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Synthesis and Characterization of 4,4'-Diaminodiphenylmethane Schiff Bases

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Five novel Schiff bases were prepared from the reaction of 4,4'-diaminodiphenylmethane with acetylacetone, 3-chloroacetylacetone, salicylaldehyde, benzaldehyde and *m*-tolualdehyde. The synthesized Schiff bases were characterized by spectroscopic methods and elemental analysis.

Key Words: Schiff bases, 4,4'-Diaminodiphenylmethane.

INTRODUCTION

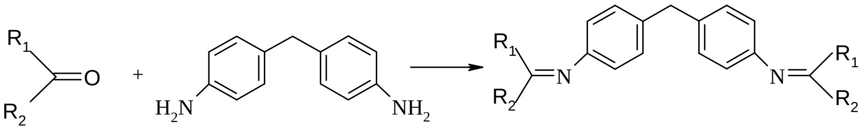
Schiff bases are important in diverse fields of chemistry owing to their interesting properties, *e.g.* thermochromism, photochromism and biological activities[1-3]. A lot of Schiff base compounds are used as ligands and catalysts in coordination and organic chemistry. Polydentate Schiff base complexes containing nitrogen and oxygen donor atoms are useful for catalytic applications[4,5]. It is known also using Schiff bases and their derivatives as reagents in pharmaceutical, dye and polymer technology are very important. Thus, the chemists are prompted to generate new Schiff base derivatives by introducing new substituents into the existing skeleton.

Herein, the synthesis and characterization of some novel 4,4'-diaminodiphenylmethane Schiff bases are reported.

EXPERIMENTAL

All the starting materials and solvents are commercially available and were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AV 400 instrument operating at the appropriate frequencies using TMS as external standard. IR spectra were obtained from a Mattson 1000 ATI Unicam FT-IR spectrometer in KBr discs. The UV-visible spectra were measured using a Unicam UV-Visible UV2 series spectrometer. Elemental analysis were performed on a Fisons EA 1108 CHNS-O instrument and melting points were determined by Gallenkamp MPD 350 BM 2.5 apparatus.

Synthetic procedures: The general procedure for the synthesis of five novel Schiff bases is given in **Scheme-I**.



1 R$_1$: CH$_3$; R$_2$: CH$_3$COCH$_2$- **2** R$_1$: CH$_3$; R$_2$: CH$_3$COCHCl-
3 R$_1$: H; R$_2$: -C$_6$H$_4$(OH) **4** R$_1$: H; R$_2$: -C$_6$H$_4$(CH$_3$) **5** R$_1$: H; R$_2$: C$_6$H$_5$-

Scheme-I Condensation reactions of 4,4'-diaminodiphenylmethane with different carbonyl groups afford 4,4'-diaminodiphenylmethane Schiff bases

N, N'-*Bis*(acetylacetone)4,4'-diaminodiphenylmethane (1): Acetylacetone (0.5 mL, 4.8 mmol) was added to a solution of 4,4'-diaminodiphenylmethane (0.48 g, 2.42 mmol) in toluene (25 mL) and the mixture was heated to reflux for 30 h. Compound **1** was obtained from the evaporation of the solvent as a viscous liquid that dissolved in a minimum amount of dichloromethane. After adding Et$_2$O to the solution, a yellow precipitate was obtained that was filtered off and recrystallized from ethyl acetate/ hexane (1:1). Yield: 0.56 g (63.4 %). m.p. 103-105ºC. Anal. Calcd. (%) for $C_{23}H_{26}N_2O_2$; C, 76.2; H, 7.2; N, 7.7. Found (%): C, 76.1; H, 7.3; N, 7.6. Selected FT-IR ν(cm^{-1}): 3080w, 2999w, 1617s ν(C=N), 1592s, 1567s, 1523m, 1496m, 1446m, 1413m, 1361m, 1323m, 1284s, 1195s, 1028m, 918s, 797m, 764m. ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm, 12.36 (s, 2H, =C–O–H····N); 7.23-7.11 (m, 8H, Ar-H); 5.06 (s, 2H, C=C–H), 3.86 (s, 2H, CH$_2$); 2.00 (s, 6H, CH$_3$); 1.91 (s, 6H, CH$_3$). ^{13}C NMR (acetone-d$_6$, 100.6 MHz): δ ppm, 195.1 (C=O keto form), 159.8 (C=N), 138.4, 137.1, 129.6, 124.2, 97.2 (C=C enol form), 40.2 (CH$_2$), 29.3 (CH$_3$), 18.9 (CH$_3$). UV-Vis (nm): 330.

