



Synthesis and Structural Characterization of Four Novel Bisoxime-Type Compounds Based on 2,2'-(Ethylenedioxy)bisbenzaldehyde

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A series of bisoxime compounds have been synthesized by the reaction of 2,2'-(ethylenedioxy)bisbenzaldehyde with hydroxylamine hydrochloride, methoxyamine hydrochloride, ethoxyamine hydrochloride or 3-aminoacetophenone oxime in hot ethanol medium, respectively and characterized by elemental analyses, IR, UV-visible spectra and ¹H NMR spectroscopy.

Keywords: 2,2'-(Ethylenedioxy)bisbenzaldehyde, Bisoximes-type ligand, Synthesis, Characterization.

INTRODUCTION

Bisoxime-type compounds are a kind of multidentate chelating ligands and easily obtained by the reaction of bisamine and aldehyde or alkone, which can coordinated to transition metal ions to afford stable metal complexes¹. However the oxime-type compounds play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures²⁻⁵. In recent years, the research of the metal-organic complexes with these bisoxime-type ligands and transition metal ions have made great progress⁶⁻⁸. In order to investigating the structural properties of the bisoxime-type compounds more deeply, we have recently studied a series of bisoxime compounds from 2,2'-(ethylenedioxy)bis-benzaldehyde with hydroxylamine hydrochloride, methoxyamine hydrochloride, ethoxyamine hydrochloride or 3-aminoacetophenone oxime, respectively and the characterizations have also been studied.

EXPERIMENTAL

Salicylaldehyde ($\geq 98\%$), 1,2-dibromoethane, hydroxylamine hydrochloride, methoxyamine hydrochloride, ethoxyamine hydrochloride and 3-aminoacetophenone were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. The methods are the same as literature early⁸.

General procedure: Synthetic route to bisoxime compounds H_2L^1 , L^2 , L^3 and H_2L^4 are shown in Fig. 1.

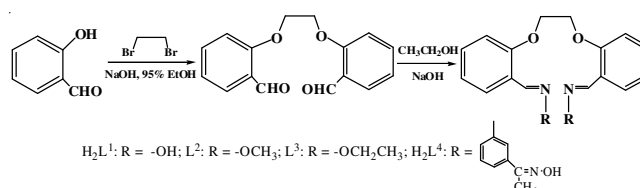


Fig. 1. Synthetic route to bisoximes-type compounds H_2L^1 , L^2 , L^3 and H_2L^4

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 72 h⁹. ¹H NMR (400 MHz, DMSO-*d*₆, δ /ppm), 4.50 (s, 4H, CH₂O), 6.96 (t, 2H, $J = 7.7$ Hz, ArH), 7.15 (d, $J = 7.7$ Hz, 2H, ArH), 7.36 (t, $J = 7.7$ Hz, 2H, ArH), 7.76 (d, $J = 7.7$ Hz, 2H, ArH), 10.08 (s, 2H, CH=O).

Preparation of 2,2'-(ethylenedioxy)bisbenzaldehyde dioxime (H_2L^1): To a hot ethanolic solution (15 mL) of 2,2'-(ethylenedioxy)bisbenzaldehyde (270.3 mg, 1 mmol) was added an ethanolic solution (15 mL) of hydroxylamine hydrochloride (278 mg, 4 mmol). After the solution had been stirred at 55 °C for 1 h, sodium hydroxide (400 mg, 10 mmol) was added slowly with shaking. The mixture was then refluxed for 15 min, cooled to room temperature and poured into a solution of concentrated hydrochloric acid (60 mL) and water (250 mL). The formed precipitate was separated by filtration and washed three times successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain white powder H_2L^1 . Yield 82.5 %. m.p. 445-446 K.

Preparation of N,N'-bismethoxy-2,2'-(ethylenedioxy)-bisbenzaldehyde dioxime (L^2): To a hot ethanolic solution

(15 mL) of 2,2'-(ethylenedioxy)bisbenzaldehyde (270.8 mg, 1 mmol) was added an ethanolic solution (15 mL) of methoxyamine hydrochloride (334.3 mg, 4 mmol). After the solution had been stirred at 55 °C for 1 h, sodium hydroxide (400 mg, 10 mmol) was added slowly with constant shaking. The mixture was then refluxed for 25 min, cooled to room temperature and poured into a solution of concentrated hydrochloric acid (60 mL) and water (300 mL). The formed precipitate was separated by filtration and washed three times successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain white powder L². Yield 79.1 %. m.p. 369-370 K.

Preparation of N,N'-bisethoxy-2,2'-(ethylenedioxy)bisbenzaldehyde dioxime (L³): To a hot ethanolic solution (15 mL) of 2,2'-(ethylenedioxy)bisbenzaldehyde (270.3 mg, 1 mmol) was first added an ethanolic solution (10 mL) of ethoxyamine hydrochloride (390.2 mg, 4 mmol), then NaOH (400 mg, 10 mmol). After the mixture had been stirred under reflux for 4 h, 10 mL distilled water was added. The solution was filtered and concentrated to about 15 mL over night at 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 white powder L³. Yield 68.1 %. m.p. 337-338 K.

