NOTE

Synthesis and Crystal Structure of 4,4'-Dimethyl-1,1'-[butane-1,4-diylldioxy]bis(nitrilomethylidyne)dibenzene

WEN-KUI DONG*, YANG ZHANG, ZHENG-KUN WANG, YIN-XIA SUN and PENG-FEI LIU

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

*Corresponding author: E-mail: dongwk@126.com

(Received: 12 July 2012;

Accepted: 14 May 2013)

AJC-13499

A new bisoxime compound, 4,4'-dimethyl-1,1'-[butane-1,4-diylldioxy]bis(nitrilomethylidyne)dibenzene, has been synthesized and characterized structurally. There is a crystallographic twofold rotation axis passing through the middle point of the -CH₂-CH₂-CH₂-CH₂- linkage. The molecule adopts a *trans*-congration with respect to the methyldiene unit. There are no intramolecular and intermolecular hydrogen bonds. The two phenyl rings in each molecule are parallel to each other with a perpendicular interplanar spacing of *ca* 1.266(3) Å.

Key Words: Bisoxime compound, Synthesis, Crystal structure.

Particular attention has recently been paid to the synthesis and crystal structure of salen and its analogues, which consist two nitrogen and two oxygen donors and can easily form stable metal complexes¹⁻³. These complexes have wide applications, such as catalysts in various organic reactions⁴, magnetism⁵, nonlinear optical materials⁶ and biological models in understanding the structure of biomolecules and biological processes^{7,8}. Herein, we report the synthesis and crystal structure of a bisoxime compound, 4,4'-dimethyl-1,1'-[butane-1,4-diylldioxy]bis(nitrilomethylidyne)dibenzene.

4-Methyl benzaldehyde was purchased from Alfa Aesar and used without further purification. 1,4-Bis(aminooxy)-butane was synthesized according to an analogous method reported earlier⁹. The other reagents and solvents were analytical grade reagents from Beijing 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'-Dimethyl-1,1'-[butane-1,4-diylldioxy]bis(nitrilomethylidyne)dibenzene was synthesized according to reported method⁸. To an ethanol solution (3 mL) of 1,4-bis(aminooxy)butane (125.0 mg, 1.0 mmol) was added an ethanol solution (5 mL) of 4-methyl benzaldehyde (243.7 mg, 2.0 mmol). The reaction mixture was stirred at 328-333 K for 10 h. The formed precipitate was separated by filtration and washed successively

with ethanol and *n*-hexane. The product was dried under vacuum to yield 196.6 mg of the title compound. Yield, 60.6 %. m.p. 338.5-339.5 K. Anal. calcd. for C₂₀H₂₄N₂O₂: C, 74.04; H, 7.46; N, 8.64. Found: C, 74.08; H, 7.43; N, 8.61.

A solution of the title compound was dissolved in *n*-hexane and allowed to stand at room temperature for about two weeks, several colourless block-like single crystals suitable for X-ray crystallographic analysis were obtained.

X-ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.48 × 0.40 × 0.10 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 F² 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: 757706.

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 title compound crystallizes in the triclinic system, space group P-1. The single-crystal structure of the title compound is built up by discrete C₂₀H₂₄N₂O₂ molecules, in which all bond lengths are in normal ranges. There is a crystallographic two-fold rotation axis passing through the middle point of the

-CH₂-CH₂-CH₂-CH₂- linkage. The molecule adopts a *trans* conformation with respect to the methylenide unit. The two phenyl rings in each molecule are parallel to each other with a perpendicular interplanar spacing of about 1.266(3) Å and a C1-O1-N1-C3 torsion angle of -177.2(3)°. A view of the crystal packing of the title compound is given in Fig. 2.

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

Empirical formula	C ₂₀ H ₂₄ N ₂ O ₂
Formula weight	324.41
Temperature, K	298(2)
Wavelength, Å	0.71073
Crystal system	Triclinic,
Space group	P 2 ₁ /c
Cell dimensions, (Å°)	a = 4.7594(5), b = 9.579 (1), c = 10.567 (1); α = 102.284(2), β = 98.826(1), γ = 98.944(1)
Volume, Å ³	456.21(8)
Z	1
Density (calculated), mg/m ³	1.181
Absorption coefficient, mm ⁻¹	0.077
F(000)	174
Index ranges	-5 ≤ h ≤ 5, -11 ≤ k ≤ 10, -11 ≤ l ≤ 12
Reflections collected	2373/1590 [R(int) = 0.0266]
Independent reflections	599
Data/restraints/parameters	1590/0/109
Goodness of fit indicator	1.014
R [I > 2σ(I)]	R ₁ = 0.0576, wR ₂ = 0.1023
Largest diff. peak and hole, e ⁻ Å ⁻³	0.155 and -0.204

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

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

Bond	Lengths	Bond	Lengths
N(1)-C(3)	1.257(3)	C(4)-C(5)	1.383(3)
N(1)-O(1)	1.404(2)	C(5)-C(6)	1.372(3)
O(1)-C(1)	1.419(3)	C(6)-C(7)	1.380(3)
C(1)-C(2)	1.496(3)	C(7)-C(8)	1.368(3)
C(2)-C(2)	1.524(5)	C(7)-C(10)	1.500(3)
C(3)-C(4)	1.452(3)	C(8)-C(9)	1.380(3)
C(4)-C(9)	1.382(3)		
Bond	Angles	Bond	Angles
C(3)-N(1)-O(1)	110.3(2)	C(6)-C(5)-C(4)	120.6(2)
N(1)-O(1)-C(1)	109.9(2)	C(5)-C(6)-C(7)	121.8(2)
O(1)-C(1)-C(2)	108.2(2)	C(8)-C(7)-C(6)	117.2(2)
C(2)-C(2)-C(2)	113.3(3)	C(8)-C(7)-C(10)	121.4(3)
N(1)-C(3)-C(4)	123.1(2)	C(6)-C(7)-C(10)	121.4(3)
C(9)-C(4)-C(5)	117.9(2)	C(7)-C(8)-C(9)	121.9(2)
C(9)-C(4)-C(3)	122.9(2)	C(8)-C(9)-C(4)	120.5(2)
C(5)-C(4)-C(3)	122.9(2)

Fig. 2. A view of the crystal packing of the title compound

ACKNOWLEDGEMENTS

The authors acknowledged the Support of Science and Technology Fund of Lanzhou Jiaotong University (ZC2012003) and the Fundamental Research Funds for the Gansu Province Universities (212086).

REFERENCES

1. J.P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.*, **39**, 165 (2000).
2. W.K. Dong, X.N. He, Y.X. Sun, L. Xu and Y.H. Guan, *Acta Cryst.*, **E64**, o1917 (2008).
3. P. Pfeiffer, E. Breith, E. Lubbe and T.L. Tsumaki, *Ann. Chem.*, **503**, 84 (1933).
4. S. Akine, T. Taniguchi and T. Nabeshima, *Angew. Chem. Int. Ed.*, **41**, 4670 (2002).
5. N.C. Hoshino, *Chem. Rev.*, **174**, 77 (1998).
6. S.D. Bella and I. Fragalà, *Synth. Met.*, **115**, 191 (2000).
7. W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010).
8. 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).
9. W.K. Dong, G. Wang, S.S. Gong, J.F. Tong, Y.X. Sun and X.H. Gao, *Transition Met. Chem.*, **37**, 271 (2012).