



SYNTHESIS OF SOME UNSYMMETRICAL NEW SCHIFF BASES FROM AZO DYES

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Keywords: Schiff base, azo dye, diaminomaleonitrile, salicylaldehyde, antimicrobial, *o*-hydroxy azoaldehydes

A simple and satisfactory environment friendly procedure for synthesis of some antimicrobial azo-Schiff bases is presented. The condensation of *o*-hydroxy azoaldehydes and diaminomaleonitrile in the presence of a catalytic amount of acetic acid produced desired Schiff bases in high yields.

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Synthesis of azo dyes precursors. A general procedure

To a solution of an aniline derivative (10 mmol) in water (5 mL), concentrated hydrochloric acid (20 mL) was added slowly with stirring. The clear solution was poured into ice-water mixture, diazotied with sodium nitrite (0.69 g, 10 mmol), dissolved in water (3.5 mL), during a period of 15 min at 0-5 °C. The cold diazo solution was added dropwise to the solution of salicylaldehyde (1.05 mL, 10 mmol) in water (50 mL) containing sodium hydroxide (0.4 g) and sodium carbonate (7.3 g) during a period of 30 min at 0-5 °C. The reaction mixture was stirred for 1 h in ice bath, allowed to warm slowly to room temperature and subsequently stirred for 4 h at this temperature. The product was collected by filtration and recrystallized from mixture of EtOH and H₂O (Scheme 1, Table 1).

5-Phenylazosalicylaldehyde 1a. Brown solid; Yield 1.76 g, 78%; M.p. 128-129 °C; IR (KBr, ν cm⁻¹): 3200 (O-H stretch), 3030 (aromatic C-H stretch), 1660 (aromatic aldehyde C=O stretch), 1618, 1568 (aromatic C=C stretch), 1478 (N=N stretch), 1280 (C-O stretch); ¹H NMR (400 MHz, CDCl₃, ppm) δ : 7.15 (d, J=8.8 Hz, 1H, H_e), 7.48-7.57 (m, 3H, H_g, H_h), 7.93 (dd, J=8.4 Hz, J=1.2 Hz, 2H, H_f), 8.21 (dd, J=8.8 Hz, J=2.4 Hz, 1H, H_d), 8.23 (d, J=2.4 Hz, 1H, H_c), 10.06 (s, 1H, H_b), 11.35 (s, 1H, H_a); UV-Vis (EtOH): λ_{\max} =240 nm, 350 nm, Exact mass (M): Calcd. for C₁₃H₁₀N₂O₂ 226.0742 found 226.0751.

INTRODUCTION

Schiff bases derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represented in important series of widely-studied organic ligands. A variety of applications such as biological,¹⁻⁴ clinical,⁵⁻⁸ analytical,⁹⁻¹² industrial¹³ and catalytical¹⁴⁻¹⁷ of Schiff bases and their metal complexes have been reported. Aromatic aldehyde Schiff bases have also attracted much attention due to their diverse biological activities, such as antimicrobial, antibacterial, antiviral, and anticancer activities.¹⁸ They are used in optical and electrochemical sensors, in various chromatographic methods and to enhance selectivity and sensitivity of the organic reagents. Schiff bases are easily characterized. They possess structural-similarities with natural biological substances. Their preparation procedures are relatively simple and have synthetic flexibility that enables tuning of suitable structural properties.¹⁹⁻²³ In the present investigation, some new Schiff bases have been in one-stage through a reaction of diaminiomaleonitrile with *o*-hydroxy azoaldehydes in the presence of acetic acid as catalyst.

Experimental Section

The UV-Vis spectra were measured on a Shimadzu UV-2100 spectrometer. The ¹H NMR (500 MHz) spectra were obtained with a Bruker 500 DRX-Avance NMR and the others (400 MHz) were registered with a Bruker 400 Avance 3 spectrometer. The IR spectra were taken with a Shimadzu 470 spectrometer using KBr pellets. Melting points of crystalline dicyano compounds were measured with a Electrothermal melting point apparatus and are not corrected. Mass spectra were recorded on a GC-MS Agilent Technologies QP-5973N MSD instrument. Typical reaction procedures and spectroscopic data for all products are described below.

