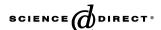
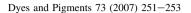


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Synthesis of Schiff base ligands derived from condensation of salicylaldehyde derivatives and synthetic diamine

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Abstract

Three Schiff base ligands have been prepared by condensation of 3-methyl, 4-methyl and 5-methyl salicylaldehyde with 4,4'-diaminoazobenzene (1), respectively. Diamine (1) from p-aminoacetanilide in the presence of glacial acetic acid, boric acid and sodium perboratetetrahydrate has been prepared. The products have been characterized by FT-IR, 1 H NMR, and 13 C NMR spectra. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Schiff base; 4,4'-Diaminoazobenzene; Salicylaldehyde derivatives

1. Introduction

Schiff base ligands have significant importance in chemistry, specially in the development of Schiff base complexes, because Schiff base ligands are potentially capable of forming stable complexes with metal ions [1,2]. Schiff bases that have solvent dependent UV/vis spectra (solvatochromicity) can be suitable NLO (nonlinear optical active) materials [3]. These ligands can be useful materials in solid phase extraction [4] and synthesis of ionselective electrodes for the determination of anions in analytical samples [5–8].

They are also useful in enantioselective [9,10] and regioselective [11] ring opening of epoxides, enantioselective epoxidation of alkenes [12] and asymmetric oxidation of methyl phenyl sulfide [13]. 4,4'-Diaminoazobenzene is useful as a model compound for studies of the chemistry of colored diamines, specifically for the preparation of colored disocyanates.

In this research the diamine (1) was synthesized according to the literature [14] (Scheme 1).

Then Schiff base ligands 2, 3 and 4 were prepared by the reaction of salicylaldehyde derivatives with diamine (1), as shown in Scheme 2.

2. Results and discussion

The overall yield of the diamine (1) from p-aminoacetanilide is 52%. The presence of $-NH_2$ stretching bonds in the 3300–3420 cm⁻¹ IR region, the lack of HNC=O stretching bond in the 1720 cm⁻¹ IR region and 1H NMR data for diamine (1) are completely consistent with the formulation indicated in Scheme 1. The diamine (1) was chosen to synthesize Schiff base ligands 2, 3 and 4 through the reaction with 3-methyl salicylaldehyde, 4-methyl salicylaldehyde and 5-methyl salicylaldehyde, respectively.

The Schiff base ligands **2**, **3** and **4** were easily prepared with 72–85% yield by refluxing two equivalents of the hydroxy aldehydes with one equivalent of the diamine (**1**) in anhydrous methanol. Complete condensation of all primary amino groups is confirmed by the lack of NH₂ stretching bonds in the 3300–3420 cm⁻¹ IR region and the presence of strong stretching bonds in the 1595–1605 cm⁻¹ IR region. The ¹H NMR, ¹³C NMR and IR data for **2**, **3** and **4** are completely consistent with the formulation indicated in Scheme 2.

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$$\begin{array}{c|c} & & & & \\ H_2N & & & \\ \hline & N & \\ & & \\$$

Scheme 1.

3. Experimental

Chemicals were purchased from the Fluka and Merck Chemical companies. Melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. ¹H NMR spectra were obtained at 500 MHz using a Bruker Avance 500 NMR in CDCl₃-d and DMSO-*d*₆ as the solvents. ¹³C NMR (500 MHz) spectra of compounds were obtained on a 500 MHz Avance Bruker spectrometer. The infrared spectra were determined on a Nicolet Magna series FT-IR 550 spectrometer using KBr pellets.

Preparation of 4,4'-diaminoazobenzene was carried out by the reaction of p-aminoacetanilide in the presence of glacial acetic acid, boric acid and sodium perboratetetrahydrate with hydrolysis the resulting 4,4'-bis(acetamido)azobenzene (Scheme 1).

In this method, the product was prepared as a yellow crystalline with 52% yield, mp: 238–241 °C; IR (KBr)cm⁻¹: 3350, 3110, 1585, 1400; ¹H NMR (DMSO- d_6 ; 500 MHz) δ (ppm): 7.82 (d, 4H), 6.74 (d, 4H), 5.72 (s, 4H), ¹³C NMR (DMSO- d_6) δ (ppm): 149, 145, 125, 114.

3.1. Preparation of N,N'-bis(n-methyl salicylidine)-4,4'-diaminoazobenzene (n = 3,4,5)

4,4'-Diaminoazobenzene (212 mg, 1.00 mmol) was added into a 50 ml round-bottom flask with 10 ml absolute methanol

and the temperature was raised to 60 °C and stirring was continued at this temperature until the diamine dissolved. Then n-methylsalicylaldehyde (n=3,4,5) (272 mg, 2.00 mmol) in 5 ml absolute methanol was added to the mixture in a round-bottom flask. The resulting mixture was refluxed for about 8–12 min. When the reaction was complete (checked by TLC), the mixture was cooled and the products were filtered, washed with absolute methanol and dried.

3.1.1. N,N'-Bis(3-methyl salicylidine)-4.4'-diaminoazobenzene (2)

Yield 85%; decomposition point: >300 °C; FT-IR (KBr)cm⁻¹: 3300–3500, 3020, 2900, 1605, 1150; ¹H NMR (DMSO- d_6 ; 500 MHz) δ (ppm): 13.38 (s, 2H), 8.71 (s, 2H), 8.02 (d, 4H), 7.40 (d, 4H), 7.29 (dd, 4H), 6.90 (t, 2H), 2.35 (s, 6H), ¹³C NMR (DMSO- d_6) δ (ppm): 163.4, 159.6, 151.28, 150.72, 134.65, 130.27, 126.42, 125.21, 124.29, 123.65, 122.0, 118.81, 118.39, 15.53.

3.1.2. N,N'-Bis(4-methyl salicylidine)-4,4'-diaminoazobenzene (3)

Yield 72%; decomposition point: >300 °C; FT-IR (KBr)cm⁻¹: 3330–3510, 3010, 2920, 1610, 1130; ¹H NMR (DMSO- d_6 ; 500 MHz) δ (ppm): 13.33 (s, 2H), 8.82 (s, 2H), 7.99 (d, 4H), 7.38 (d, 4H), 7.31 (d, 2H), 6.72 (d, 2H), 6.69 (s, 2H), 2.39 (s, 6H), ¹³C NMR (DMSO- d_6) δ (ppm): 159.1,

Scheme 2.

158.2, 150.24, 149.7, 141.12, 135.16, 130.2, 127.14, 124.53, 123.90, 122.11, 121.45, 119.22, 18.72.

3.1.3. N,N'-Bis(5-methyl salicylidine)-

4,4'-diaminoazobenzene (4)

Yield 70%; decomposition point: >300 °C; FT-IR (KBr)cm⁻¹: 3315–3450, 3015, 2900, 1610, 1135; ¹H NMR (DMSO- d_6 ; 500 MHz) δ (ppm): 13.42 (s, 2H), 8.47 (s, 2H), 7.95 (d, 4H), 7.32 (d, 4H), 7.26 (d, 2H), 6.83 (d, 2H), 6.64 (s, 2H), 2.41 (s, 6H), ¹³C NMR (DMSO- d_6) δ (ppm): 160.2, 158.4, 150.7, 149.36, 133.70, 131.84, 127.90, 126.40, 125.11, 123.22, 122.93, 119.54, 118.40, 17.50.

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