

NOTE

Synthesis and Characterization of 4,4'-Dimethoxy-1,1'-[(butane-1,4-diylldioxy)bis(nitrilomethylidyne)]dibenzene

YU-JIE DING^{1,*}, YANG WANG² and JIAN-GANG GAO¹

¹College of Biochemical Engineering, Anhui Polytechnic University, Wuhu 241000, P.R. China

²Material Examination Department, State Intellectual Property Office, Beijing 100088, P.R. China

*Corresponding author: E-mail: yujieding123@163.com

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The compound 4,4'-dimethoxy-1,1'-[(butane-1,4-diylldioxy)bis(nitrilomethylidyne)]dibenzene with the molecular formula $C_{20}H_{24}N_2O_4$ was synthesized by the reaction of 4-methoxybenzaldehyde with 1,4-bis(aminooxy)butane in ethanol medium and characterized structurally by X-ray crystallography. Intermolecular C-H...O hydrogen bonding is observed between C-H of methoxy groups and O atom from methoxy groups of the neighboring compound molecules. It is noted that the distances between the nearest benzene rings, which are parallel to that of another molecule, are about 2.466(2) Å in the crystal structure, exhibiting strong intermolecular π - π stacking interactions, which forms two-dimensional structures of the title compound.

Key Words: 4,4'-Dimethoxy-1,1'-[(butane-1,4-diylldioxy)bis(nitrilomethylidyne)]dibenzene, Synthesis, Crystal structure.

N_2O_2 type ligands such as salen-type bisoxime compound are easily obtained by the reaction of salicylaldehyde with diamines, coordinate to *d*-block transition metals in a tetradentate fashion to afford stable mononuclear¹, dinuclear², trinuclear³, tetranuclear⁴ and octanuclear⁵ complexes. Herein, a bisoxime compound, 4,4'-dimethoxy-1,1'-[(butane-1,4-diylldioxy)bis(nitrilomethylidyne)]dibenzene was designed and synthesized, which may be useful as a build block for larger supramolecules^{6,7}.

4-Methoxybenzaldehyde was purchased from Alfa Aesar and was used without further purification. 1,4-Bis(aminooxy)butane was synthesized according to a method reported earlier⁷. 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.

4,4'-Dimethoxy-1,1'-[(butane-1,4-diylldioxy)bis(nitrilomethylidyne)]dibenzene was synthesized according to a method reported earlier⁷. To an ethanolic solution (8 mL) of 4-methoxybenzaldehyde (408.44 mg, 3.0 mmol) was added an ethanol (8 mL) solution of 1,4-bis(aminooxy)butane (180.23 mg, 1.50 mmol). The mixture solution was stirred at 328 K for 3 h. The precipitate was filtered, washed successively with

ethanol/hexane (1:4) and hexane, respectively. The product was dried under vacuum and purified with recrystallization from ethanol to yield 284.77 mg of the title compound. Yield, 79.9%. m.p. 367-368 K. Anal. calcd. (%) for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found (%): C, 67.28; H, 7.00; N, 7.84.

Colourless block-shaped single crystals suitable for X-ray diffraction studies were obtained after *ca.* 2 months by slow evaporation at room temperature from a chloroform solution of 4,4'-dimethoxy-1,1'-[(butane-1,4-diylldioxy)bis(nitrilomethylidyne)]dibenzene.

X-Ray structure determination: The single crystal of the present compound, with approximate dimensions of 0.30 mm × 0.28 mm × 0.27 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 ($\lambda = 0.71073$ 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: 693775.

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

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

BOND	LENGTHS	BOND	LENGTHS	BOND	LENGTHS
N(1)-C(3)	1.265(7)	C(1)-C(2)	1.465(8)	C(5)-C(6)	1.382(7)
N(1)-O(1)	1.422(6)	C(2)-C(2) ^{#1}	1.480(12)	C(6)-C(7)	1.386(7)
O(1)-C(1)	1.413(7)	C(3)-C(4)	1.453(7)	C(7)-C(8)	1.383(7)
O(2)-C(7)	1.366(6)	C(4)-C(5)	1.380(7)	C(8)-C(9)	1.376(7)
O(2)-C(10)	1.436(7)	C(4)-C(9)	1.383(7)		
BOND	ANGLES	BOND	ANGLES	BOND	ANGLES
C(3)-N(1)-O(1)	111.1(5)	C(5)-C(4)-C(9)	118.0(5)	O(2)-C(7)-C(6)	115.0(5)
C(1)-O(1)-N(1)	110.1(4)	C(5)-C(4)-C(3)	123.0(5)	C(8)-C(7)-C(6)	119.4(5)
C(7)-O(2)-C(10)	118.2(5)	C(9)-C(4)-C(3)	118.9(5)	C(9)-C(8)-C(7)	119.8(5)
O(1)-C(1)-C(2)	110.4(5)	C(4)-C(5)-C(6)	121.2(5)	C(8)-C(9)-C(4)	121.7(5)
C(1)-C(2)-C(2) ^{#1}	115.0(7)	C(5)-C(6)-C(7)	119.9(5)		
N(1)-C(3)-C(4)	121.6(5)	O(2)-C(7)-C(8)	125.6(5)		

