Synthesis of Di and Tetraoximes from the Reaction of Phenylendiamines with Dichloroglyoxime

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ABSTRACT: 2,5,10,13-Tetraazatricyclo $[12,2,2,2^{6,9}]$ icosa-1(16),6,8,14,17,19-hexene-3,4,11,12tetraone tetraoxime (**1a**) and 2,5,11,14-tetraazatricyclo $[13,3,1,1^{6,10}]$ icosa-1(19),6,8,10(20),15,17hexaene-3,4,12,13-tetraonetetraoxime (**1b**) were obtained from condensation of 1,4- and 1,3phenylendiamine with dichloroglyoxime, respectively. The reaction of 1,2-phenylendiamine with dichloroglyoxime resulted in the production of (2Z,3Z)-1,4-dihydroquinoxaline-2,3-dione dioxime (**2**). The x-ray structure determination of compound **2** shows the piprazine ring is rather planar relative to the fused aromatic ring. The results show that a resonance occurs between the aromatic ring and the C=N bond, through N₄ and N₃ atoms of the molecule. The results from x-ray data, indicated that the molecules **2** could exist as a dimmer by intermolecular hydrogen bonding between NH and OH groups.

KEY WORDS: *Phenylendiamine, Dichloroglyoxime, vic-Dioximes, Crystal Structure, Intermolecular hydrogen bonds.*

INTRODUCTION

vic-Dioximes have been used as general industrial chemicals [1]. Oxime ligands are used as analytical reagents [2,3] and serve as models for biological systems [4-7] as well as catalysts in chemical processes [8,10]. Dioxime ligands are also successful sequestering agents for transition metals and other ions [11]. *vic*-Dioximes and their complexes constitute an important class of compounds having versatile reactivity [8-9]. Since the discovery of cobaloximes as the model compound for coenzyme B_{12} many advances have been made in structural and spectroscopic methodologies [6-10]. Tetraoxime molecules have been reported before as rare

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EXPERIMENTAL

All chemical reagents were obtained from Merck and were used without further purification. Melting points were measured on an Electrothermal 9200 apparatus and are uncorrected. Elemental analyses for C, H and N were performed using a Heraeus CHN-O Rapid analyzer. Mass spectra were recorded on a Finnigan-Matt 8430 GC-Mass and Shimatzu 5050 QD spectrometers. ¹H and ¹³C NMR

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^{[12,13].} In this report we describe a facile condensation of phenylendiamines with dichloroglyoxime to produce a new di and tetraoximes rings.

spectra were recorded with a Brucker DRX-500 AVANCE, DMSO- d_6 was used as solvent. IR spectra were recorded on a Shimadzu IR-460 spectrometer.

Synthesis of 5,8,13,16-tetrahydrodibenzo[b,h] [1,4,7,10] tetraazacyclododecine [6,7,14,15] tetraonetetraoxime (1a)

To a stirring solution of 1,4-phenylenediamine (1.08 g, 10 mmole), 0.2 g, Na₂CO₃ in 40 ml MeCN a solution of dicholoroglyoxime (1.57 g, 10 mmole) in 20 ml MeCN was added at 0-5 °C. After 2 h stirring at room temperature, the mixture was filtered and precipitate was washed with cold MeCN. Recrystallization from MeCN. Yield: 1.91 g (94%), mp 230-231 °C. IR (KBr) cm⁻¹: 3400(NH), 2500-3500(OH), 1620(C=N), 960(N-O). ¹H-NMR, ppm: 10.22(4H,OH), 8.83, 7.79(4H, NH), 6.56, 6.58(dd, 8H). ¹³C-NMR, ppm: 143.65, 134.59, 122.17, and 120.29. The EI-MS, m/z: $385(m+1)^+$. Elemental analysis calculated for C₁₆H₁₆N₈O₄: C, 50; H, 4.16; N, 29.16. Found: C, 50.03; H, 4.16; N, 29.15.