Preparation of N,N'-phenyl-3-acetyl oxime -2,2'-(ethylenedioxy)bisbenzaldehyde (H₂L⁴): 3-Aminoacetophenone oxime was synthesized analogously to the method reported in the previous literature¹⁰. To a hot ethanolic solution (7 mL) of 3-aminoacetophenone (818.2 mg, 6 mmol) was added a mixed ethanolic solution (15 mL) of hydroxylamine hydrochloride (423.5 mg, 6 mmol) and sodium acetate trihydrate (480.4 mg, 10 mmol), the colour of the mixing solution turned to pale-yellow. The mixture was stirred at 55 °C for 12 h. After cooling to room temperature, the mixture was filtered, washed successively with ethanol and *n*-hexane, respectively. The product was dried under reduced pressure to obtained brown needle-like solid. Yield, 68.2 %. m.p. 408-409 K. Anal. Calcd. for C₈H₁₀N₂O (%): C, 63.98; H, 6.71; N, 18.65; Found: C, 63.91; H, 6.74; N, 18.62.

H₂L⁴: A solution of 3-aminoacetophenone oxime (480.4 mg, 10 mmol) in ethanol (10 mL) was added dropwise to a solution of 2,2'-(ethylenedioxy)bisbenzaldehyde (270.4 mg, 1 mmol) in ethanol (10 mL) at room temperature. After the solution had been stirred and condensing refluxed at 55 °C for 6 h and reduced to half by vacuum distillation, then put it in the refrigerator overnight, the formed precipitate was separated by filtration and washed successively with ethanol/hexane (1:4) and hexane, respectively. The product was dried under reduced pressure for 72 h to obtain pale pink powder H₂L⁴. Yield, 86.9 %. m.p. 472-473 K.

RESULTS AND DISCUSSION

A series of bisoximes-type compounds H₂L¹, L², L³ and H₂L⁴ have been synthesized with good yields and the compositions are confirmed by elemental analyses, IR and UV-visible spectra.

Physical and chemical properties of bisoximes compounds

H₂L¹, L², L³ and H₂L⁴: The colour, yields and elemental analytical results of the synthesized bisoximes compounds H₂L¹, L², L³ and H₂L⁴ are presented in Table-1.

Bisoximes-type compounds H₂L¹, L², L³ are white solid, H₂L⁴ is a pale pink solid and all the compounds stable in air and compounds H₂L¹, L², L³ soluble in ethanol, dichloromethane, THF and DMF, slightly soluble in acetone and methanol, insoluble in acetonitrile and *n*-hexane. Bisoximes-type compound H₂L⁴ soluble in acetone, ethanol and DMF, slightly soluble in acetone, THF and methanol and insoluble in acetonitrile and *n*-hexane.

IR spectra: The most important IR spectral data for the bisoximes compounds H₂L¹, L², L³ and H₂L⁴ are given in Table-2.

In the IR spectra of the the bisoximes compounds H₂L¹, L², L³ and H₂L⁴, the bands due to characteristic C=N stretching absorption bands appear at 1613-1607 cm⁻¹, respectively^{8,10}. The Ar-O stretching frequencies appear within 1264-1243 cm⁻¹ as reported for similar bisoxime compounds⁸. These provide evidence for the formation of the title compounds. The O-H stretching frequency of the bisoxime compound is expected in the 3300-3800 cm⁻¹ region⁸, here a strong band at 3684-3656 cm⁻¹ was observed in the title compounds H₂L¹ and H₂L⁴

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA
FOR THE BISOXIMES-TYPE COMPOUNDS H₂L¹, L², L³ AND H₂L⁴

Compound	Colour	m.p. (K)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (Calcd.)		
					C	H	N
H ₂ L ¹	White	354-355	82.5	C ₁₆ H ₁₆ N ₂ O ₄ (300.30)	63.92 (63.99)	5.33 (5.37)	9.36 (9.33)
L ²	White	445-445.5	79.1	C ₁₈ H ₂₀ N ₂ O ₄ (328.36)	65.81 (65.84)	6.17 (6.14)	8.59 (8.53)
L ³	White	337-338	68.1	C ₂₀ H ₂₄ N ₂ O ₄ (356.42)	67.57 (67.40)	6.61 (6.79)	7.72 (7.86)
H ₂ L ⁴	Pale pink	472-473	86.9	C ₃₂ H ₃₀ N ₄ O ₄ (534.61)	71.91 (71.89)	5.63 (5.66)	10.45 (10.48)

TABLE-2
KEY IR BANDS (cm⁻¹) FOR THE BISOXIMES-TYPE COMPOUNDS H₂L¹, L², L³ AND H₂L⁴

Compound	ν(C=N)	ν(Ar-O)	ν(O-H)	ν(C=C) _{benzene ring}	ν(CH _{arom})	ν(CH ₂)
H ₂ L ¹	1609	1255	3656	1596, 1545, 1462	3072	2930, 2857
L ²	1612	1246	-	1590, 1553, 1438	3074	2933, 2858
L ³	1613	1243	-	1592, 1548, 1442	3070	2936, 2851
H ₂ L ⁴	1607	1264	3684	1596, 1550, 1445	3075	2937, 2848

