



Research Article

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## Synthesis, spectroscopic studies of new azo ligands Schiff base and amines derived of 5-phenylazo-2-hydroxybenzaldehyde

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### ABSTRACT

Three new azoimine ligands, namely bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl ether(**1**), bis[5-phenylazo-2-hydroxy benzaldehyde]-4,4'-diiminophenyl methane(**2**), bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl ethane(**3**) and their reduced imine form bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl ether(**4**), bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl methane(**5**), bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl ethane(**6**) were synthesized by reducing the imine groups of the azoimine (**1-3**) with Sodium borohydride. The azoimine (**1-3**) and their reduced form (**4-6**) were characterized using elemental analyses, IR, UV-Visible spectroscopy, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra.

**Keywords:** Azo dyes, Schiff base, Amines, Uv-visible.

### INTRODUCTION

Azo compounds are very important molecules and have attracted much attention in both academic and applied research [1-3]. These compounds are key chromophores in the chemical industry as dyes and pigments, food additives, indicators, radical reaction initiators and therapeutic agents [4-6]. The spectral properties of azo dyes depend on the nature of both the azo and the coupling components. For example, azometine compounds which have some interesting structural properties and uses can be prepared by coupling of azo and methine groups [7-10]. Furthermore, considerable attentions have been paid to the study of azo-azomethine dyes containing hydroxyl groups in recent years due to their metabolites are toxic, carcinogenic, and mutagenic [11-14]. These compounds have the ability to form different type of intra- and intermolecular hydrogen bond and intramolecular proton transfer between their nitrogen atoms. This tautomerization can be induced either by light, heat or the solvent [15-19]. Herein, new azo (**1-3**) were prepared of 5-phenylazo-2-hydroxybenzaldehyde with 4,4'(diaminodiphenyl) derivatives and their reduced form (**4-6**) were prepared by reducing the imine groups of the azoimine (**1-3**) with Sodium borohydride.

### EXPERIMENTAL SECTION

#### 1.1. Material and methods

All reactions were monitored by thin-layer chromatography and experiments were repeated at least in triplicates. The chemicals used for the synthesis were of analytical reagent grade and was used without further purification. The solvents were of spectroscopic grade. IR spectra were recorded on a Shimadzu 8000S FTIR spectrophotometer using

KBr pellets. Nuclear Magnetic Resonance ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR) spectra were recorded on a Bruker (ARX-500) spectrometer (400 MHz) in  $\text{DMSO}-d_6$ . The mass spectra were recorded on Os\_MSMS\_20CE.m, Acquisition SW 6200 series TOF/6500, Version series Q-TOF B.05.01(B5125.1) mass spectrometer. The electronic spectra were obtained using Unicam Spectrophotometer. Elemental carbon, nitrogen and hydrogen analyses were performed with a Leco CHNS-932 analyzer.

## 1.2. Synthesis and Characterization

### 1.2.1. Synthesis of 5-phenylazo-2-hydroxybenzaldehyde (ALD)

The 5-phenylazo-2-hydroxybenzaldehyde was synthesized using the known coupling methods [20]. Yellow solid, yield 63.09 %, mp  $128^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3100-3300 (OH), 3040 (C-H, aromatic), 1664 (C=O), 1570 (C=C, aromatic), 1478 (N=N), 1380, 1284 (C-O), 1155 (C-N), 682.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  = 11.51 (s, H-10), 10.37 (s, H-9), 8.19 (d,  $J$  = 2.4 Hz, H-3), 8.10 (dd,  $J$  = 2.6, 8.8 Hz, H-2), 7.86 (m, 2H, H-4, H-8), 7.56 (m, 3H, H-5, H-6, H-7), 7.20 (d,  $J$  = 8.8 Hz, H-1).  $^{13}\text{C}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  = 118.19, 122.14, 122.39, 123.51, 129.22, 129.51, 130.92, 144.57, 151.63, 163.08, 190.35. Elemental analysis calcd (%) For  $(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2)$ : C 69.02, H 4.46, N 12.38, found: C 68.76, H 4.63 and N 12.29.

### 1.2.2. General procedure for synthesis of azoimine ligands (1-3)

Three ligands (1-3) were prepared by refluxing of (0.01 mol) of 5-phenylazo-2-hydroxybenzaldehyde with (0.005 mol) of 4,4'-(diaminodiphenyl) derivatives in 100 mL of absolute ethanol for 1 h. pure compound was obtained as yellow precipitate by cooling the reaction mixture to room temperature. The precipitate was filtered off and washed with absolute ethanol and dry in desiccators.

#### Bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl ether (1)

Yellow – Orange solid, yield 93.18 %, mp  $256^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3415 (OH), 3055 (C-H, aromatic), 2918 (C-H, aliphatic), 2846, 1618 (C=N), 1573 (C=C, aromatic), 1500 (N=N), 1349, 1272 (C-O), 1194 (C-N), 838, 686. Elemental analysis calcd (%) For  $(\text{C}_{38}\text{H}_{28}\text{O}_3\text{N}_6)$ : C 74.01, H 4.58, N 13.63, found: C 73.58, H 4.51 and N 13.45.

#### Bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl methane (2)

Orange Solid, yield 94.27 %, mp  $> 260^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3424 (OH), 3034 (C-H, aromatic), 2918 (C-H, aliphatic), 2852, 1617 (C=N), 1569 (C=C, aromatic), 1495 (N=N), 1353, 1280 (C-O), 1188 (C-N), 832, 683. Elemental analysis calcd (%) For  $(\text{C}_{39}\text{H}_{30}\text{O}_2\text{N}_6)$ : C 76.20, H 4.92, N 13.67, found: C 76.06, H 4.84 and N 13.38.

#### Bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl ethane (3)

Orange - Yellow solid, yield 90.73 %, mp  $> 260^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3418 (OH), 3022 (C-H, aromatic), 2919 (C-H, aliphatic), 2854, 1618 (C=N), 1572 (C=C, aromatic), 1490 (N=N), 1351, 1281 (C-O), 1187 (C-N), 830, 680. Elemental analysis calcd (%) For  $(\text{C}_{40}\text{H}_{32}\text{O}_2\text{N}_6)$ : C 76.41, H 5.13, N 13.37, found: C 76.01, H 4.87 and N 13.44.

## 1.3. General procedure for synthesis of the reduce form (4-6)

The reduce form (4-6) where as follow (0.001 mol) of the azoimine ligands (1-3) were dissolved in 100 mL absolute ethanol and then 0.075g (0.002 mol) of Sodium borohydride, was added. The mixture was stirred at room temperature for 72h and the solvent was removed by rotary evaporation to dryness. The solid was dissolved in about 150 mL of distilled water, and extracted with 3×50 mL portions of  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  layer was dried by standing with ~ 40g of anhydrous sodium sulfate powder for about 30 min, filtered and the  $\text{CHCl}_3$  removed by rotary evaporation. The isolated brown-yellow powder was stored in desiccators.

#### Bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl ether (4)

Brown Solid, yield 83.80 %, mp  $185^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3436 (OH), 3284 (N-H), 3033 (C-H, aromatic), 2922 (C-H, aliphatic), 2857, 1594 (C=C, aromatic), 1506 (N=N), 1251 (C-O), 830, 683.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  = 10.49 (s, H-10), 7.84 (br s, H-3), 7.76 (d,  $J$  = 7.6 Hz, H-4, H-8), 7.69 (d,  $J$  = 8.7 Hz, H-2), 7.51 (m, 3H, H-5, H-6, H-7), 7.00 (d,  $J$  = 8.6 Hz, H-1), 6.69 (m,  $J$  = 8.7 Hz, H-12, H-13), 6.55 (m,  $J$  = 8.8 Hz, H-11, H-14), 5.98 (br s, N-H), 4.22 (br s, 2H, H-9).  $^{13}\text{C}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  = 158.83, 152.29, 148.43, 145.17, 130.38, 129.29, 127.15, 123.20, 122.93, 122.04, 119.05, 115.35, 113.00. ESI-TOF MSMS  $m/z$  (%):  $[\text{M}]^+$  = 621 molecular ion peak is not observed, but 305.15  $[\text{M}]^{+2}$   $[\text{C}_6\text{H}_4\text{-N=NH-C}_6\text{H}_3\text{OH-CH}_2\text{-NH}_2\text{-C}_6\text{H}_5]$ . Elemental analysis calcd (%) For  $(\text{C}_{38}\text{H}_{32}\text{O}_3\text{N}_6)$ : C 73.53, H 5.20, N 13.54, found: C 73.17, H 5.53 and N 13.42.

#### Bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl methane (5)

Yellow Solid, yield 88.44 %, mp  $156^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3420 (OH), 3268 (N-H), 3034 (C-H, aromatic), 2910 (C-H, aliphatic), 2857, 1591 (C=C, aromatic), 1508 (N=N), 1258 (C-O), 769, 691.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  = 10.51 (s, H-10), 7.82 (s, H-3), 7.76 (d,  $J$  = 7.2 Hz, H-4, H-8), 7.67 (dd,  $J$  = 2, 8.5 Hz, H-2), 7.50 (m, 3H, H-5, H-6, H-7), 6.99 (d,  $J$  = 8.6 Hz, H-1), 6.85 (d,  $J$  = 8.3 Hz, H-12, H-13), 6.50 (d,  $J$  = 8.1 Hz, H-11, H-14), 5.98 (m, N-H),

4.22 (s, 2H, H-9), 3.57 (s, H-R).  $^{13}\text{C}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  = 158.58, 151.88, 146.48, 144.88, 130.10, 129.20, 129.06, 128.82, 127.04, 123.07, 122.55, 121.81, 115.14, 111.96. ESI-TOF MSMS  $m/z$  (%):  $[\text{M}]^+ = 619$  molecular ion peak is not observed, but 305.15  $[\text{M}]^{+2}$   $[\text{C}_6\text{H}_4\text{-N=NH-C}_6\text{H}_3\text{OH-CH}_2\text{-NH}_2\text{-C}_6\text{H}_5]$ . Elemental analysis calcd (%) For  $(\text{C}_{39}\text{H}_{34}\text{O}_2\text{N}_6)$ : C 75.71, H 5.54, N 13.58, found: C 75.45, H 5.83 and N 13.35.

