Synthesis and Crystal Structure of 2,2'-(1,2-Ethylenedioxy)bisbenzaldehyde *O,O'*-Diethyldioxime

LI ZHAO*, YU-JIE ZHANG, SHOU-TING ZHANG, HONG-XIA GUO and QIAN CHENG

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

*Corresponding author: E-mail: zhaoli_72@163.com

(Received: 25 September 2012;

Accepted: 20 March 2013)

AJC-13141

The compound, 2,2'-(1,2-ethylenedioxy)-*bis*-benzaldehyde *O,O'*-diethyldioxime, has been synthesized by 2,2'-(1,2-ethylenedioxy)-*bis*-benzaldehyde *O,O'*-diethyldioxime and ethoxyamine hydrochloride in ethanolic solution and characterized structurally by X-ray crystallography. The molecule of the title compound adopts an extended conformation where the two oxime groups are apart from each other. The two benzene rings are parallel to each other. In the crystal structure, intermolecular C7-H7...O2 hydrogen bonds link the molecules forming an infinite 1D chain-like supramolecular structure.

Key Words: Bisoxime compound, Synthesis, Crystal structure.

INTRODUCTION

Oxime-type compounds ($-C=N-OR$) are a kind of important ligands containing N atoms, they are usually synthesized by the condensation of ketones or aldehydes with hydroxylamine *etc.*¹. Much attention has recently been paid to the synthesis and crystal structure of oxime-type compounds and their derivatives² because they can provide new topologies for functional materials, in which coordination forms and functionality are significant variables³, they also can accommodate one, two or more metal centers and form homo- and heteronuclear metal complexes serving as catalysts⁴, models of reaction centers of metalloenzymes⁵, models of reaction centers of metalloenzymes⁶, nonlinear optical materials and molecular recognition and biological agents⁷. They are also useful in constructing supramolecular structures⁸. Thus, new materials can be produced by using these compounds, which seem to be suitable candidates for further chemical modifications^{9,10}. Here, the synthesis and crystal structure of 2,2'-(1,2-ethylenedioxy)-bisbenzaldehyde *O,O'*-diethyldioxime has been reported carefully.

EXPERIMENTAL

The 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 400-4000 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.

2,2'-(1,2-ethylenedioxy) bisbenzaldehyde was synthesized by refluxing of salicylaldehyde, sodium hydroxide and 1,2-dibromoethane in ethanol-water mixture under nitrogen for *ca.* 48 h¹¹.

2,2'-(1,2-Ethylenedioxy)bisbenzaldehyde *O,O'*-diethyldioxime was synthesized analogously to the method reported in the previous literature¹². To a hot ethanol solution (15 mL) of 2,2'-(1,2-ethylenedioxy)-*bis*-benzaldehyde (270.3 mg, 1.0 mmol) was first added an ethanolic solution (10 mL) of ethoxyamine hydrochloride (390.2 mg, 4.0 mmol), then NaOH (400 mg, 10 mmol). After the mixture had been stirred under reflux for 4 h, 10 mL distilled water was added. Then the solution was filtered and concentrated to about 15 mL over night in 271 K. The resulting pale-yellow solid product was filtered and washed successively with distilled water and ethanol/hexane (1:4). The isolated compound was dried under vacuum to yield 242.7 mg of the title compound. Yield 68.1 %. m.p. 337-338 K. Anal. calcd. for $C_{20}H_{24}N_2O_4$ (%): C, 67.40; H, 6.79; N, 7.86. Found (%): C, 67.57; H, 6.61; N, 7.72.

Colourless needle-like single crystals suitable for X-ray diffraction studies were obtained after about one week by slow evaporation from a ethanol/ H_2O (3:1) solution of the title compound.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of $0.43 \times 0.09 \times 0.06$ mm³ 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-97¹³. 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: 901642.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT
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	Monoclinic
Space group	C2/c
Cell dimensions	a = 15.5401(2) Å, b = 4.8750(4) Å, c = 26.330(2) Å, β = 105.4710(1)°
Volume	1922.4(3) Å ³
Z	4
Density (calculated)	1.231 mg/m ³
Absorption coefficient	0.086 mm ⁻¹
F(000)	760
Index ranges	-18 ≤ h ≤ 12, -5 ≤ k ≤ 5, -29 ≤ l ≤ 31
Reflections collected/unique	4547/1679 [R(int) = 0.0802]
Independent reflections	1160
Data/restraints/parameters	1679/0/120
Goodness of fit indicator	1.054
R [I > 2σ(I)]	R ₁ = 0.0437, wR ₂ = 0.0962
Largest diff. peak and hole	0.032 and -0.264 e.Å ⁻³

