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Synthesis of New Dioximes and Tetraoximes from Reaction of Aminothiophenoles with Dichloroglyoxime

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The reaction of 2-aminothiophenol with dichloroglyoxime in alkaline solution of MeOH led to (2E,3E)-2H-1,4-benzothiazine-2,3(4*H*)dionedioxime (**1**). The compounds (2Z,6Z)-1,4-*bis*(2-mercaptophenyl)-piprazine-2,3,5,6-tetraone tetraoxime (**2**), (1Z,2Z)-$N^{1'}$,$N^{2'}$-dihydroxy-N^1,N^2-*bis*-(2-mercaptophenyl)ethanediimidamide (**3**), *bis*(2-aminophenyl) (1Z,2Z)-N^1,N^2-dihydroxyethane *bis*-(imidothioate) (**4**) and 2-aminophenyl (1Z,2Z)-N-hydroxy-2-hydroxyimino-2-[(2-mercaptophenyl)amino]ethanimidothioate (**5**), were obtained from the reaction of 1,2-aminothiophenol with dichloroglyoxime in different condition. The compounds (**3, 4** and **5**) can be converted to (**1**) in the presence of dichloroglyoxime. But, In the same condition compounds (3E,4E,11E, 12E)-2,10-dithia-5,13-diazatricyclo[12.2.2.$2^{6,9}$]icosa-1(16),6,8,14,17,19-hexaene-3,4,11,12-tetraone tetraoxime (**6a**) and (3E,4E,12E, 13E)-2,11-dithia-5,14-diazatricyclo-[13.3.1.$1^{6,10}$]icosa-1(19), 6(20), 7,9,15,17-hexaene-3,4,12,13-tetraonetetraoxime (**6b**) were synthesized from the reaction of 1,4- and 1,3-aminothiophenol with dichloroglyoxime, respectively.

Key Words: *vic*-Dioxime, Tetraoxime, Aminothiophenol, X-Ray crystallography.

INTRODUCTION

The reaction of amines or thiols with dichloroglyoxime (DCGO) has yielded various substituted di, tetra, polyamino or thioglyoximes derivatives[1-5]. Recently metal containing oxime complexes are utilized in medicine as well. Technetium(V) and copper(II) complexes containing *vicinal* dioxime are used as cerebral and myocardial perfusion imaging agents[6-9]. The chemistry of *vic*-dioxime and their numerous transition metal complexes have been

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widely investigated as analytical reagent[10-13], model for biological systems such as vitamin B_{12}[14-17], as well as catalysts in chemical processes[18,19]. The reported tetraoxime molecules are rare. These molecules are used to prepared polynuclear complexes[2-3,5]. The chemistry of multidentate aminothia macrocycles and mutidentate dioximes, and also their interactions to each other could be interested for researchers. Thus, in this work, we reported a facile condensation of aminothiophenols with dichloro-glyoxime (DCGO) to produce new *vic*-dioxime systems and tetraoximes rings.

EXPERIMENTAL

All commercially available chemical reagents were obtained from Merck and used without further purification. Melting points were measured with electrothermal 9200 apparatus and were uncorrected. Elemental analyses for C, H, N and S were performed using a Heraeus CHN-O rapid analyzer. MS were recorded with a Shimadzu 5050 QD spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Brucker DRX-500 Avance instrument at 500.1 and 125.7 MHz, respectively. The NMR spectra were carried out in DMSO-d_6. IR spectra were recorded with a Shimadzu IR-460 spectrometer.