N,N'-*Bis*(3-chloroacetylacetone)4,4'-diaminodiphenylmethane (2): 3-Chloroacetylacetone (1.0 mL, 8.8 mmol) was added to a solution of 4, 4'-diaminodiphenylmethane (0.88 g, 4.4 mmol) in toluene (30 mL) and the mixture was heated to reflux for 20 h. Compound **2** was obtained from the evaporation of the solvent and it was recrystallized from acetone as a yellowish crystal. Yield: 0.65 g (34.2 %). m.p. 115-116ºC. Anal. Calcd. (%) for $C_{23}H_{24}N_2O_2Cl_2$; C, 64.0; H, 5.6; N, 6.5. Found (%): C, 64.4; H, 5.9; N, 6.3. Selected FT-IR ν(cm^{-1}): 3128w, 3036w, 2924w, 1609s ν(C=N), 1556s, 1516s, 1417s, 1358s, 1272s, 1206s, 1007m, 915m, 750m, 506m. ^{1}H NMR (CDCl$_3$): δ ppm, 12.83 (very small, ClC=C–O–H···N); 7.34-7.23 (m, 8H, Ar-H); 7.16 (s, 2H, ClCH); 4.03 (s, 2H, CH$_2$); 2.28 (s, 6H, CH$_3$); 2.07 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ ppm, 189.3 (C=O), 153.2 (C=N), 133.6, 131.5, 124.5, 120.3, 99.2 (ClCH), 35.7 (CH$_2$), 23.4 (CH), 13.1 (CH$_3$). UV-Vis (nm): 344, 241.

N,N'-*Bis*(salicylidene)4,4'-diaminodiphenylmethane (3): Salicylaldehyde (1.0 g, 8.2 mmol) was added to a solution of 4,4'-diaminodiphenylmethane (0.81 g, 4.1 mmol) in ethanol (25 mL) and the mixture was stirred for 1 h at room temperature. Compound **3** was obtained from evaporation of ethanol and it was recrystallized from dichloromethane as a bright yellow crystal. Yield: 1.65 g (99 %). m.p. 212-213ºC. Anal. Calcd. (%) for $C_{27}H_{22}N_2O_2$; C, 79.8; H, 5.4; N, 6.9. Found (%): C, 79.7; H, 5.2; N, 6.8. Selected FT-IR ν(cm^{-1}): 3446b (OH), 3023w, 2931m, 2857w, 1623s (C=N), 1576s, 1503s, 1370m, 1285s, 1186m, 1166m, 756s, 644m. ^{1}H NMR ($CDCl_3$): δ ppm, 13.31 (broad, Ar–O–H···N); 8.65 (s, 2H, N=CH) 7.51-6.93 (m, 16H, Ar-H); 4.07 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ ppm, 162.2 (C=N), 161.1, 146.7, 139.8, 133.1, 132.2, 129.1, 121.4, 119.3, 119.0, 117.3, 41.0 (CH_2). UV-Vis (nm): 344, 272.

N,N'-*Bis*(*m*-toluilidene)4,4'-diaminodiphenilmethane (4): *m*-Tolualdehyde (1.02 g, 8.1 mmol) was added to a solution of 4,4'-diaminodiphenylmethane (0.8 g, 4.0 mmol) in methanol (20 mL) and the mixture was stirred for 24 h at room temperature. Compound **4** was obtained from evaporation of methanol and it was recrystallized from methanol as a white crystal. Yield: 0.65 g (40 %). m.p. 190ºC. Anal. Calcd. (%) for $C_{29}H_{26}N_2$; C, 86.6; H, 6.5; N, 7.0. Found (%): C, 86.3; H, 6.4; N, 6.85. Selected FT-IR ν(cm^{-1}): 3023w, 2917w, 2852w, 1629s, 1595s ν(C=N), 1503s, 1417w, 1212m, 1146s, 789s, 696s. ^{1}H NMR ($CDCl_3$): δ ppm, 8.27 (s, 2H, N=CH); 7.59-6.99 (m, 16H, Ar–H); 3.86 (s, 2H, CH_2); 2.27 (s, 6H, CH_3). ^{13}C NMR (acetone-d_6, 100.6 MHz): δ ppm, 159.7 (C=N), 150.2, 139.4, 138.3, 136.7, 131.9, 129.56, 12.0, 128.6, 126.0, 121.0, 40.6 (CH_2), 20.4 (CH_3). UV-Vis (nm): 323.8, 269.2, 230.8

