

## Synthesis and Crystal Structure of 5,5'-Dinitro-2,2'-[(1,4-butylene)dioxybis(nitrilomethylidene)]diphenol

LI WANG\*, YIN-XIA SUN, XIU-YAN DONG, LI ZHAO and LI XU

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

\*Corresponding author: E-mail: wangl@mail.lzjtu.cn; wangli\_78@126.com

(Received: 17 April 2012;

Accepted: 24 December 2012)

AJC-12608

The compound, 5,5'-dinitro-2,2'-[(1,4-butylene)dioxybis(nitrilomethylidene)]diphenol, was synthesized by the reaction of 5-nitrosalicylaldehyde with 1,4-bis(aminoxy)butane in ethanol and characterized structurally by single crystal X-ray diffraction method. The molecule lies across a crystallographic inversion centre and assumes a Z configuration with respect to the C=N bond. The strong intramolecular O3-H3...N1 and O6-H6...N2 hydrogen bonds play an important role in the stability for the crystal structure of 5,5'-dinitro-2,2'-[(1,4-butylene)dioxybis(nitrilomethylidene)]diphenol. It is noteworthy that the two benzene rings of present compound form a dihedral angle of 6.59 (3) Å and the distance between the two intramolecular benzene rings is 3.701 (2) Å, revealing weak intramolecular *p-p* stacking interaction along b axis.

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

### INTRODUCTION

The condensation of primary amines with salicylaldehyde and its derivatives yields salen-type compounds that are important versatile tetradentate chelating ligands in modern coordination chemistry<sup>1,2</sup>. In the past few decades, the synthesis, structure and properties of metallosalen complexes have stimulated much interest for their noteworthy contributions in single molecule-based magnetism, materials science, catalysis of many reactions like epoxidation, aziridination, *etc.*<sup>3-5</sup>. In comparison to the salen-type ligands, only a relatively small number of free salen-type bisoxime ligands have been characterized<sup>6,7</sup>. As an extension of our work<sup>8</sup> on the synthesis and structural characterization of salen-type bisoxime ligands, 5,5'-dinitro-2,2'-[(1,4-butylene)dioxybis(nitrilomethylidene)]diphenol, (Fig. 1), is reported here.

### EXPERIMENTAL

**Synthesis:** 5,5'-Dinitro-2,2'-[(1,4-butylene)dioxybis(nitrilomethylidene)]diphenol was synthesized according to an analogous method reported earlier. To an ethanolic solution (4 mL) of 5-nitrosalicylaldehyde (167.4 mg, 1 mmol) was added an ethanol solution (2 mL) of 1,4-bis(aminoxy)butane (60.07 mg, 0.50 mmol). The mixed solution was stirred at 338 K for 5 h. The precipitate was filtered and washed successively with ethanol and ether, respectively. The product was dried under vacuum to yield 160.3 mg of the title compound. Yield 76.6 %. m.p. 462.5-463.5 K. Anal. calcd. (%) for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>8</sub>:

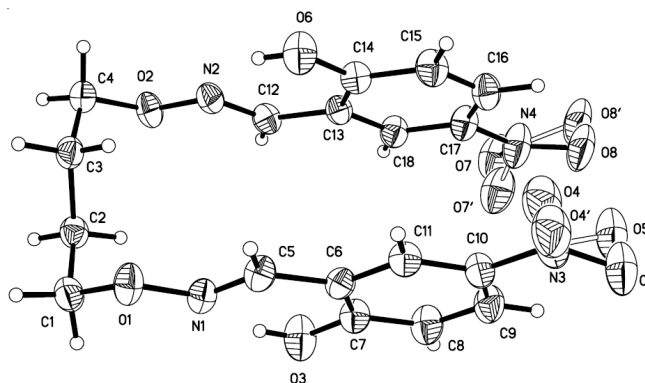


Fig. 1. Molecular structure of 5,5'-dinitro-2,2'-[(1,4-butylene)dioxybis(nitrilomethylidene)]diphenol with the atomic numbering scheme

C, 51.68; H, 4.34; N, 13.39. Found (%): C, 51.42; H, 4.51; N, 13.16. Colourless prismatic single crystals suitable for X-ray diffraction studies were obtained after one weeks by slow evaporation from a acetonitrile solution of the title compound.