Synthesis of (2Z,6Z)-1,4-*bis*(2-mercaptophenyl)piprazine-2,3,5,6-tetraone tetraoxime (2) and (1Z,2Z)-N$^{1'}$,N$^{2'}$-dihydroxy-N^1,N^2-*bis*(2-mercaptophenyl)ethanedi imidamide (3): During 15 min period, a solution of dichloroglyoxime (1.57g, 10 mmole) in 15 mL EtOH was added dropwise to a stirring solution of 2-aminothiophenol (5 g, 40 mmol) in 15 mL EtOH at -5 °C. The solution was stirred for 10 min and then kept in a refrigerator overnight (16-18 h). The precipitated product was removed by filtration and washed with cold THF. The crude product of **2** was agitated twice in 15 mL of cold THF and then filtered. Yield 1.30 g (31.10 %), m.p. 200.5-200.7 °C. IR (KBr, ν_{max}, cm^{-1}): 3100-2400 (OH), 2580 (SH) 1631 (C=N). ^{1}H NMR, ppm: 9.85 (6H, OH, SH, exchangeable with D_2O), 7.11-7.45 (8H, CH_{Ar}). ^{13}C NMR, ppm: 140.95, 136.87, 134.67, 133.59, 131.16, 130.61, 127.41, 126.67, 126.19, 125.78, 123.83, 122.43, 118.74 and 114.91. MS: m/z; 418 (m$^+$). Elemental analysis for $C_{16}H_{14}N_6O_4S_2$ calculated: C, 45.93; H, 3.35; N, 20.09; S, 15.31; found: C, 46.04; H, 3.35; N, 19.98; S, 15.30.

The filtrated solution was concentrated to a volume of 15 mL and placed in the refrigerator for 24 h. The brown precipitate of **3** was collected by filtration and recrystallized in THF. Yield: 1.09 g (32.63 %), m.p. 202.4-202.6 °C. IR (KBr, ν_{max}, cm^{-1}): 3400 (NH), 3400-2500 (OH), 2570 (SH), 1605 (C=N), ^{1}H NMR, ppm: 12.43 (1H, OH), 9.44 (1H, OH, exchangeable with D_2O), 6.44-7.40 (8H, CH_{Ar}), 5.41 (4H, NH, SH, exchangeable with D_2O). ^{13}C NMR, ppm: 149.07, 137.75, 137.12, 135.44, 133.54, 131.22, 126.98, 125.90, 121.11, 117.22, 116.79, 116.74, 115.37 and 112.96. MS: m/z; 335 (m+1), 334 (m$^+$).

Synthesis of *bis*(2-aminophenyl) (1Z,2Z)-N^1,N^2-dihydroxyethane-*bis*(imidothioate) (4): During 1.5 h period, a solution of DCGO (1.57 g, 10 mmol) in 15 mL aqueous 2-propanol (90 %) and 0.15 g $NaHCO_3$ was added dropwise to a stirring solution of 2-aminothiophenol (5 g, 40 mmol) in 15 mL 2-propanole at -5 °C. The solution was stirred for 2 h at -5 °C. The mixture was placed in the refrigerator for 24 h. The white precipitate product was collected by filtration. The crude product was agitated twice in 20 mL MeCN and then filtered. Yield: 2.38 g (71.25 %), m.p. 203-203.2 °C. IR (KBr, ν_{max}, cm^{-1}): 3300 (NH), 3400-2600 (OH), 1630 (C=N), ^{1}H NMR, ppm: 11.92 (2H, OH, exchangeable with D_2O), 6.50-7.25 (8H, CH_{Ar}), 5.16 (4H, NH, exchangeable with D_2O). ^{13}C NMR, ppm: 150.79, 144.59, 138.00, 131.23, 116.82, 115.17 and 110.05 MS: m/z; 335 $(m+1)^+$, 268, 242, 209, 194 and 150[19].