Synthesis 2,5,11,14-tetraazatricyclo [13,3,1,1^{6,10}] icosa-1(19),6,8,10(20),15,17-hexaene-3,4,12,13-tetraonetetraoxime (1b)

It was prepared according to the same procedure as described for the preparation of **1a** at room temperature. Yield: 69%, mp178 °C. IR (KBr) cm⁻¹: 3240(NH), 2500-3500(OH), 1610(C=N), 940(N-O). ¹H-NMR, ppm: 10.72(s, 4H, OH), 8.49(bs, 4H, NH), 6.23-7.18(m, 8H). ¹³C-NMR, ppm: 138.16, 134.49, 122.06, 119.30 and 116.90. The EI-MS, m/z: $385(m+1)^+$. Elemental analysis calculated for C₁₆H₁₆N₈O₄. C, 50; H, 4.16; N, 29.16. Found: C, 49.98; H, 4.17; N, 29.13.

Synthesis of (2Z,3Z)-1,4-dihydroquinoxaline-2,3-dione dioxime (2)

The reaction of 1,2-phenylendiamine with dicholoroglyoxime under similar condition of 1**a**, leads to **2**. Recrystallization from EtOH (70%). Yield: 1.78 g (93%), mp 239-240 °C. IR (KBr) cm⁻¹: 3400 (NH), 2500-3500(OH), 1640(C=N), 980(N-O). ¹H-NMR, ppm: 10.13(bs, 2H, OH), 9.46(bs, 2H, NH), 6.71, 7.18(dd, 4H). ¹³C-NMR, ppm: 138.45, 125.90, 121.03, and 114.57. The EI-MS, m/z: 384 (2m⁺), 192(m⁺), 193(m+1). Elemental analysis calculated for $C_8H_8N_4O_2$: C, 50; H, 4.16; N, 29.16. Found: C, 50.01; H, 4.17; N, 29.14. It should be

noted, that compound **2** has been synthesized via another procedure but resulting in low yield [12].

X-ray structure analysis of 2

The clear colorless crystal with dimensions 0.4×0.2×0.2 mm crystallized from MeCN /H2O was used for data collection on a Bruker SMART 1000 CCD diffractommeter with graphite monochromated MoKa (λ=0.71073 Å). C₈H₈N₄O₂, FW= 192.18. Triclinic crystals in a P1 Space group, a=8.3998 (16) Å, b=8.3888(13) Å, c=13.129(4) Å, α = 102.68(6)°, β =102.666(4)°, γ = 108.316(3)°, V=814.2(2) Å⁻³. Z=4, $D_{calc} = 1.568 \text{ g/cm}^3$. $\mu = 0.118 \text{ mm}^{-1}$, F (000) = 400, T=120 (2) K. Of the 9581 total reflections 4648 were unique $(R_{int} = 0.0539)$. The structure was solved by direct methods (SHELEXTL)[15] and refined by full-matrix least-squares on F^2 (isotropic refinement of the molecule and location of remaining non-hydrogen atoms from a difference Fourier map and subsequent anisotropy refinement on all atoms; H atoms were found after highangle refinement in a difference Fourier map and their positions included in the final stages of refinement), factors of R1=0.0671, wR2=0.1347 for 2491 reflections with I $<2\sigma$ (I). No significant features, only ripples from -0.290 to 0.341 e Å⁻³, were observed in the final difference map. The nonhydrogen atoms were refined anisotropically. Atomic coordinate, temperature factors, bond distances, bond and torsion angles have been deposited at the Cambridge Crystallographic Data Center (CCDC No; 271443). These data can be obtained free of charge via WWW.ccdc.cam.ac.uk/conts/retrieving; html (or from Cambridge Crystallographic Data Center; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The compounds 2,5,10,13-tetraazatricyclo $[12,2,2,2^{6,9}]$ icosa -1(16),6,8,14,17,19-hexene-3,4,11,12-tetraonetetraoxime (**1a**) and 2,5,11,14-tetraazatricyclo $[13,3, 1,1^{6,10}]$ icosa-1(19),6,8,10(20),15,17-hexaene-3,4,12,13-tetraone tetraoxime (**1b**) were obtained from condensation of dichloroglyoxime with 1,4-phenylendiamine and 1,3phenylendiamine in alkaline solution of MeCN at 0-5 °C and room temperature, respectively (scheme 1).

But, in the similar conditions, the reaction of 1,2phenylendiamine with dichloroglyoxime leads to product (2Z,3Z)-1,4-dihydroquinoxaline-2,3-dione dioxime (**2**).





Scheme 2.



Fig. 1: ORTEP diagram of (2Z,3Z)-1,4-dihydroquinoxaline-2,3-dione dioxime (2).