5-(4-Nitrophenylazo)salicylaldehyde 1b. Orange solid; Yield 2.41g, 89%; M.p. 184-186 °C; IR (KBr, ν cm⁻¹): 3400 (O-H stretch), 3100 (aromatic C-H stretch), 1660 (aromatic aldehyde C=O stretch), 1600, 1570 (aromatic C=C stretch), 1520 (NO₂ asymmetric stretch), 1475 (N=N stretch), 1340 (NO₂ symmetric stretch), 1280 (C-O stretch), 850 (aromatic out of plane bend); ¹H NMR (500 MHz, CDCl₃, ppm) δ : 7.21 (d, J=8.95 Hz, 1H, H_c), 8.06 (d, J=8.96 Hz, 2H, H_f), 8.26 (dd, J=8.96 Hz, J=2.3 Hz, 1H, H_d), 8.33 (d, J=2.3 Hz, 1H, H_e), 8.43 (d, J=8.94 Hz, 2H, H_g), 10.10 (s, 1H, H_b), 11.50 (s, 1H, H_a); UV-Vis (CHCl₃): λ_{\max} =255 nm, 360 nm, Exact mass (M): Calcd. for C₁₃H₉N₃O₄ 271.0593 found 271.0582.

5-(4-methylphenylazo)salicylaldehyde 1c. Brown solid; Yield 2.1 g, 87%; M.p. 150-152 °C; IR (KBr, ν cm^{-1}): 3200 (O-H stretch), 3030 (aromatic C-H stretch), 2910 (aliphatic C-H stretch), 1650 (aromatic aldehyde C=O stretch), 1618, 1600, 1567 (aromatic C=C stretch), 1478 (N=N stretch), 1278 (C-O stretch), 820, 740, 690 (aromatic out of plane bend). $^1\text{H NMR}$ (500 MHz, CDCl_3 , ppm) δ : 2.49 (s, 3H, H_h), 7.16 (d, $J = 8.7$ Hz, 1H, H_e), 7.37 (d, $J = 8.2$ Hz, 2H, H_g), 7.86 (d, $J = 8.3$ Hz, 2H, H_f), 8.21 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1H, H_d), 8.23 (d, $J = 2.3$ Hz, 1H, H_c), 10.07 (s, 1H, H_b), 11.34 (s, 1H, H_a); UV-Vis: (EtOH) $\lambda_{\text{max}} = 240$ nm, 350 nm Exact mass (M): calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$, 240.0899 found 240.0872.

5-(4-acetylphenylazo)salicylaldehyde 1d. Brown solid; Yield 2.46 g, 92%; M.p. 176-178 °C; IR (KBr, ν cm^{-1}): 3200 (O-H stretch), 1675 (ketone C=O stretch), 1660 (aromatic aldehyde C=O stretch), 1617, 1595, 1567 (aromatic C=C stretch), 1480 (N=N stretch), 1260 (C-O stretch), 840, 735 (aromatic out of plane bend). $^1\text{H NMR}$ (500 MHz, CDCl_3 , ppm) δ : 2.71 (s, 3H, H_h), 7.19 (d, $J = 8.9$ Hz, 1H, H_e), 8 (d, $J = 8.4$ Hz, 2H, H_f), 8.15 (d, $J = 8.4$ Hz, 2H, H_g), 8.25 (dd, $J = 8.9$ Hz, $J = 2.2$ Hz, 1H, H_d), 8.29 (d, $J = 2.1$ Hz, 1H, H_c), 10.09 (s, 1H, H_b), 11.44 (s, 1H, H_a); UV-Vis: (EtOH) $\lambda_{\text{max}} = 258$ nm, 364 nm; Exact mass (M): Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3$ 268.0847 found 268.0864.

Synthesis of unsymmetrical Schiff bases. A general procedure

Different azo dyes (1mmol) in EtOH (7 mL) were added to a solution of diaminomaleonitrile (1 mmol, 0.11 g) in EtOH (7 mL) and then a catalytic amount of acetic acid (two or three drops) was added to mixture at room temperature. The reaction mixture was stirred for 2 h. The products were collected by filtration and recrystallized from ethanol (Scheme 2, Table 2).

Synthesis of 2a. Orange solid; Yield 0.30 g, 95 %; M.p. 248-250 °C; IR (KBr, ν cm^{-1}): 3300, 3400 (NH_2 stretch), 3190 (aromatic C-H stretch), 2200 (-CN stretch) 1627 (C=N stretch), 1600, 1555 (aromatic C=C stretch), 1478 (N=N stretch), 1280 (C-O stretch). $^1\text{H NMR}$ (500 MHz, DMSO, ppm) δ : 7.11 (d, $J = 8.85$ Hz, 1H, H_e), 7.53 (dd, $J = 8.35$ Hz, $J = 9.42$ Hz, 1H, H_i), 7.57 (d, $J = 7.72$ Hz, 2H, H_g), 7.85 (d, $J = 7.76$ Hz, 2H, H_h), 7.87 (dd, $J = 2.54$ Hz, $J = 8.82$ Hz, 1H, H_f), 8.03 (s, 2H, H_a), 8.66 (s, 1H, H_b), 8.70 (d, $J = 2.47$ Hz, 1H, H_d), 11.24 (s, 1H, H_c); UV-Vis: (DMSO) $\lambda_{\text{max}} = 257$ nm, 331 nm; Exact mass (M): Calcd. for $\text{C}_{17}\text{H}_{12}\text{N}_6\text{O}$ 316.1072 found 316.1055.