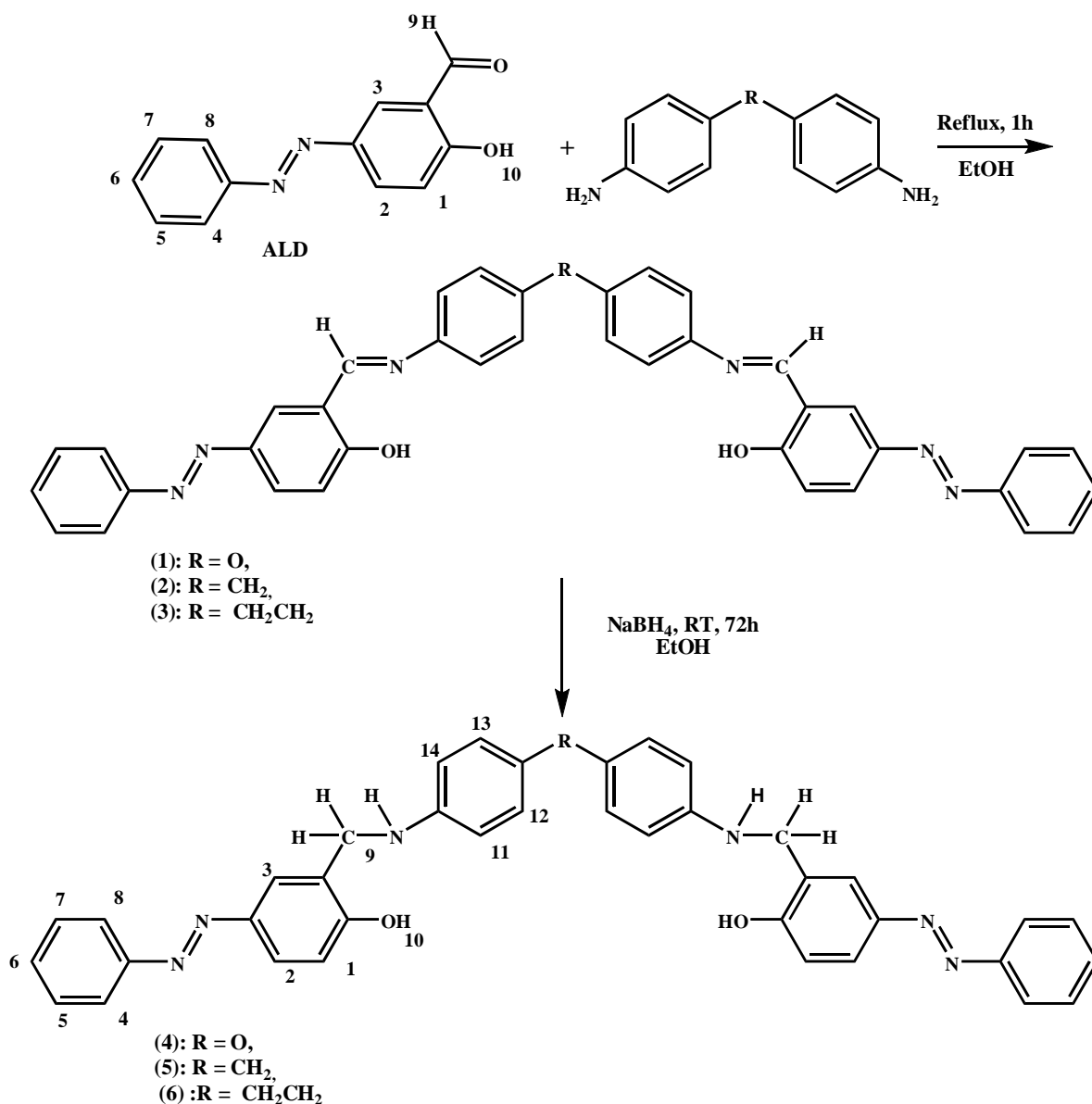


Fig. 1 Synthesized azo ligands dyes (1 - 6)

#### Bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl ethane (6)

Yellow Solid, yield 86.15 %, mp 199 °C. IR (KBr,  $\text{cm}^{-1}$ ): 3432 (OH), 3285 (N-H), 3032 (C-H, aromatic), 2914 (C-H, aliphatic), 1586 (C=C, aromatic), 15022 (N=N), 1226 (C-O), 832, 684.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  = 10.50 (br s, H-10), 7.82 (s, H-3), 7.76 (d,  $J$  = 7.6 Hz, H-4, H-8), 7.68 (d d,  $J$  = 2.3, 8.6 Hz, H-2), 7.49 (m, 3H, H-5, H-6, H-7), 7.00 (d,  $J$  = 8.6 Hz, H-1), 6.88 (d,  $J$  = 8.3 Hz, H-12, H-13), 6.50 (d,  $J$  = 8.4 Hz, H-11, H-14), 5.98 (br s, N-H), 4.23 (s, 2H, H-9), 2.58 (s, 2H, H-R).  $^{13}\text{C}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  = 158.66, 152.09, 146.66, 145.15, 130.35, 129.28, 129.15, 128.73, 122.66, 122.02, 122.69, 122.02, 115.34, 112.14. ESI-TOF MSMS  $m/z$  (%):  $[\text{M}]^+ = 633$  molecular ion peak is not observed, but 305.15  $[\text{M}]^{+2}$   $[\text{C}_6\text{H}_4\text{-N=NH-C}_6\text{H}_3\text{OH-CH}_2\text{-NH}_2\text{-C}_6\text{H}_5]$ . Elemental analysis calcd (%) For  $(\text{C}_{40}\text{H}_{36}\text{O}_2\text{N}_6)$ : C 75.93, H 5.73, N 13.28, found: C 75.55, H 6.12 and N 13.02.

## RESULTS AND DISCUSSION

Treatment of 5- phenylazo -2- hydroxybenzaldehyde (ALD) with 4,4'(diaminodiphenyl) derivatives in refluxing ethanol afforded the new azoimine ligand (1-3) in a good yield (Fig 1). Pure products were characterized by IR, Uv-visible spectroscopy and elemental analyses. These organic compounds can act as tetradentate  $\text{N}_2\text{O}_2$  and pentadentate

N<sub>2</sub>O<sub>3</sub> ligands. There new azo ligands (4-6) can be obtained by redcuig the imine groups of the azoimine ligands (1-3) with with Sodium borohydride. The azoimine (1-3) and their reduced form (4-6) were characterized using elemental analyses, IR, UV-visble spectroscopy, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra.

## 2.1. FT-IR

The vibration bands with the wave numbers 3415, 3424, 3418, 3436, 3420 and 3432 cm<sup>-1</sup> are assigned to  $\nu$  (O–H) vibration mode. The N–H bond was observed at 3284, 3268 and 3285 for the azoimine ligands (1-3). 2900 - 3055 (C–H aliphatic, C–H aromatic); 1573, 1569, 1572, 1594, 1591 and 1586 cm<sup>-1</sup> (C=C) and 1272, 1280, 1281, 1251, 1258 and 1226 cm<sup>-1</sup> (C–O) were observed for compounds (1–6), respectively. The C=N bond was observed at 1618, 1617 and 1618 cm<sup>-1</sup> the azoimine ligands (1-3). The N=N bond was observed at 1500, 1495, 1490, 1506, 1508 and 1522 cm<sup>-1</sup> for compounds (1–6) respectively. The stretching frequency observed at 2846–2897 cm<sup>-1</sup> in compounds (1–6) showed the presence of O–H...N intramolecular hydrogen bonds [21, 22]. The results are given in Table 1.