TABLE-3
UV-VISIBLE SPECTRAL DATA FOR THE BISOXIMES-TYPE COMPOUNDS H₂L¹, L², L³ AND H₂L⁴

Compound	C (× 10 ⁻⁵ mol L ⁻¹)	First band	Second band
		λ _{max1} (nm)	λ _{max2} (nm)
H ₂ L ¹	5.00	272	327
L ²	5.00	270	325
L ³	5.00	271	328
H ₂ L ⁴	5.00	275	316

TABLE-4
¹H NMR DATA FOR THE BISOXIMES-TYPE COMPOUNDS H₂L¹, L², L³ AND H₂L⁴

Compound	¹ H NMR (400 MHz, CDCl ₃ , δ/ppm)
H ₂ L ¹	C ₁₆ H ₁₆ N ₂ O ₄ (300.30) 4.51 (s, 4H, CH ₂ O), 6.97 (t, 2H, J = 7.8 Hz, ArH), 7.16 (d, J = 7.6 Hz, 2H, ArH), 7.35 (t, J = 7.5 Hz, 2H, ArH), 7.74 (d, J = 7.5 Hz, 2H, ArH), 8.42 (s, 2H, CH=N), 10.23 (s, 2H, OH)
L ²	C ₁₈ H ₂₀ N ₂ O ₄ (328.36) 4.06 (s, 6H, CH ₃ O), 4.50 (s, 4H, CH ₂ O), 6.96 (t, 2H, J = 7.7 Hz, ArH), 7.15 (d, J = 7.7 Hz, 2H, ArH), 7.36 (t, J = 7.7 Hz, 2H, ArH), 7.76 (d, J = 7.7 Hz, 2H, ArH), 8.36 (s, 2H, CH=N)
L ³	C ₂₀ H ₂₄ N ₂ O ₄ (356.42) 3.92 (s, 6H, CH ₃), 4.17 (m, J = 7.2 Hz, 4H, CH ₂ O), 4.52 (s, 4H, CH ₂ O), 6.95 (t, 2H, J = 7.6 Hz, ArH), 7.12 (d, J = 7.9 Hz, 2H, ArH), 7.39 (t, J = 7.2 Hz, 2H, ArH), 7.78 (d, J = 7.0 Hz, 2H, ArH), 8.35 (s, 2H, CH=N)
H ₂ L ⁴	C ₃₂ H ₃₀ N ₄ O ₄ (534.61) 3.97 (s, 6H, CH ₃), 4.55 (s, 4H, CH ₂ O), 6.86 (d, J = 7.2 Hz, 2H, ArH), 6.95 (t, 4H, J = 7.5 Hz, ArH), 7.14 (d, J = 7.0 Hz, 4H, ArH), 7.32 (t, J = 7.2 Hz, 4H, ArH), 7.66 (d, J = 7.2 Hz, 2H, ArH), 8.42 (s, 2H, CH=N), 10.38 (s, 2H, OH)

and assigned to phenolic alcohol stretching absorption bands. In addition, in the 1596-1442 cm⁻¹ region, the observed bands were attributed to aromatic C=C vibrations.

UV-visible and ¹H NMR Spectra: The absorption spectra of the bisoximes compounds H₂L¹, L², L³ and H₂L⁴ (Table-3), in diluted dichloromethane solution show that the spectra of H₂L¹, L², L³ and H₂L⁴.

The UV-visible spectra of the bisoximes compounds H₂L¹, L², L³ and H₂L⁴ in 5 × 10⁻⁵ DMF solution are presented in Table-3. The bisoximes compounds H₂L¹, L², L³ and H₂L⁴ exhibit two intense peaks at around 272 and 327 nm. The former absorption peak at about 272 nm can be assigned to the π-π* transition of the benzene rings, while the latter can be attributed to the intra-ligand π-π* transition of the C=N bonds^{11,12}. It is of note that there was no absorption around 400 nm, which is seen in the corresponding Salen derivatives. The absorption is ascribed to the quinoid form of H₂Salen¹³.

The ¹H NMR spectra showed a singlet at about 8.35-8.42 ppm indicating the existence of oxime bonds¹³ (Table-4).

Conclusion

In this paper, a series of bisoximes-type compounds H₂L¹, L², L³ and H₂L⁴ have been designed and synthesized by the reaction of 1 equivalents of 2,2'-(ethylenedioxy)bisbenzaldehyde with hydroxylamine hydrochloride, methoxyamine hydrochloride, ethoxyamine hydrochloride or 3-aminoacetophenone oxime under hot ethanol conditions, respectively. It is shown that an O-alkyl oxime moiety is much more useful to assemble supramolecular systems. Further investigation on the synthesis and structures of bisoximes-type complexes with transition metal ions, are now in progress.

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