Synthesis of 2b. Orange solid; Yield 0.33 g, 92 %; M.p. 248-250 °C; IR (KBr, ν cm^{-1}): 3300, 3400 (NH_2 stretch), 3100 (aromatic C-H stretch), 2200 (-CN stretch) 1627 (C=N stretch), 1600, 1558 (aromatic C=C stretch), 1520 (NO_2 asymmetric stretch), 1480 (N=N stretch), 1340 (NO_2 symmetric stretch), 1280 (C-O stretch)); $^1\text{H NMR}$ (500 MHz, DMSO, ppm) δ : 7.13 (d, $J = 8.83$ Hz, 1H, H_e), 7.89 (d, $J = 8.82$ Hz, 1H, H_f), 8.00 (d, $J = 8.84$ Hz, 2H, H_g), 8.05 (s, 2H, H_a), 8.39 (d, $J = 8.78$ Hz, 2H, H_h), 8.63 (s, 1H, H_b), 8.77 (s, 1H, H_d), 11.56 (s, 1H, H_c); UV-Vis (DMSO); $\lambda_{\text{max}} = 259$ nm, 354 nm; Exact mass (M) Calcd. for $\text{C}_{17}\text{H}_{11}\text{N}_7\text{O}_3$ 361.0923 found 361.0912.

Synthesis of 2c. Yellow solid; Yield 0.28 g, 86%, M.p. 256-258 °C; IR (KBr, ν cm^{-1}): 3300, 3400 (NH_2 stretch), 3030 (aromatic C-H stretch), 2910 (aliphatic C-H stretch), 2200 (-CN stretch), 1625 (C=N stretch), 1600, 1555 (aromatic C=C stretch), 1480 (N=N stretch), 1280 (C-O stretch); $^1\text{H NMR}$ (500 MHz, DMSO, ppm) δ : 2.39 (s, 3H, H_i), 7.10 (d, $J = 11$ Hz, 1H, H_e), 7.38 (d, $J = 10$ Hz, 2H, H_h), 7.76 (d, $J = 10$ Hz, 2H, H_g), 7.85 (dd, $J = 3$ Hz, $J = 11$ Hz, 1H, H_f), 8.04 (s, 2H, H_a), 8.69 (s, 1H, H_b), 8.67 (d, $J = 3.5$ Hz, 1H, H_d); UV-Vis (DMSO): $\lambda_{\text{max}} = 252$ nm, 332 nm; Exact mass (M): Calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_6\text{O}$ 330.1229 found 330.1289.

Synthesis of 2d. Yellow solid; Yield 0.28 g, 80%; M.p. 262 °C_{dec.}; IR (KBr, ν cm^{-1}): 3300, 3400 (NH_2 stretch), 1675 (ketone C=O stretch), 1625 (C=N stretch), 1600, 1557, (aromatic C=C stretch), 1480 (N=N stretch), 1260 (C-O stretch); $^1\text{H NMR}$ (500 MHz, DMSO, ppm) δ : 2.63 (s, 3H, H_i), 7.12 (d, $J = 8.8$ Hz, 1H, H_e), 7.89 (dd, $J = 8.3$ Hz, $J = 2.1$ Hz, 1H, H_f), 7.93 (d, $J = 8.3$ Hz, 2H, H_g), 8.04 (s, 2H, H_a), 8.17 (d, $J = 8.3$ Hz, 2H, H_h), 8.64 (s, 1H, H_b), 8.75 (d, $J = 1.9$ Hz, 1H, H_d), 11.40 (s, 1H, H_c); UV-Vis (DMSO): $\lambda_{\text{max}} = 365$ nm, 549 nm; Exact mass (M): Calcd. for $\text{C}_{19}\text{H}_{14}\text{N}_6\text{O}_2$ 358.1178 found 358.1197.