**Crystal data and structure determination:** A colourless single crystal of the title compound, with approximate dimensions of 0.45 mm × 0.30 mm × 0.20 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<sub>α</sub> radiation (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXS-97<sup>9</sup> and Fourier difference techniques and refined by full-matrix least-squares method on F<sup>2</sup> using SHELXL-97<sup>10</sup>. Details of

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

Empirical formula	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>8</sub>
Formula weight	418.36
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)/c
Cell dimensions	a = 11.1627(12) Å, b = 14.0873(18) Å, c = 24.768(3) Å
Volume	3894.8(8) Å <sup>3</sup>
Z	8
Density (calculated)	1.427 mg/m <sup>3</sup>
Absorption coefficient	0.114 mm <sup>-1</sup>
F <sub>(000)</sub>	1744
Index ranges	-12 ≤ h ≤ 13, -16 ≤ k ≤ 16, -29 ≤ l ≤ 16
Reflections collected	15918/3439 [R <sub>(int)</sub> = 0.0464]
Independent reflections	3124
Data/restraints/parameters	3439/0/309
Goodness of fit indicator	1.079
R [I > 2σ(I)]	R <sub>1</sub> = 0.0505, wR <sub>2</sub> = 0.1135
Largest diff. peak and hole	0.154 and -0.169 e. Å <sup>-3</sup>

the data collection and refinements of title compound are given in Table-1. The non-hydrogen atoms were refined aniso-

tropically. Hydrogen atoms were added theoretically. CCDC: 644785.

## RESULTS AND DISCUSSION

A molecular structure with atom-numbering scheme and the packing diagram of C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>8</sub> are shown in Figs. 1 and 2, respectively. Selected bond lengths and bond angles are listed in Tables 2 and 3.

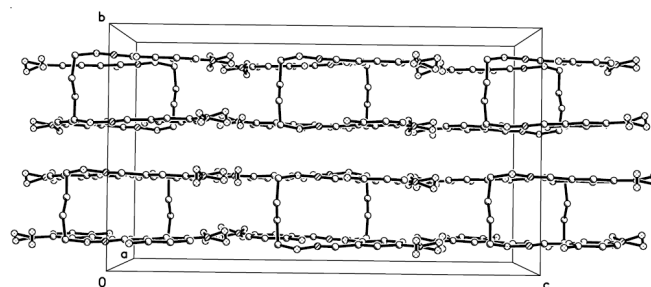


Fig. 2. Molecular packing arrangement in the unit cell

The molecule of the title compound lies across a crystallographic inversion centre (symmetry code: -x, -y, -z) to give 1/2 molecule per asymmetric unit, it assumes a Z configuration

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

Atom	Distance	Atom	Distance	Atom	Distance
N(1)-C(4)	1.271(3)	N(4)-O(7)	1.26(5)	C(6)-C(7)	1.409(4)
N(1)-O(1)	1.390(3)	N(4)-C(17)	1.459(4)	C(7)-C(8)	1.382(4)
N(2)-C(12)	1.273(4)	O(1)-C(1)	1.444(3)	C(8)-C(9)	1.354(4)
N(2)-O(2)	1.395(3)	O(2)-C(4)	1.445(3)	C(9)-C(10)	1.384(4)
N(3)-O(4')	1.22(6)	O(3)-C(7)	1.346(3)	C(10)-C(11)	1.365(4)
N(3)-O(4')	1.23(8)	O(3)-H(3)	0.8200	C(12)-C(13)	1.448(4)
N(3)-O(4)	1.24(4)	O(5)-C(14)	1.350(3)	C(13)-C(18)	1.385(4)
N(3)-O(4)	1.26(5)	C(1)-C(2)	1.509(4)	C(13)-C(14)	1.408(4)
N(3)-C(10)	1.457(4)	C(2)-C(3)	1.516(4)	C(14)-C(14)	1.383(4)
N(4)-O(8)	1.23(4)	C(3)-C(4)	1.499(4)	C(14)-C(15)	1.364(4)
N(4)-O(8')	1.24(6)	C(4)-C(5)	1.452(4)	C(15)-C(17)	1.385(4)
N(4)-O(7')	1.26(5)	C(5)-C(11)	1.386(4)	C(17)-C(18)	1.369(4)