Synthesis of 2-aminophenyl(1Z,2Z)-N-hydroxy-2-hydroxyimino-2-[(2-mercaptophenyl)amino]ethanimidothioate (5): During 1 h, solution of 2-aminothiophenol (5 g, 40 mmol) in 20 mL EtOH was added dropwise to a stirring solution of DCGO (1.57 g, 10 mmol) in 15 mL EtOH (90 %) and 0.1 g $NaHCO_3$ at -5 °C. The solution was stirred for 0.5 h at -5 °C. The mixture was placed in the refrigerator for 1 week. The orange precipitate was collected by filtration. The crude product was agitated twice in 15 mL hot THF and then filtered. Yield: 2.05 g (61.37 %), m.p. 204.5-204.7 °C. IR (KBr, ν_{max}, cm^{-1}): 3550, 3450 (NH), 3500-3400 (OH), 2950-2800 (OH), 2585 (SH), 1662, 1638 (C=N), ^{1}H NMR, ppm: 12.49 (1H, OH), 10.87 (1H, OH, exchangeable with D_2O), 9.58 (2H, NH, SH, exchangeable with D_2O), 6.82-7.41 (8H, CH_{Ar}), 4.72 (2H, NH_2, exchangeable with D_2O). ^{13}C NMR, ppm: 138.39, 137.31, 135.67, 133.74, 131.61, 127.45, 126.35, 121.76, 118.61, 118.18, 117.32, 116.55, 113.50. MS: m/z; 335 (m+1).

Synthesis of (2E,3E)-2H-1,4-benzothiazine-2,3(4*H*)dionedioxime (1) from reaction of 3 with DCGO: To a stirring solution of **3** (0.334 g, 1 mmol) in 20 mL THF, a solution of DCGO (0.156 g, 1 mmol) in 10 mL aqueous THF (80 %) and 0.05 g $NaHCO_3$ was added at room temperature. The solution was stirred for 4 h and then the mixture was filtered. The filtrate was placed at room temperature for 24 h. The precipitate was removed by filtration and precipitate was washed with cold THF. Recrystallization from 2-propanol gave gray crystals of **1**. Yield: 0.31 g (74.16 %), m.p. 219-219.3 °C. IR (KBr, ν_{max}, cm^{-1}): 3400 (NH), 3200-2800 (OH), 1635, 1600 (C=N). ^{1}H NMR, ppm: 12.35 (1H, OH, exchangeable with D_2O), 10.76 (1H, OH, exchangeable with D_2O), 9.35 (bs, 1H, NH, exchangeable with D_2O), 6.82-7.37 (4H, CH_{Ar}). ^{13}C NMR, ppm: 137.50, 137.24, 133.64, 126.97, 125.89, 120.97, 116.62 and 112.81 MS: m/z; 418 (2m), 335, 209 (m^+), 193 and 150. Elemental analysis for $C_{16}H_{14}N_6O_4S_2$ calculated: C, 45.93; H, 3.35; N, 20.10; S, 15.31; found: C, 45.91; H, 3.37; N, 20.12; S, 15.30.

Synthesis of 1 from the reaction of 4 with DCGO: To a stirring solution of 4 (0.835 g, 2.5 mmol) in 50 mL EtOH (85 %) and $NaHCO_3$ (0.1 g), 0.39 g of DCGO (2.5 mmol) was added at room temperature. The solution was stirred for 4 h and then the mixture was filtered. The filtrated mixture was placed at room temperature for 3 d. The precipitate was collected by filtration and washed with cold THF. Recrystallization from 2-propanol gave gray crystals of **1**. Yield: 0.86 g (82.3 %), m.p. 219.-219.3 °C.

Synthesis of 1 from the reaction of 5 with DCGO: To a stirring solution of **5** (0.334 g, 1 mmol) in 20 mL THF, a solution of DCGO (0.157 g, 1 mmol) in 15 mL aqueous THF (50 %) was added at room temperature. The solution was stirred for 1 h, then 3 mL $NaHCO_3$ (0.1 molar) was added and stirred for 1 h. The mixture was placed at room temperature for 3 d. The precipitate was removed by filtration and washed with cold MeCN. Yield: 0.2 g (47.84 %), m.p. 219.-219.3 °C.

