained after several weeks by slow evaporation from a methanol-acetonitrile mixed solution of 3,3'-dibromo-1,1'-[butane-1,4-diylldioxybis(nitrilomethylidene)]dibenzene.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.48 mm \times 0.38 mm \times 0.30 mm was placed on a Bruker Smart 1000 diffractometer equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated

MoK α radiation ($\gamma = 0.71073 \text{ \AA}$) at 298(2) K. The structure was solved by using the program SHELXS-97⁹ and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97¹⁰. 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: 696136.

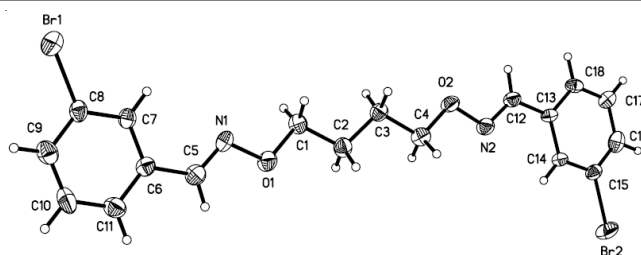


Fig. 1. Molecule structure of the title compound

TABLE-1 CRYSTAL DATA AND REFINEMENT PARAMETERS FOR THE TITLE COMPOUND	
Empirical formula	C ₁₈ H ₁₈ N ₂ O ₂ Br ₂
Formula weight	454.16
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Cell dimensions	a = 11.9330(16) Å, b = 4.8703(5) Å, c = 32.423(3) Å $\beta = 99.706(2)^\circ$
Volume	1857.4(4) Å ³
Z	4
Density (calculated)	1.624 mg/m ³
Absorption coefficient	4.377 mm ⁻¹
F ₍₀₀₀₎	904
Index ranges	-14 ≤ h ≤ 11, -5 ≤ k ≤ 5, -38 ≤ l ≤ 34
Reflections collected	8610/3256 [R _(int) = 0.0505]
Independent reflections	3256
Data/restraints/parameters	3256/0/217
Goodness of fit indicator	1.005
R [I > 2σ(I)]	R ₁ = 0.0766, wR ₂ = 0.1515
Largest diff. peak and hole	0.524 and -0.538 e. Å

RESULTS AND DISCUSSION

X-Ray crystallographic analysis revealed the crystal structure of 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 C₁₈H₁₈N₂O₂Br₂ molecules and all bond lengths and angles are in normal ranges^{6,7}. The molecule assumes an extended

conformation in which two benzaldehyde moieties are well separated from each other with a crystallographic inversion center (symmetry code: -x, -y, -z). Within the molecule, the two aromatic rings are aligned with the angle of 5.57(3)°, but extend in opposite directions from the tetramethylene bridge.

In the crystal structure, C-H... π (Ph) stacking interactions and weak intermolecular C-H...O hydrogen bonds link the neighboring molecules into an infinite three-dimensional supramolecular network structure. The title molecules are linked by a pair of intermolecular C9-H9... π_{centroid} (C13-C18) hydrogen bond interactions into a 1D infinite zigzag chain along the c-axis. Furthermore, this linkage is further stabilized by a pair of intermolecular C16-H16... π_{centroid} (C6-C11) hydrogen bond interactions to form an infinite 2D crapy layer parallel to the bc-plane (Fig. 2). The intermolecular C-H... π_{centroid} separations are *ca.* 3.214 Å for C16-H16... π_{centroid} (C6-C11) and *ca.* 3.231 Å for C9-H9... π_{centroid} (C13-C18), respectively (Table-3) and lie in the accepted distance range for this type of contacts¹¹. In addition, the adjacent crapy layers are further linked by the intermolecular C18-H18...O2 hydrogen bonds between the oxime oxygen atom and the methylene groups of the benzene ring. It is noteworthy that an infinite helices chain along the b-axis is formed by the C18-H18...O2 hydrogen bond interactions (Figs. 3 and 4). To sum up, with the help of intermolecular C-H...O and C-H... π hydrogen-bonding interactions, the crystal packing shows a self-assembling 3D supramolecular network structure.