The structures of **1** and **2** were deduced from their elemental analyses and their IR, ¹H and ¹³C NMR spectra. The mass spectra of these compounds are fairly similar, and confirm their molecular weights, as expected. In alkaline solutions the products are stable. But, compounds **1** are decomposed in acidic media (pH<4). The structure of the compound **2** was established by X-ray crystallography (Fig. 1).

There are unusual structural features in the molecule. The C-N bonds are smaller than usual values and bond



Fig. 2: Unit cell showing π - π stacking interaction between aromatic rings and hydrogen bonding in compound 2.



Fig. 3: Possible isomer of cyclic vic-Dioximes.

angles around the N₃ or N₄ have sp^2 characteristics (table 1). Torsion angles for N₄-C₈-C₃-N₃, C₈-C₃-N₃-C₂ C₃-C₈-N₄-C₁ are 2.2°, 3.0° and 3.0° respectively. The piprazine ring is rather planar relative to fused aromatic ring. These results show that a resonance occurs between aromatic ring and C=N bond, through N₄ and N₃ atoms of the molecule. This could be the result of influence on bond lengths, angles, pyramidal and planarity of piprazine ring.

The torsion angles of N_1 - C_1 - C_2 - N_2 , N_4 - C_1 - C_2 - N_3 , and C_1 - C_2 - N_3 - C_3 are 14.1°, 16.6°, and -12.3° respectively.

Bond lengths	(Å)	Bond lengths	(Å)
C ₁ -N ₁	1.290(3)	C ₃ -C ₈	1.392
C1-N4	1.360(3)	N ₄ -C ₈	1.420(3)
C ₁ -C ₂	1.481(3)	N2-O2	1.420(2)
C ₂ -N ₂	1.287(3)	O ₁ -H ₁₀	0.8661
C ₂ -C ₃	1.361	O ₂ -H _{2O}	0.8364
N ₃ -C ₃	1.403(3)	N ₃ -H _{3N}	1.0465
Bond angles	(°)	Bond angles	(°)
N ₁ -C ₁ -N ₄	124.8(2)	C1-N4-C8	122.97(19)
N ₁ -C ₁ -C ₂	117.94(18)	C ₁ -N ₄ -H _{4N}	119.6
N ₄ -C ₁ -C ₂	117.20(19)	C ₈ -N ₄ -H _{4N}	116.3
N ₂ -C ₂ -N ₃	125.02	N ₃ -C ₃ -C ₈	118.88(19)
N ₂ -C ₂ -C ₁	117.86(19)	C ₃ -C ₈ -N ₄	118.82(19)
N ₃ -C ₂ -C ₁	117.16(18)	C ₁ -N ₁ -O ₁	110.04(17)
C ₂ -N ₃ -C ₃	123.06	N ₁ -O ₁ -H ₁₀	105.5
C ₂ -N ₃ -H ₃	121.0	C ₂ -N ₂ -O ₂	109.92(17)
C ₃ -N ₃ -H	113.1	N ₂ -O ₂ -H ₂₀	103.6
Torsion angles	(°)	Torsion angles	(°)
N ₁ -C ₁ -C ₂ -N ₂	14.1(3)	C ₁ -C ₂ -N ₂ -O ₂	-178.4(18)
N ₄ -C ₁ -C ₂ -N ₃	16.6(3)	N ₂ -C ₂ -N ₃ -C ₃	168.9(2)
N ₃ -C ₃ -C ₈ -N ₄	2.2(3)	C ₁ -C ₂ -N ₃ -C ₃	-12.3(3)
N_4 - C_1 - N_1 - O_1	0.1(3)	C ₈ -C ₃ -N ₃ -C ₂	3.0(3)
$C_2-C_1-N_1-O_1$	178.44(18)	N ₁ -C ₁ -N ₄ -C ₈	169.1(2)
N ₃ -C ₂ -N ₂ -O ₂	0.4(3)	C ₂ -C ₁ -N ₄ -C ₈	-12.3(3)

Table 1: Selected bond lengths (Å), bond angles (°) and torsion angles (°).