Synthesis of (3E,4E,,11E,12E)-2,10-dithia-5,13-diazatricyclo-[12.2.2.2^{6,9}]icosa-1(16),6,8,14,17,19-hexaene-3,4,11,12-tetraonetetra-oxime (6a): To a stirring solution of 4-aminothiophenol (1.25 g, 10 mmol) in 25 mL of MeOH a solution of DCGO (1.57 g, 10 mmol) in 25 mL MeOH (45 % aqueous) was added at room temperature. The solution was stirred for 10 min, then $NaHCO_3$ (0.1 g) was added. After 3 h stirring at room temperature, the mixture was filtered and the precipitate was then washed with hot EtOH to give pure crystals.Yield: 1.46 g (69.8 %); m.p. 219-219.3 °C. IR (KBr, ν_{max}, cm^{-1}): 3320 (NH), 3200-2800 (OH), 1650, 1620 (C=N), 950 (N-O). ^{1}H NMR, ppm: 10.59 (2H, OH, exchangeable with D_2O), 10.76 (2H, OH, exchangeable with D_2O), 8.40 (bs, 2H, NH, exchangeable with D_2O), 6.74-6.76, 7.16-7.18 (dd, 8H, J = 8.25 Hz, CH_{Ar}). ^{13}C NMR, ppm: 141.99, 140.25, 130.26, 127.59, 119.38, and 114.23. MS: m/z; 418 (m^+), 335, 268, 209 and 150. Elemental analysis for $C_{16}H_{14}N_6O_4S_2$ calculated: C, 45.93; H, 3.35; N, 20.10; S, 15.31; Found: C, 45.91; H, 3.37; N, 20.12; S, 15.30.

Synthesis of (3E,4E,12E,13E)-2,11-dithia-5,14-diazatricyclo-[13.3.1.1^{6,10}]icosa-1(19),6(20),7,9,15,17-hexaene-3,4,12,13-tetraonetetra-oxime (6b): To a stirring solution of 3-aminothiophenol (1.25 g, 10 mmol) in 25 mL of MeCN a solution of DCGO (1.57 g, 10 mmol) in 25 mL MeOH (45 % aqueous) was added at room temperature. The solution was stirred for 10 min, then $NaHCO_3$ (0.1 g) was added. After 12 h stirring at 35 °C, the mixture was filtered and precipitate was washed with cold MeCN. Recrystallization from propanol gave crystals of **6b**. Yield: 0.93 g (44.50 %); m.p. 210-211 °C. IR (KBr, ν_{max}, cm^{-1}): 3379 (NH), 3132-2854 (OH), 1589 (C=N), 972 (N-O). ^{1}H NMR, ppm: 12.29 (bs, 2H, OH, exchangeable with D_2O), 12.25 (bs, 2H, OH, exchangeable with D_2O), 10.86 (bs, 2H, NH, exchangeable with D_2O), 6.74-7.53 (m, 8H, CH_{Ar}). ^{13}C NMR, ppm: 143.40,

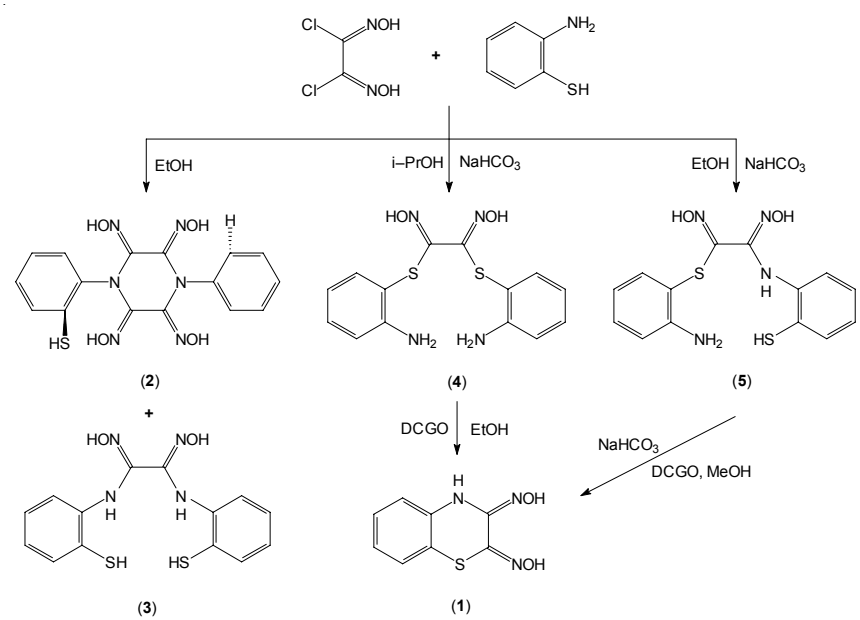
141.23, 133.60, 133.33, 129.99, 129.75, 127.83 and 123.22. MS: m/z; 418 (m^+), 209, 150. Elemental analysis for $C_{16}H_{14}N_6O_4S_2$ calculated: C, 45.93; H, 3.35; N, 20.10; S, 15.31. Found: C, 45.90; H, 3.34; N, 20.01; S, 15.31.