TABLE-3  
SELECTED BOND ANGLES (°) FOR THE TITLE COMPOUND

Atom	Angle	Atom	Angle	Atom	Angle
C(5)-N(1)-O(1)	111.8(2)	C(1)-C(2)-C(3)	112.9(3)	C(10)-C(11)-C(6)	119.3(3)
C(12)-N(2)-O(2)	111.9(2)	C(4)-C(3)-C(2)	113.5(3)	N(2)-C(12)-C(13)	121.9(3)
O(5')-N(3)-O(4')	124(4)	O(2)-C(4)-C(3)	112.5(2)	C(18)-C(13)-C(14)	118.6(3)
O(5')-N(3)-O(4)	120(3)	N(1)-C(5)-C(6)	122.1(3)	C(18)-C(13)-C(12)	118.6(3)
O(4')-N(3)-O(4)	24(5)	C(11)-C(6)-C(7)	118.6(3)	C(14)-C(13)-C(12)	122.9(3)
O(5')-N(3)-O(5)	30(6)	C(11)-C(6)-C(5)	119.0(3)	O(6)-C(14)-C(15)	118.2(3)
O(4')-N(3)-O(5)	114(3)	C(7)-C(6)-C(5)	122.4(3)	O(6)-C(14)-C(13)	121.8(3)
O(4)-N(3)-O(5)	124(2)	O(3)-C(7)-C(8)	118.3(3)	C(15)-C(14)-C(13)	120.0(3)
O(5')-N(3)-C(10)	116(3)	O(3)-C(7)-C(6)	121.9(3)	C(16)-C(15)-C(14)	120.8(3)
O(4')-N(3)-C(10)	121(3)	C(8)-C(7)-C(6)	119.8(3)	C(15)-C(16)-C(17)	119.0(3)
O(4)-N(3)-C(10)	117(2)	C(9)-C(8)-C(7)	121.2(3)	C(18)-C(17)-C(16)	121.6(3)
O(5)-N(3)-C(10)	119.0(1)	C(8)-C(9)-C(10)	118.5(3)	C(18)-C(17)-N(4)	118.6(3)
O(8)-N(4)-O(8')	23(3)	C(11)-C(10)-C(9)	122.0(3)	C(16)-C(17)-N(4)	119.8(3)
O(8)-N(4)-O(7')	113.7(2)	C(11)-C(10)-N(3)	118.7(3)	C(17)-C(18)-C(13)	120.0(3)
O(8')-N(4)-O(7')	129(4)	C(9)-C(10)-N(3)	119.3(3)	O(8)-N(4)-O(7)	121(2)
O(8')-N(4)-O(7)	122(4)	O(8')-N(4)-C(17)	113(3)	N(1)-O(1)-C(1)	109.7(2)
O(7)-N(4)-O(7)	34(2)	O(7')-N(4)-C(17)	116.8(2)	N(2)-O(2)-C(4)	109.6(2)
O(8)-N(4)-C(17)	121(2)	O(7)-N(4)-C(17)	117.3(1)	O(1)-C(1)-C(2)	111.4(2)

with respect to the azomethine (C=N) bond. This structure is not similar to what was observed in our previously reported series salen-type compounds containing four-methene bridge, which often adopt an E or linear configuration. The four carbon atoms in the C1-C2-C3-C4 bridge are almost in the same plane with slight deviation of 0.037 Å below for C1 and C4, 0.036 and 0.038 Å above the plane for C2 and C3, respectively. The oxygen atoms of two nitro groups (O4, O5, O7 and O8) are disordered unequally over two different positions. The strong intramolecular O3-H3...N1 and O6-H6...N2 hydrogen bonds play an important role in the stability for the crystal structure of the title compound<sup>11-13</sup>. Noteworthy is that the two benzene rings of (I) form a dihedral angle of 6.59 (3) Å and the distance between the two intramolecular benzene rings is 3.701 (2) Å, revealing weak intramolecular  $\pi$ - $\pi$  stacking interaction along b axis.

#### ACKNOWLEDGEMENTS

This work was supported by the Foundation of the Education Department of Gansu Province (No. 0904-11), which is gratefully acknowledged.

#### REFERENCES

1. S. Akine, T. Takanori, W.K. Dong and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005).
2. W.K. Dong, J.H. Feng and X.Q. Yang, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **37**, 189 (2007).
3. P. Zhang, M. Yang and X.P. Lu, *Asian J. Chem.*, **19**, 2083 (2007).
4. N.S. Venkataramanan, G. Kuppuraj and S. Rajagopal, *Coord. Chem. Rev.*, **249**, 1249 (2005).
5. H.K. Fun, R. Kia, H. Kargar and A. Jamshidvand, *Acta Cryst.*, **E65**, o706 (2009).
6. W.K. Dong, J.G. Duan, H.L. Wu, J.Y. Shi and T.Z. Yu, *Z. Kristallogr. NCS*, **221**, 555 (2006).
7. W.K. Dong, J.G. Duan and G.L. Liu, *Transition Met. Chem.*, **32**, 702 (2007).
8. W.K. Dong, J.Y. Shi, J.K. Zhong, Y.Q. Tian and J.G. Duan, *Chin. J. Inorg. Chem.*, **24**, 10 (2008).
9. G.M. Sheldrick, SHELXS97, Program for Crystal Structure Determination, University of Göttingen, Germany (1996).
10. G.M. Sheldrick, *Acta Cryst.*, **A64**, 112 (2008).
11. W.K. Dong, C.E. Zhu, H.L. Wu, Y.J. Ding and T.Z. Yu, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **37**, 61 (2007).
12. H.L. Wu, K.T. Wang, F. Kou, F. Jia, B. Liu, J.K. Yuan and Y. Bai, *J. Coord. Chem.*, **64**, 2676 (2010).
13. W.K. Dong and Y.J. Ding, *Cryst. Res. Technol.*, **43**, 321 (2008).