RESULTS AND DISCUSSION

X-ray crystallographic analysis revealed the crystal structure of the title compound. The structure is shown in Fig. 1 and C7-H7...O2 hydrogen bonds interactions are shown in Fig. 2 and The 1D chain-like supermolecular model of the compound is shown in Fig. 3. Crystal data and structure refinement for the title compound are listed in Table-1. Selected bond distances and angles are listed in Table-2. The crystal structure of the title compound is only built up by the C₂₀H₂₄N₂O₄ molecules, in which all bond lengths are in normal ranges. The molecule adopts an extended conformation where the two oxime groups are apart from each other. The two benzene rings are parallel to each other. In the crystal structure, intermolecular C7-H7...O2

hydrogen bonds link the molecules forming an infinite 1D chain-like supramolecular structure¹⁴⁻¹⁶.

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

Fig. 2. C7-H7...O2 intermolecular hydrogen bond along c axis

Fig. 3. 1D chain-like supermolecular model of the title compounds

ACKNOWLEDGEMENTS

This work was supported by the Foundation of Preparative Research of Jin-Chuan Corporation (No. 209125-1104), which is gratefully acknowledged.

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
N(1)-C(2)	1.235(8)	O(2)-C(9)	1.406(8)	C(4)-C(5)	1.365(1)
N(1)-O(2)	1.381(7)	C(1)-C(1)	1.468(1)	C(5)-C(6)	1.399(1)
O(1)-C(4)	1.335(8)	C(3)-C(4)	1.400(9)	C(6)-C(7)	1.334(9)
O(1)-C(1)	1.403(7)	C(3)-C(8)	1.436(9)	C(9)-C(10)	1.457(1)
C(2)-C(3)	1.421(1)	C(7)-C(8)	1.318(9)		
Bond	Angles	Bond	Angles	Bond	Angles
C(2)-N(1)-O(2)	114.3(8)	C(4)-C(3)-C(8)	116.0(9)	C(7)-C(6)-C(5)	121.2(9)
C(4)-O(1)-C(1)	118.1(6)	C(2)-C(3)-C(8)	124.2(8)	C(8)-C(7)-C(6)	118.2(9)
N(1)-O(2)-C(9)	111.2(7)	O(1)-C(4)-C(5)	125.5(7)	C(7)-C(8)-C(3)	124.5(8)
O(1)-C(1)-C(3)	105.3(8)	O(1)-C(4)-C(3)	116.1(8)	O(2)-C(9)-C(10)	108.6(8)
N(1)-C(2)-C(3)	123.3(9)	C(5)-C(4)-C(3)	118.4(8)		
C(4)-C(3)-C(2)	119.8(8)	C(4)-C(5)-C(6)	121.6(8)		

REFERENCES

1. W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.*, **67b**, 197 (2012).
2. W.K. Dong, J.F. Tong, Y.X. Sun, S.S. Gong and L. Li, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **41**, 155 (2011).
3. W.K. Dong, G. Wang, S.S. Gong, J.F. Tong, Y.X. Sun and X.H. Gao, *Transition Met. Chem.*, **37**, 271 (2012).
4. W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009).
5. 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).
6. J.P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.*, **39**, 165 (2000).
7. S.S. Sun, C.L. Stern, S.T. Nguyen and J.T. Hupp, *J. Am. Chem. Soc.*, **126**, 6314 (2004).
8. A.K. Sharma, F. Lloret and R. Mukherjee, *Inorg. Chem.*, **46**, 5128 (2007).
9. C. Policar, F. Lambert, M. Cesario and I. Morgenstern-badarau, *Eur. J. Inorg. Chem.*, **12**, 2201 (1999).
10. D.A. Atwood and M.J. Harvey, *Chem. Rev.*, **101**, 37 (2001).
11. I.M. Atkinson, L.F. Lindoy, O.A. Matthews, G.V. Meehan, A.N. Sobolev and A.H. White, *Aust. J. Chem.*, **47**, 1155 (1994).
12. W.K. Dong, J. Yao, Y.X. Sun, L. Li and J.C. Wu, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **40**, 521 (2010).
13. G.M. Sheldrick, *Acta Crystallogr.*, **A64**, 112 (2008).
14. W.K. Dong, Y.X. Sun, G.H. Liu, L. Li, X.Y. Dong and X.H. Gao, *Z. Anorg. Allg. Chem.*, **638**, 1370 (2012).
15. W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009).
16. H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu and Y. Bai, *Z. Naturforsch.*, **66b**, 1049 (2011).