X-ray structure analysis of 1: The clear colourless crystal with the dimensions 0.5 × 0.5 × 0.1 mm^3 was used for data collection on a Bruker SMART 1000 CCD diffractometer with graphite monochromated MoK_α (λ = 0.71073 Å). $C_8H_{11}N_3O_4S$, FW = 245.26. Orthorhombic crystals in a Pbca space group, a = 9.1636(18) Å, b = 9.8195(18) Å, c = 24.165(4) Å, β = 93.08(1)°, V = 1284.07(16) $Å^{-3}$. Z = 8, D (X-ray, calcd.) = 1.498 Mg/m^3. μ = 0.302 mm^{-1}, F (000) = 1024, T = 120(2)º K. Of the 15018 total reflections, 2337 were unique. R_{int} = 0.0823. The structure was dissolved by direct methods (SHELEXTL PC)[20] and refined by full-matrix least-squares (isotropic refinement of the molecule and location of remaining non-hydrogen atoms from a difference Fourrier and subsequent anisotropic refinement on all atoms; H atoms were found after high-angle refinement in a difference Fourrier and their positions included in the final stages of refinement), factors of R1 = 0.0458, Rw2 = 0.0962 for 1482 unique observed reflections (another reflections, with $I > 2\sigma$ (I), were considered unobserved). No significant features, only ripples from -0.251 to 0.433 e $Å^{-3}$, were observed in the final difference map. The nonhydrogen atoms were refined anisotropically. Atomic coordinate, temperature factors, bond distances, bond angles and torsion have been deposited at the Cambridge crystallographic data center. Number CCDC 299488. 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 reaction of 2-aminothiophenol with dichloroglyoxime (DCGO) in an alkaline solution of MeOH lead to (2E,3E)-2H-1,4-benzothiazine-2,3(4*H*)dionedioxime (**1**)[3]. However, reaction of 1 mole of DCGO with 4 mole of 2-aminothiophenol in EtOH at -2 °C, resulted in the formation of (2Z,6Z)-1,4-*bis*(2-mercaptophenyl)piprazine-2,3,5,6-tetraonetetraoxime (**2**) and (1Z,2Z)-$N^{1'}$, $N^{2'}$-dihydroxy-N^1,N^2-*bis*(2-mercaptophenyl)ethane diimidamide (**3**). They were separated in cold THF (**Scheme-I**). But, in an alkaline solution of 2-propanol, at -5 ºC, the product of the reaction was *bis*(2-aminophenyl)-(1Z,2Z)-N^1,N^2-dihydroxyethane*bis*(imidothioate) (**4**). In addition, while we added 4 mole of the solution of 2-aminothiophenol to 1 mole of the solution DCGO dropwise during 1 h in an alkaline solution of EtOH (90 %) at -5 ºC, the orange precipitate of 2-aminophenyl(1Z,2Z)-N-hydroxy-2-hydroxyimino-2-[(2-mercaptophenyl)amino]ethanimidothioate (**5**) was slowly formed in a week. Compounds (**3**), (**4**) and (**5**) in the presence of DCGO, can be converted to **1** (**Scheme-I**). Best yields were obtained by