These data show that C_1 and C_2 atoms are not coplanar, therefore the C_1 - C_2 bond shows a single bond characteristic and there is not a resonance between them. The results from x-ray data, as shown in Fig. 1, indicated that the molecule **2** could exist as a dimmer by intermolecular hydrogen bonding between NH and OH groups. The corresponding distance and angle for hydrogen bonds are given in table 2. The unit cell of the resulting crystal, shown in Fig. 2, clearly revealed that a three dimensional network is formed owing to the presence of intermolecular hydrogen bonding interaction. There is a face to face π - π stacking [14]. The experimental data and structural models show the existence of three possible cyclic *vic*-dioximes configurations (anti, amphi and syn) (Fig. 3). The isomer distribution depends on steric effects of substitutions and the possibility of hydrogen bonding between the oxime groups [16]. The torsion angles of molecule **2**, N_3 - C_2 - C_1 - N_1 , C_2 - C_1 - N_1 - O_1 , N_4 - C_1 - C_2 - N_2 , C_1 - C_2 - N_2 - O_2 , confirm an anti configuration and the oxime groups will not be coplanar unless they are linked by a hydrogen bond. Mass spectra of **2** show a molecular ion peak at 384 m/z.

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D-H	D (D-H) Å	d (HA) Å	<dha°< th=""><th>d (DA) Å</th><th>А</th></dha°<>	d (DA) Å	А
O ₁ -H ₁₀	0.866	1.981	149.41	2.762	\mathbf{N}_1
O ₂ -H ₂₀	0.836	2.003	151.13	2.765	N_2
O _{1A} -H _{10A}	0.866	1.973	151.42	2.765	N _{1A}
O _{2A} -H _{20A}	0.845	1.986	152.94	2.766	N _{2A}
O _{2A} -H _{20A}	0.845	2.649	128.25	3.241	O _{2A}
N _{3A} -H _{3NA}	1.069	2.430	131.26	3.237	O ₁
N _{3A} -H _{3NA}	1.069	2.558	147.07	3.504	O_2
N ₃ -H _{3N}	1.081	2.428	130.89	3.240	O _{1A}
N ₃ -H _{3N}	1.081	2.546	146.71	3.500	O _{2A}
N ₄ -H _{4N}	1.047	2.546	123.19	3.241	O _{2A}
N ₄ -H _{4NA}	1.015	2.495	129.62	3.238	O ₂
N ₄ -H _{4NA}	1.047	2.544	151.56	3.500	O _{1A}

Table 2: Hydrogen bonds D-H...A in the crystal of (2Z,3Z)-1,4-dihydroquinoxaline-2,3-dione dioxime (2).

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REFERENCES

- [1] Kanno, H. and Yammamoto, H. *European Patent*, 0,636,605A1 (1994).
- [2] Banks, C.V., Rec. Chem. Prog., 25, 85 (1964).
- [3] Singh, R.B., Garg, B.S. and Singh, R. P., *Talanta*, 26, 425 (1979).
- [4] Ramadan, A.E., El-Mehasseb, I.M. and Isssa, R.M., *Transition Met. Chem.*, **22**, 529 (1997).
- [5] Lance, K.A., Dzugan, S., Busch, D.H. and Alcock, N.W., *Gazz. Chim. Ital.*, **126**, 251 (1996).
- [6] Schrauzer, G.N., Acc. Chem. Res., 1, 97 (1968).
- [7] Tovrog, B.S., Kitko, D.J. and Drago, R.S., *J. Am. Chem. Soc.*, **98**, 5144 (1976).
- [8] Boyer, J.H., Chem. Rev., 80, 495 (1980).
- [9] Chakravorty, A., Coord. Chem. Rev., 13, 1 (1974).
- [10] Schrauzer, G.N. and Kohnle, J., Chem. Ber., 97, 3056 (1964).
- [11] Luneau, D., Oshio, H., Okawa, H. and Kida, S., *Chem. Lett.*, 443 (1989).
- [12] Grundman, G., Justus. Liebigs. Ann. Chem, 687, 191 (1965).
- [13] Coburn, M, D., J. Heterocyclic. Chem. 5, 83 (1968).
- [14] Greenwood, N. N., and Earnshaw, A., "Chemistry of the Elements", pergamon press, oxford, 235 (1986).
- [15] Sheldrick, G. M., SHELXTL (1998 b) v. 5.10,

"Structure Determination Software Suite", Bruker AXS, Madison, Wisconsin, USA.

[16] Willer, R., Moore, D. W., J. Org. Chem. 50, 5123 (1985).