TABLE-2 SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE TITLE COMPOUND					
Bond	Lengths	Bond	Lengths	Bond	Lengths
Br(1)-C(8)	1.901(8)	C(9)-C(10)	1.368(12)	O(2)-C(4)	1.419(8)
N(1)-C(5)	1.253(9)	C(12)-C(13)	1.480(10)	C(2)-C(3)	1.524(10)
N(2)-C(12)	1.265(9)	C(13)-C(18)	1.413(9)	C(5)-C(6)	93(11)
O(1)-C(1)	1.438(8)	C(15)-C(16)	1.387(11)	C(6)-C(11)	1.411(11)
C(1)-C(2)	1.520(10)	C(17)-C(18)	1.383(10)	C(8)-C(9)	1.380(11)
C(3)-C(4)	1.510(9)	Br(2)-C(15)	1.861(7)	C(10)-C(11)	1.342(11)
C(6)-C(7)	1.376(10)	N(1)-O(1)	1.419(7)	C(13)-C(14)	1.372(9)
C(7)-C(8)	1.387(10)	N(2)-O(2)	1.422(8)	C(14)-C(15)	1.386(10)
C(16)-C(17)	1.376(11)	-	-	-	-
C(5)-N(1)-O(1)	108.6(7)	C(14)-C(13)-C(18)	119.8(7)	C(11)-C(6)-C(5)	118.2(8)
N(1)-O(1)-C(1)	109.7(6)	C(18)-C(13)-C(12)	118.0(7)	C(9)-C(8)-C(7)	121.0(8)
O(1)-C(1)-C(2)	106.6(6)	C(14)-C(15)-C(16)	118.9(8)	C(7)-C(8)-Br(1)	119.4(6)
C(4)-C(3)-C(2)	110.7(6)	C(16)-C(15)-Br(2)	121.8(6)	C(11)-C(10)-C(9)	123.5(9)
N(1)-C(5)-C(6)	122.2(8)	C(16)-C(17)-C(18)	119.0(8)	N(2)-C(12)-C(13)	120.1(7)
C(7)-C(6)-C(5)	121.0(7)	C(12)-N(2)-O(2)	111.1(6)	C(14)-C(13)-C(12)	122.2(7)
C(6)-C(7)-C(8)	118.7(8)	C(4)-O(2)-N(2)	108.3(5)	C(13)-C(14)-C(15)	120.5(7)
C(9)-C(8)-Br(1)	119.6(6)	C(1)-C(2)-C(3)	112.3(7)	C(14)-C(15)-Br(2)	119.3(6)
C(10)-C(9)-C(8)	118.0(8)	O(2)-C(4)-C(3)	108.4(6)	C(17)-C(16)-C(15)	121.9(8)
C(10)-C(11)-C(6)	117.7(9)	C(7)-C(6)-C(11)	120.8(7)	C(17)-C(18)-C(13)	119.9(7)