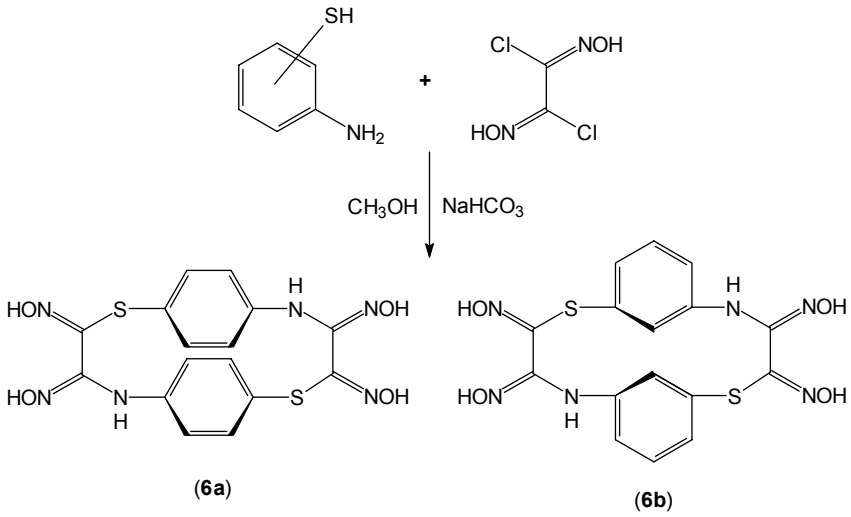
the addition of reactants over a 2 h period. The yields of the products were dependent on the reaction conditions. Factors were examined including solvent, reactant concentrations, rate of mixing, reaction temperature and time. The structure of product depends on the concentration of DCGO in reaction mixture. The products were stable in aprotic solvents or alkaline solutions. But, in acidic media (pH < 5), compounds (**3**), (**4**) and (**5**) are decomposed.



Scheme-I

Furthermore, the compounds (3E,4E,11E,12E)-2,10-dithia-5,13-diazatricyclo[12.2.2.2^{6,9}]icosa-1(16),6,8,14,17,19-hexaene-3,4,11,12-tetraonetetraoxime (**6a**) and (3E,4E,12E,13E)-2,11-dithia-5,14-diaza-tricyclo[13.3.1.1^{6,10}]icosa-1(19),6(20),7,9,15,17-hexaene-3,4,12,13-tetra-onetetraoxime (**6b**) were obtained from the reaction of 1,4- and 1,3-amino-thiophenol with DCGO in an alkaline solution of MeOH or MeCN, respectively (**Scheme-II**).

The structure of compound (**1**) was established by X-ray crystallography (experimental section for details). The atomic coordinates and thermal parameters are reported in the supplementary pages (Fig. 1).



Scheme-II

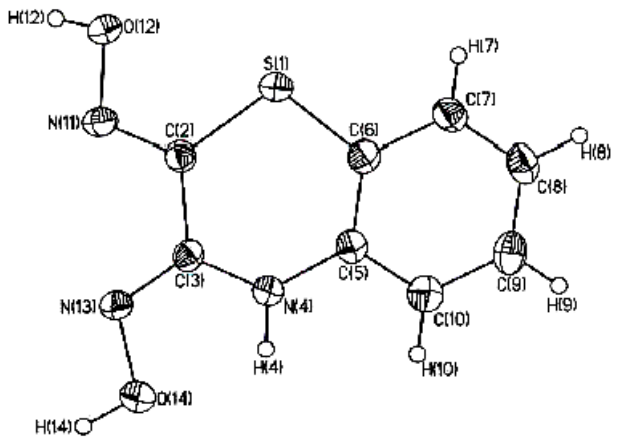


Fig. 1. ORTEP drawing of (**1**)

There are some unusual structural features in the molecule. The C-N, C-S, bonds are smaller than usual values and bond angles around the N_4 or S_1 have sp^2 characteristics (Table-1). Torsion angles for N_4-C_5-C_6-S_1 and C_5-C_6-N_4-C_3 C_5-C_6-S_1-C_2 are –2.1º, 3.4º and -7.6º, respectively. The thiazine ring is essentially planar with respect to the fused aromatic ring. These results show a resonance between aromatic ring and C=N bond, through N and S atoms of the compound. This can be attributed to the influence of bond lengths, bond angles, pyramid and planarity of thiazine ring. The torsion angles of N_{13}-C_3-C_2-N_{11}, N_4-C_3-C_2-S_1 and C_6-C_5-C_2-C_3 are -16.8º, -19.9º and 9.93º, respectively. These data show that C_2 and C_3 are not coplanar and the C_2-C_3 bond shows a single bond characteristic.