## 2.2. <sup>1</sup>H NMR and <sup>13</sup>C NMR

The OH protons were observed as singlets at 10.49, 10.51 and 10.50 ppm for the ligands (1-3). The phenyl protons were observed as singlets I the range at 6.55 –7.84. The imine protons were found as singlets at 5.98 ppm. The azomethine protons were (which proton) observed as singlets around 4.22. The singlet of the R–H protons was observed at 3.57, 2.58 ppm for compounds 2 and 3, respectively. The <sup>13</sup>C-NMR spectra of compounds 1, 2 and 3 have 13, 14 and 14 signals, respectively.

## 2.3. MS

In the mass spectrum, the m/z 620, 618 and 632 can be assigned to the molecular ions M<sup>+</sup> and the peaks at m/z 621, 619 and 633 to the [M + 1]<sup>+</sup> ions for the ligands 1, 2 and 3, respectively [23]. The most intense peaks at 305 [M + 2]<sup>+</sup>, for the ligands (1-3) is assigned to [C<sub>6</sub>H<sub>4</sub>–N=NH–C<sub>6</sub>H<sub>3</sub>OH–CH<sub>2</sub>–NH<sub>2</sub>–C<sub>6</sub>H<sub>5</sub>] fragment.

## 2.4. UV–Vis

The electronic spectra of all synthesized compounds are measured (in the range of 200–900 nm) in solvent DMF, at room temperature (Fig 2). The UV–vis absorption spectra of ALD and compounds (1-6) show two bands in the range 338 - 358 nm and 452 nm. The results are given in (Table1). Which are assigned to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic transition of azo–aromatic chromophore of the aromatic ring and intramolecular charge transfer interaction [24].

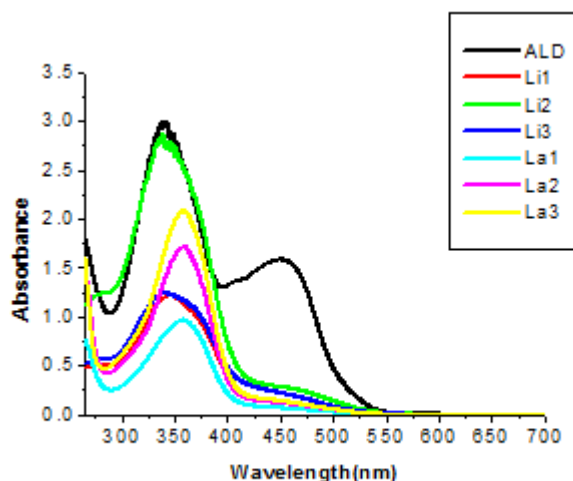


Fig. 2: Absorption spectra of ALD and azo ligands dyes (1-6) in DMF

Table 01: Tentative assignments of some selected IR (KBr, cm<sup>-1</sup>) and UV-Vis data of the prepared azo ligands

compounds	$\nu$ (N=N)	$\nu$ (C=C, ar)	$\nu$ (C=N)	$\nu$ (C=O)	$\nu$ (C-H, ar)	$\nu$ (N-H)	$\lambda_{\text{max}}$ (nm)
ALD	1478	1570	-	1664	3040	-	342, 453
1	1500	1573	1618	-	3055	-	344
2	1495	1569	1617	-	3034	-	338
3	1490	1572	1618	-	3022	-	343
4	1506	1594	-	-	3033	3284	358
5	1508	1591	-	-	3034	3268	357
6	1522	1586	-	-	3032	3285	356

## CONCLUSION

In this research work, we have prepared three new azoimine ligands, namely bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl ether (**1**), bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl methane (**2**), bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl ethane (**3**) and their reduced imine form bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl ether (**4**), bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl methane (**5**), bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diaminophenyl ethane (**6**).

All synthesized compounds were characterized using elemental analyses, IR, Uv-visble spectroscopy,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectra.

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