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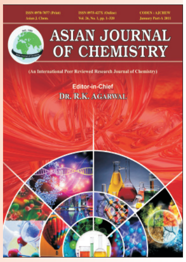

Bromo-Substituted Salamo-Type Compounds Possessing More Flexible O-Alkyl Chain: Synthesis and Sructural Characterization

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A series of bromo-substituted Salamo-type compounds have been synthesized by the reaction of 5-bromo-2-hydroxybenzaldehyde with 1,7-*bis*(aminooxy)heptane, 1,8-*bis*(aminooxy)octane, 1,9-*bis*(aminooxy)nonane or 1,10-*bis*(aminooxy)decane in hot ethanol medium, respectively, and characterized by elemental analyses, IR, UV-visible spectra and ^{1}H NMR spectroscopy.

Keywords: Salamo-type bisoxime ligand, Synthesis, Characterization.

INTRODUCTION

Oxime-type chelate ligands, condensed by oxyammonia and aldehyde or alkone, were widely used as the donor materials in the modern metal-organic coordinating chemistery[1]. Especially, the bisoxime-type compounds have drawn increasing attentions for their diverse structures and broad applications prospects in medicine, catalysis, optoelectronic and magnetism[2-5]. In recent years, the research of the metal-organic complexes with these Salamo-type bisoxime ligands and transition metals have made great progress[6-8]. In order to investigating the structural properties of the bisoxime-type compounds, we have synthesized a serial of bisxiome compounds from 5-bromo-2-hydroxybenzaldehyde and *bis*(aminooxy)alkane with different long-chain alkane molecules, 4,4'-bibromo-2,2'-[1,7-(heptanediyldioxy)*bis*-(nitrilomethylidyne)]diphenol, 4,4'-bibromo-2,2'-[1,8-(octanediyldioxy)*bis*(nitrilomethylidyne)]diphenol, 4,4'-bibromo-2,2'-[1,9-(nontanediyldioxy)*bis*(nitrilomethylidyne)]diphenol, 4,4'-bibromo-2,2'-[1,10-(decanediyldioxy)*bis*(nitrilomethylidyne)]diphenol and the characterizations have also been studied.

EXPERIMENTAL

5-Bromo-2-hydroxy-benzaldehyde (≥ 98 %), 1,7-dibromoheptane, 1,8-dibromooctane, 1,9-dibromononane and 1,10-dibromodecane were purchased from Alfa Aesar and used without further purification. The other 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. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (4000-400 cm^{-1}) pellets. UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer and the thermometer was uncorrected. ^{1}H NMR spectra were recorded on a Mercury-400BB spectrometer.

General procedure: Synthetic route to Salamo-type bisoxime compounds H_2L^1-H_2L^4 are shown in Fig. 1. 1,7-*bis*-(aminooxy)heptanes, 1,8-*bis*(aminooxy)octane, 1,9-*bis*(aminooxy)nonane and 1,10-*bis*(aminooxy)decane were synthesized according to an analogous method reported earlier[9-11].

Preparation of 4,4'-dibromo-2,2'-[1,7-(heptanediyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^1): To a hot ethanolic solution (10 mL) of 5-bromo-2-hydroxy-benzaldehyde (201.3 mg, 1 mmol) was added a hot ethanolic solution (10 mL) of 1,7-*bis*(aminooxy)heptane (81.1 mg, 0.50 mmol). After the solution had been stirred at 60 °C for 6 h, then cooled to room temperature. The white precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane (1/4) and dried under vacuum to obtain the compound H_2L^1. Yield (%): 82.7; m.p.: 384-385 K.

Preparation of 4,4'-dibromo-2,2'-[1,8-(octanediyldioxy)*bis*(nitrilomethylidyne)]diphenol, (H_2L^2): To a hot ethanolic solution (10 mL) of 5-bromo-2-hydroxy-benzaldehyde (201.3 mg, 1 mmol) was added a hot ethanolic solution (10 mL) of 1,8-*bis*(aminooxy)octane (88.1 mg, 0.50 mmol).