TABLE-1
SELECTED BAND LENGTHS (Å), BOND ANGLES (º)
AND TORSION ANGLES (º)

Bond lengths	(Å)	Bond lengths	(Å)
S1-C6	1.7660(13)	N4-C3	1.3550(3)
S1-C2	1.7510(3)	N4-H4	0.8600
C2-N11	1.2800(3)	C3-N13	1.2990(3)
N11-O12	1.3880(3)	N13-O14	1.4110(3)
O12-H12	0.8200	C2-C3	1.4790(3)
N4-C5	1.3970(3)	C5-C6	1.3840(4)
Bond angles	(º)	Bond angles	(º)
C2-S1-C6	102.14(13)	C5-N4-C3	127.80(2)
S1-C2-C3	121.55(19)	C3-N4-H4	116.10
S1-C2-N11	120.7(2)	N4-C3-C2	123.10(2)
N11-C2-C3	117.70(2)	N4-C3-C2	119.90(2)
C2-N11-O12	110.50(2)	N13-C3-C2	117.00(2)
N11-O12-H12	109.50	C3-N13-O14	108.20(2)
C5-N4-H4	116.10	N13-O14-H14	109.50
Torsion angles	(º)	Torsion angles	(º)
N4-C5-C6-S1	-2.10(3)	C6-S1-C2-C3	18.00(2)
N4-C3-C2-S1	-19.90(3)	H4-N4-C5-C10	-6.51
C6-C5-N4-C3	3.40(3)	H10-C5-N4-H4	-0.61
C5-C6-S1-C2	-7.60(2)	N13-C2-C4-C4	-3.98
C5-S1-C3-N4	1.15(1)	S1-C2-C3-N13	160.38(7)
C3-S1-C6-C5	0.50(17)	C2-C3-N13-O14	179.59(3)
N13-C3-C2-N11	-16.80(3)	N4-C3-C2-N11	162.90(3)
C5-N4-C3-C2	8.10(3)	C3-C2-N11-O12	177.68(18)

Furthermore, the results from X-ray data as shown in Fig. 2 show that molecules **1** could be exised as a dimer by intermolecular hydrogen bonding. The corresponding distance and angle for hydrogen bonds are given in Table-2. The unit cell of the resulting crystal clearly revealed that a three

TABLE-2
HYDROGEN BOND D–H···A IN THE CRYSTAL OF **1** (Å AND º)

D–H···A	d(D-H)	d(D···H)	<DHA	d(D···A)
O(12)-H(12)···O(2w$^{\#}$2)	0.82	1.90	171	2.710(3)
O(14)-H(14)···O(1w)	0.82	1.87	179	2.690(3)
O(1w$^{\#}$3)-H(1wA$^{\#}$3)···N(11)	0.84	2.11	163	2.930(3)
O(1w$^{\#}$3)-H(1wB$^{\#}$3)···O(2w)	0.84	2.02	172	2.849(3)
O(2w$^{\#}$4)-H(2wA$^{\#}$4)···N(13)	0.84	2.02	169	2.847(3)
O(2w)-H(2wB)···O(1w)	0.84	1.95	172	2.786(3)