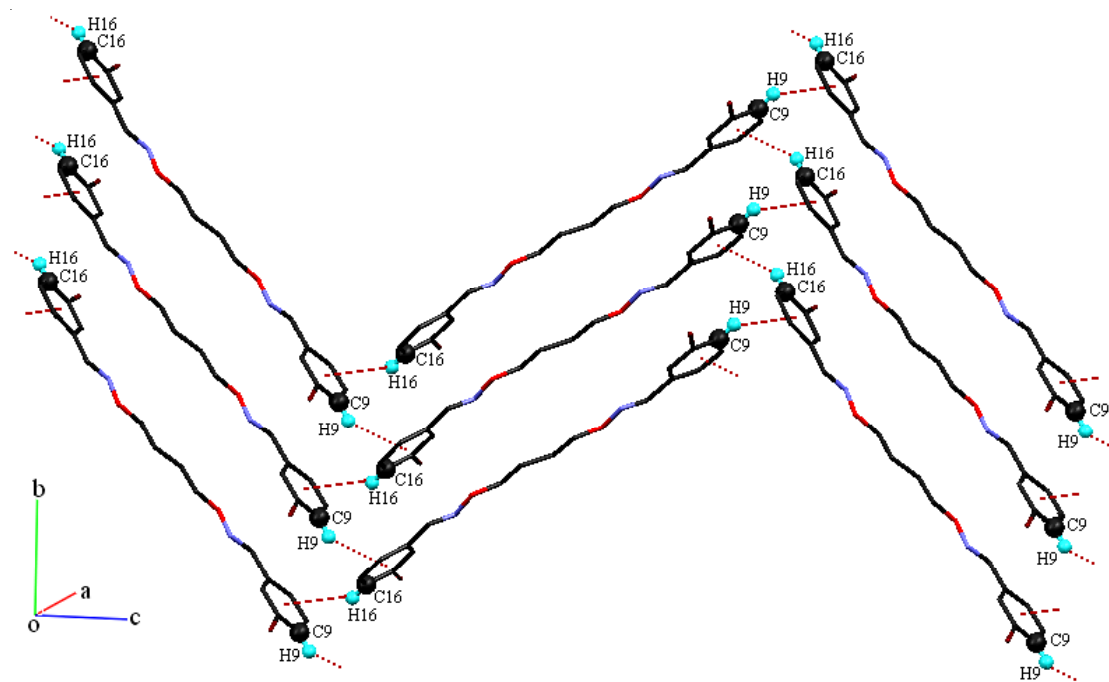


Fig. 2. View of the 1D supramolecular zigzag chain and 2D crapy layers within the title compound (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

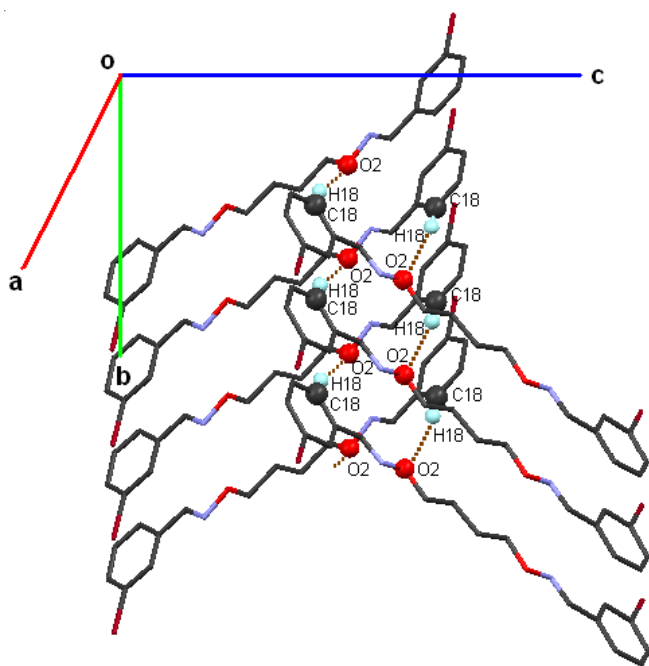


Fig. 3. Intermolecular C18-H18...O2 hydrogen bonds. For clarity, the H atoms not involved in the interactions have been omitted

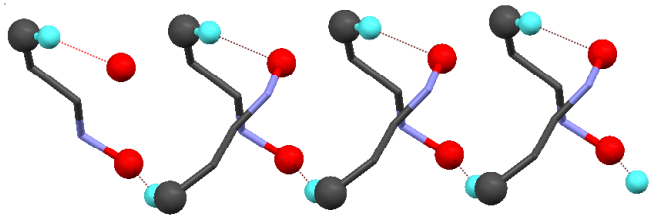


Fig. 4. Helix chain linked by C18-H18...O2 hydrogen bonds. For clarity, the non-contact atoms not involved in the interactions have been omitted

TABLE-3 HYDROGEN-BONDING DATA [Å, °]				
D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
C18-H18...O2	0.93	2.51	3.417(3)	161
C16-H16...Cg1 ^a	0.93	3.21	4.012(4)	146
C9-H9...Cg2 ^b	0.93	3.23	4.008(4)	143

^aCg1 is the C6–C11 ring centroids. ^bCg2 is the C13–C18 ring centroid.

ACKNOWLEDGEMENTS

The authors thank Young Scholars Science Foundation of Lanzhou Jiaotong University (2011007) for financial support of this work.

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