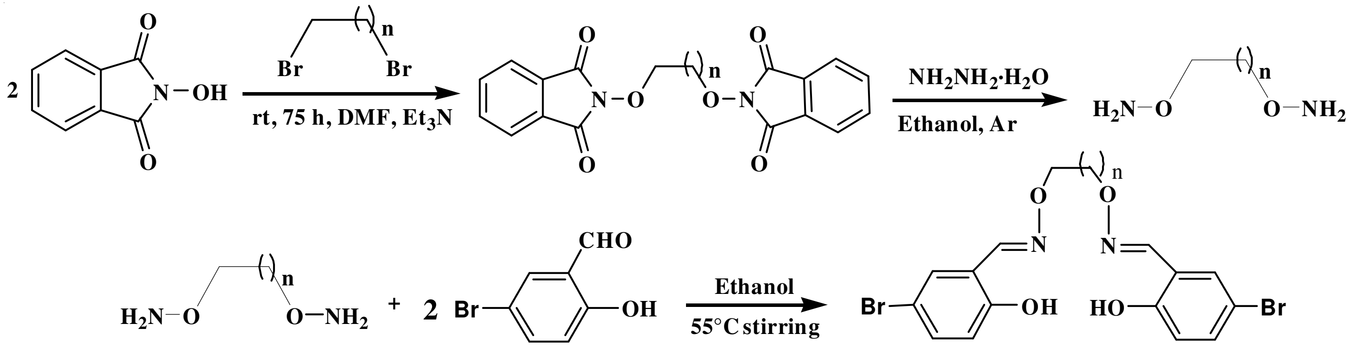

Fig. 1. Synthetic route to Salamo-type bisoxime compounds H_2L^1-H_2L^4 (n = 6-9)

After the solution had been stirred at 60 °C for 6 h, then cooled to room temperature, the white precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane (1/4) and dried under vacuum to obtain H_2L^2. Yield (%): 73.2; m.p.: 389-390 K.

Preparation of 4,4'-dibromo-2,2'-[1,9-(nonanediyldioxy)*bis*(nitrilomethylidyne)]diphenol, (H_2L^3): To a hot ethanol solution (10 mL) of 5-bromo-2-hydroxy-benzaldehyde (201.3 mg, 1 mmol) was added a hot ethanol solution (10 mL) of 1,9-*bis*(aminooxy)nonane (95.1 mg, 0.50 mmol). After the solution had been stirred at 60 °C for 6 h, then cooled to room temperature, the white precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane (1/4) and dried under vacuum to obtain H_2L^3. Yield (%): 69.1; m.p. 383-384 K.

Preparation of 4,4'-dibromo-2,2'-[1,10-(decanediyldioxy)*bis*(nitrilomethylidyne)]diphenol, (H_2L^4): To a hot ethanol solution (10 mL) of 5-bromo-2-hydroxy-benzaldehyde (201.3 mg, 1 mmol) was added a hot ethanol solution (10 mL) of 1,10-*bis*(aminooxy)decane (10.2 mg, 0.50 mmol). After the solution had been stirred at 60 °C for 6 h, then cooled to room temperature, the white precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane (1/4) and dried under vacuum to obtain H_2L^4. Yield (%): 83.2; m.p.: 373-374 K.

RESULTS AND DISCUSSION

A series of Salamo-type bisoxime compounds H_2L^1-H_2L^4 have been synthesized with good yields and the compositions are confirmed by elemental analyses, IR, UV-visible spectra and ^{1}H NMR spectroscopy.

Physical and chemistry property: The colour, yields, melting points and elemental analytical results of the synthesized Salamo-type bisoxime compounds H_2L^1-H_2L^4 are presented in Table-1. Their compositions agree with the formula. All the compounds are white microcrystalline solid, stable in air and soluble in acetone, chloroform, dichloromethane, tetrahydrofuran, ethyl acetate, DMF and DMSO, insoluble in water, methanol, ethanol, ether, acetonitrile and *n*-hexane.

IR spectra: The most important IR spectra data for H_2L^1-H_2L^4 are given in Table-2. In the IR spectra of the title compounds H_2L^1-H_2L^4, the characteristic C=N stretching bands of the compounds H_2L^1-H_2L^4 appear at 1605-1613 cm^{-1}, respectively[12], indicating that 5-bromo-2-hydroxybenzaldehyde has been condensated with 1,7-*bis*(aminooxy)heptane, 1,8-*bis*(aminooxy)octane, 1,9-*bis*(aminooxy)nonane or 1,10-*bis*(aminooxy)decane, respectively and formed novel salamo-type compounds. The Ar-O stretching bands occur at 1272-1262 cm^{-1} as reported for similar bisoxime compounds[13]. The O-H stretching band of the title compounds H_2L^1-H_2L^4 appears at 3442-3432 cm^{-1} region, but this frequency is generally displaced to about 3424 cm^{-1} because of the internal hydrogen bond OH···N=C[14].

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA
OF BROMO-SUBSTITUTED SALAMO-TYPE BISOXIME COMPOUNDS H_2L^1-H_2L^4

Comp.	Colour	m.p. (K)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (Calcd.)		
					C	H	N
H_2L^1	White	384~385	82.7	$C_{21}H_{24}Br_2N_2O_4$ (446.4)	47,75 (47.52)	4.58 (4.63)	5.30 (5.37)
H_2L^2	White	389~390	73.2	$C_{22}H_{26}Br_2N_2O_4$ (460.4)	48.73 (48.64)	4.83 (4.92)	5.17 (5.23)
H_2L^3	White	383~384	69.1	$C_{23}H_{28}Br_2N_2O_4$ (474.5)	49.66 (49.17)	5.07 (5.12)	5.04 (5.06)
H_2L^4	White	373~374	83.2	$C_{24}H_{30}Br_2N_2O_4$ (502.5)	50.54 (50.03)	5.03 (5.26)	4.91 (4.93)