Table 1. Properties of azo dye compounds

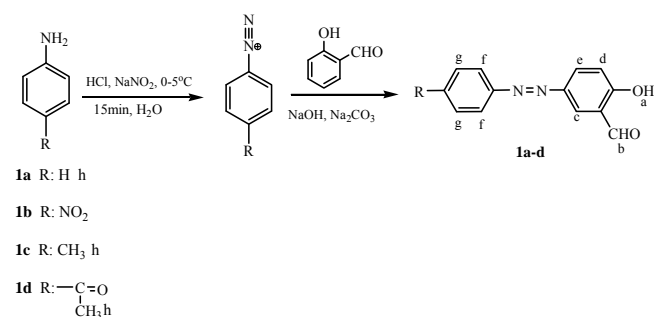
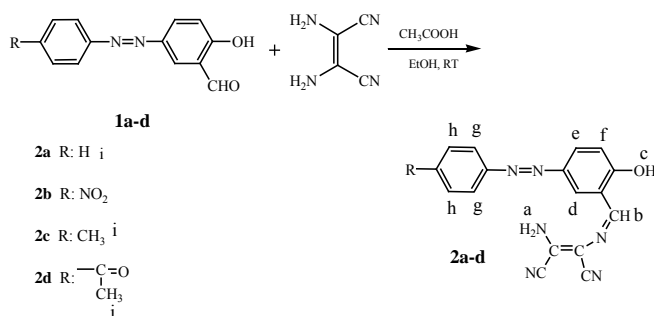
Entry	Time (h)	Yield (%)	Colour	Mp (°C)
1a	5	78	Brown solid	128-129
1b	5	89	Orange solid	184-186
1c	5	87	Brown solid	150-152
1d	5	92	Brown solid	176-178

Table 2. Properties of Schiff base compounds

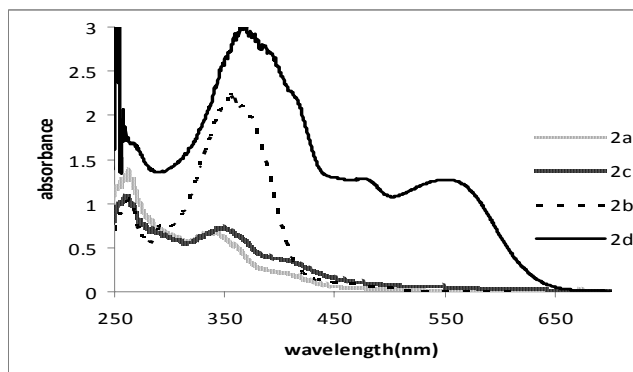
Entry	Time (h)	Yield (%)	Colour	M.p. (°C)
2a	2	95	Orange solid	248-250
2b	2	92	Orange solid	248-250
2c	2	86	Yellow solid	256-258
2d	2	80	Yellow solid	262-264

RESULTS AND DISCUSSION

Diazo coupling was accomplished selectively at the 4-position of salicylaldehyde ring to give compounds **1** in moderate to excellent yields (78-92%) (Scheme 1) (Table 1). The electronic absorption spectra of compounds **1** and **2** show intense lowest energy charge-transfer absorption band in the UV-Vis region (240-260 nm and 340-370 nm). Electron attracting substituents such as $-\text{NO}_2$, C=O in the coupler increase the polarizability. This leads to a decrease in the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), thus $\pi-\pi^*$ electronic transition with lower frequency photons, results a bathochromic shift of the visible band for azo dye and Schiff bases (Figure 1).

Scheme 1. Synthetic route for azo dye derivatives **1a-d**Scheme 2. Synthetic route for Schiff base derivatives **2a-d**

All the compounds are air stable with sharp melting points indicating the purity of the compounds. The spectra analysis of the compounds is in agreement with the composition assigned to the compounds.

Figure 1. UV-Vis Absorption spectra of **2a-d** (in DMSO)

The IR spectrum of each Schiff base compound confirms the formation of imine band (-C=N-) and absence of the original aldehyde band (-C=O). A band at $1625\text{--}1627\text{ cm}^{-1}$ is assigned to the stretching vibration of the imines group (C=N). All the compounds displayed a band at $1260\text{--}1280\text{ cm}^{-1}$ assigned to (C-O) stretching vibration of the phenol-OH. The $^1\text{H NMR}$ spectra showed singlet and sharp bands at $8.63\text{--}8.69\text{ ppm}$ which further confirmed the formation of -C=N- bonds. Reaction of DAMN with azo aldehydes readily yields the asymmetrical Schiff base compounds **2a-d** in high yields. IR and $^1\text{H NMR}$ spectra features agree with the formula assignments.

Also, the similar IR spectra of compounds **2a-d** revealed the absence of the carbonyl group band in $1650\text{--}1660\text{ cm}^{-1}$ and appearance of a strong band in $1625\text{--}1627\text{ cm}^{-1}$ region, assignable to the $\nu(\text{C=N})$ imine group. All the compounds were analyzed by melting point, IR, UV-Vis and $^1\text{H NMR}$ spectra.

ACKNOWLEDGMENTS

The partial support of this research by the Research Committee of University of Guilan is gratefully acknowledged.

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Received: 07.02. 2012.

Accepted: 07.03. 2013.