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

Empirical formula	C ₂₀ H ₂₄ N ₂ O ₄
Formula weight	356.41
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Pbca
Space group	Orthorhombic
Cell dimensions	a = 7.1042(10) Å, b = 6.1951(8) Å, c = 43.340(3) Å
Volume	1907.4(4) Å ³
Z	4
Density (calculated)	1.241 mg/m ³
Absorption coefficient	0.087 mm ⁻¹
F(000)	760
Index ranges	-8 ≤ h ≤ 8, -7 ≤ k ≤ 7, -38 ≤ l ≤ 51
Reflections collected	8685/1657 [R(int) = 0.0778]
Independent reflections	906
Data/restraints/parameters	1657/0/119
Goodness of fit indicator	1.076
R [I > 2σ(I)]	R ₁ = 0.0532, wR ₂ = 0.0819
Largest diff. peak and hole	0.270 and -0.338 e. Å ⁻³

The molecule is disposed about a crystallographic centre of symmetry and the molecule adopts an extended conformation where the two 4-methoxybenzaloxime moieties are separated from each other. The oxime groups and phenolic groups have anti-conformations and there are four weak C-H...O intermolecular hydrogen bonds, C10-H10B...O2 (d(C10-H10B) = 0.962 Å, d(H10B...O2) = 2.590(1) Å, d(C10...O2) = 3.389(2) Å, ∠C10-H10B...O2 = 127.38(2)°) in the crystal structure^{8,9}.

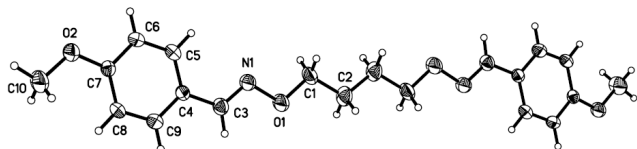


Fig. 1. Molecule structure of the title compound with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

It is noted that the distances between the nearest benzene rings, which are parallel to that of another molecule, are about 2.466(2) Å in the crystal structure, exhibiting very significantly strong intermolecular pi-pi stacking interactions, which forms two-dimensional structures of the title compound.

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REFERENCES

- W.K. Dong and Y.J. Ding, *Cryst. Res. Technol.*, **43**, 321 (2008).
- W.K. Dong, J.H. Feng and X.Q. Yang, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **37**, 189 (2007).
- S. Akine, T. Taniguchi and T. Nabeshima, *Inorg. Chem.*, **43**, 6124 (2004).
- W.K. Dong, J.H. Feng, L. Wang, L. Xu, L. Zhao and X.Q. Yang, *Transition Met. Chem.*, **32**, 1101 (2007b).
- S. Akine, W.K. Dong and T. Nabeshima, *Inorg. Chem.*, **45**, 4677 (2006).
- S.S. Sun, C.L. Stem, S.T. Nguyen and J.T. Hupp, *J. Am. Chem. Soc.*, **126**, 6314 (2004).
- (a). W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta.*, **362**, 117 (2009); (b). W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta.*, **362**, 1129 (2009); (c). W.K. Dong, X.N. He, H.B. Yan, Z.W. Lv, X. Chen, C.Y. Zhao and X.L. Tang, *Polyhedron*, **28**, 1419 (2009); (d). W.K. Dong, G. Wang, S.S. Gong, J.F. Tong, Y.X. Sun and X.H. Gao, *Transition Met. Chem.*, **37**, 271 (2012); (e). W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010); (f). W.K. Dong and J.G. Duan, *J. Coord. Chem.*, **61**, 781 (2008b).
- H.L. Wu, F. Jia, F. Kou, B. Liu, J.K. Yuan and Y. Bai, *Transition Met. Chem.*, **36**, 847 (2011).
- H.L. Wu, K.T. Wang, F. Jia, B. Liu, J.K. Yuan and Y. Bai, *J. Coord. Chem.*, **64**, 2676 (2010).