TABLE-2
KEY IR BANDS FOR THE BROMO-SUBSTITUTED SALAMO-TYPE BISOXIME COMPOUNDS H_2L^1~H_2L^4 (cm^{-1})

Compound	ν(O-H)	ν(CH_{arom})	ν(CH_2)	ν(C=N)	ν(C-C)$_{\text{benzene ring}}$	ν(Ar-O)
H_2L^1	3432	3053	2946, 2887	1605	1472	1262
H_2L^2	3438	3058	2953, 2895	1613	1479	1271
H_2L^3	3442	3056	2943, 2882	1608	1477	1272
H_2L^4	3435	3051	2944, 2883	1611	1481	1269

TABLE-3

UV-VISIBLE SPECTRAL DATA AND ^{1}H NMR DATA FOR THE BROMO-SUBSTITUTED SALAMO-TYPE BISOXIMES $\mathbf{H_2L^1}$-$\mathbf{H_2L^4}$

Compound	π-π* (nm)	^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm)
$\mathbf{H_2L^1}$	272,313	2.46-2.55 (m, 10H, CH$_2$), 4.45 (s, 4H, CH$_2$-O), 7.42 (d, *J* = 2.0 Hz, 2H, PhH), 7.56 (d, *J* = 2.0 Hz, 2H, PhH), 7.71 (d, *J* = 2.2 Hz, 2H, PhH), 8.45 (s, 2H, N=CH), 9.93 (s, 2H, OH)
$\mathbf{H_2L^2}$	272, 318	2.46-2.54 (m, 12H, CH$_2$), 4.45 (s, 4H, CH$_2$-O), 7.46 (d, *J* = 2.0 Hz, 2H, PhH), 7.55 (d, *J* = 2.0 Hz, 2H, PhH), 7.71 (d, *J* = 2.2 Hz, 2H, PhH), 8.45 (s, 2H, N=CH), 9.96 (s, 2H, OH).
$\mathbf{H_2L^3}$	274, 320	2.44-2.53 (m, 14H, CH$_2$), 4.44 (s, 4H, CH$_2$-O), 7.44 (d, *J* = 2.0 Hz, 2H, PhH), 7.54 (d, *J* = 2.0 Hz, 2H, PhH), 7.72 (d, *J* = 2.2 Hz, 2H, PhH), 8.46 (s, 2H, N=CH), 9.86 (s, 2H, OH)
$\mathbf{H_2L^4}$	276, 320	2.43-2.54 (m, 16H, CH$_2$), 4.43 (s, 4H, CH$_2$-O), 7.43 (d, *J* = 2.0 Hz, 2H, PhH), 7.51 (d, *J* = 2.0 Hz, 2H, PhH), 7.71 (d, *J* = 2.2 Hz, 2H, PhH), 8.41 (s, 2H, N=CH), 9.79 (s, 2H, OH)

UV-visible spectra: The absorption spectra of $\mathbf{H_2L^1}$-$\mathbf{H_2L^4}$ (Table-3), in diluted dichloromethane solution show that the spectra of $\mathbf{H_2L^1}$-$\mathbf{H_2L^4}$, are similar to each other.

The compounds $\mathbf{H_2L^1}$-$\mathbf{H_2L^4}$ exhibit two intense peaks at around 272 and 320 nm. The former absorption peaks at about 272 nm can be assigned to the π-π* transition of the benzene rings, while the latters can be attributed to the intra-ligand π-π* transition of the C=N bonds[15]. It is of note that there was no absorption around 400 nm, which are seen in the corresponding salen derivatives. The absorption peaks are ascribed to the quinoid form of H$_2$salen[16,17].

The ^{1}H NMR spectra of the title compounds $\mathbf{H_2L^1}$-$\mathbf{H_2L^4}$ in DMSO-d_6 are shown in Table-3. The ^{1}H NMR spectra showed a singlet at about 8.41-8.46 ppm indicating the existence of oxime bonds[16].

Conclusion

In this paper, a series of bromo-substituted Salamo-type compounds $\mathbf{H_2L^1}$-$\mathbf{H_2L^4}$ that have two oxime bonds instead of imine bonds have been designed and synthesized by the reaction of 2 equivalents of 5-bromo-2-hydroxybenzaldehyde with 1,7-*bis*(aminooxy)heptane, 1,8-*bis*(aminooxy)octane, 1,9-*bis*(aminooxy)nonane or 1,10-*bis*(aminooxy)decane under mild conditions, respectively. It is shown that an *O*-alkyl oxime moiety is much more useful to assemble supramolecular systems than a Schiff base moiety. Further investigation on the synthesis and structures of bromo-substituted Salamo-type complexes with transition metal ions, are now in progress.

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