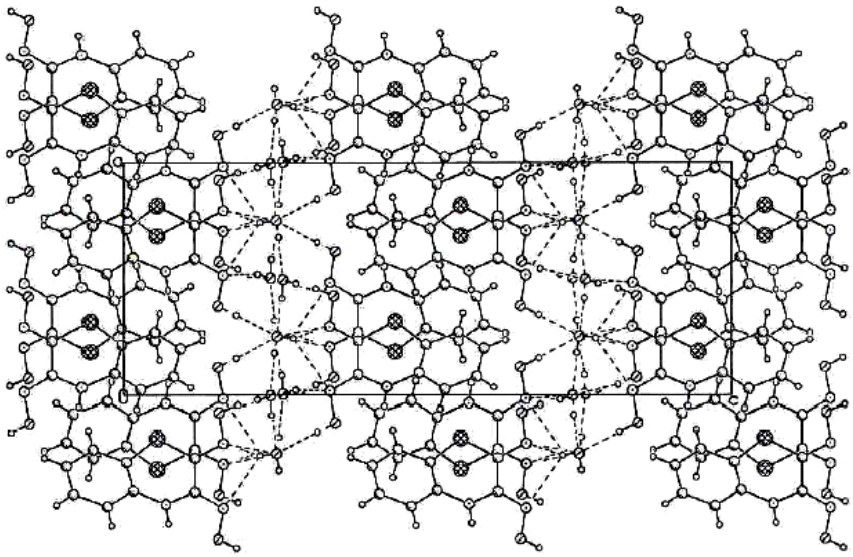


Fig. 2. Unit cell of (2E,3E)-2H-1,4-benzothiazine-2,3(4H)-dionedioxime (**1**)

dimensional network is formed owing to the presence of intermolecular hydrogen bonding interaction. The hydrogen bonding in **1** shows a face-to-edge[21] configuration. which is supported by two lattice water molecules (Figs. 2 and 3).

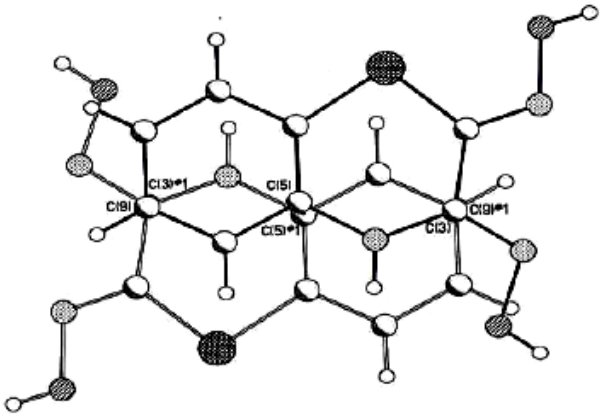


Fig. 3. Structure of (**1**), the intermolecular bond lengths (Å), C3-$C_9^{\#}$ = 3.358, C_5-$C_5^{\#}$ = 3.293 and C_9-$C_3^{\#}$ = 3.358

The experimental data and structural models show the existence of three possible cyclic *vic*-dioximes configurations (anti, amphi and syn). The isomer distribution depends on steric effects of substitutions and the possibility of hydrogen bonding between the oxime groups[4]. The torsion angles of molecule **1**, N_{11}-C_2-C_3-N_{13}, C_2-C_3-N_{13}-O_{14}, N_4-C_3-C_2-S_1, C_3-C_2-

N_{11}-O_{12}, confirm an *anti* configuration and the oxime groups will not be coplanar unless they are linked by a hydrogen bond. Mass spectra of **1** show a molecular ion peak at 418 m/z.

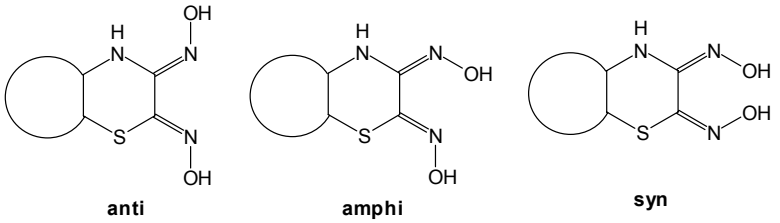


Fig. 4. Possible isomer of cyclic *vic*-dioximes

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