N,N'-*Bis*(benzylidene)4,4'-diaminodiphenilmethane (5): Benzaldehyde (1.0 mL, 9.9 mmol) was added to a solution of 4,4'-diaminodiphenylmethane (0.98 g, 4.95 mmol) in methanol (25 mL) and the mixture was stirred for 24 h at room temperature. The compound **5** was obtained from evaporation of methanol and it was recrystallized from dichloromethane as a white crystal. Yield: 0.75 g (40.5 %). m.p. 210ºC. Anal. Calcd. (%) for $C_{27}H_{22}N_2$; C, 86.6; H, 5.9; N, 7.5. Found (%): C, 86.35; H, 5.6; N, 7.2. Selected FT-IR ν(cm^{-1}): 3063w, 3030w, 2904w, 2884w, 1629s ν(C=N), 1576s, 1509s, 1451s, 1430m, 1365m, 1318w, 1199w, 1173w, 1106w, 921w, 816s, 696s. ^{1}H NMR ($CDCl_3$): δ ppm, 8.61 (s, 2H, N=C-H); 7.99-7.96, 7.53-7.23 (m, 18H, Ar–H); 4.05 (s, 2H, CH_2). ^{13}C NMR (acetone-d_6, 100.6 MHz): δ ppm, 159.6 (C=N), 150.2, 139.4, 136.7, 131.2, 129.6, 128.7, 128.6, 121.0, 40.6 (CH_2). UV-Vis (nm): 323.6, 266.2.

RESULTS AND DISCUSSION

Condensation of 4,4'-diaminodiphenylmethane with acetylacetone, 3-chloroacetylacetone, salicylaldehyde, benzaldehyde and *m*-tolylaldehyde yields five novel Schiff bases (**Scheme-I**). The structures of the compounds were elucidated by spectroscopic methods and elemental analysis. The first two ligands **1** and **2**, which are similar to each other, have been prepared from aliphatic β-diketones by refluxing in toluene for 30 and 20 h, respectively, while the other ligands have been easily obtained at room temperature. The compounds **1**, **2** and **3** are containing the similar functional groups, two nitrogen and two oxygen donor atoms, so they can be named as tetradentate (heteropolydentate) ligand, while the other two, **4** and **5** may be bi-dentate ligand.

^{13}C NMR chemical shifts (ppm) for imine moiety of the five Schiff bases change between 162.2 to 153.2 and the results are agree with the earlier studies. Recently, ^{13}C NMR chemical shifts for the same functional groups have been found as 162.0 and 158.1 for salen Schiff bases[6] and ferrocene Schiff bases[7]. ^{1}H NMR chemical shifts for the last three compounds (**3**, **4** and **5**) which contain the imino proton (N=C–H) are 8.65, 8.27 and 8.61, respectively. These values were found to be 8.6, 8.5 and 8.2 for 2-hydroxy-3-metoxybenzalideneaniline[1], salen[6] ferrocene[7] Schiff bases, respectively. The IR bands assignable to the stretching of C=N bond for the compounds were observed at frequencies range of 1629-1609 cm^{-1} and these values are in accord with those reported in the IR spectra for aromatic Schiff bases[1]. From the electronic spectra it is observed that, the N=CH groups exhibit 323.6 to 344 nm bands which may be assigned to the n→π* transitions in the compounds.

TABLE-1
DETAILS OF THE IMINE FUNCTIONAL GROUP ANALYSIS FOR 4,4'-DIAMINODIPHENYLMETHANE SCHIFF BASES

Compound	NMR, δ ($CDCl_3$)		IR, ν(cm^{-1})	UV-Vis (nm)
	C=N, ^{13}C	N=C–H, ^{1}H	C=N	λ_{max} (n→π)
1	159.8*	-	1617	330.0
2	153.2	-	1609	344.0
3	162.2	8.65	1623	344.0
4	159.7*	8.27	1629	323.8
5	159.6*	8.61	1629	323.6

* : in acetone-d_6

The first three compounds mentioned are containing C=O or –OH groups. It is known that Schiff bases containing these functional groups have different interesting properties owing to the formation of intramolecular or intermolecular hydrogen bonding[1,8-10]. Generally, there is a strong intramolecular C–O···H–N$^+$ hydrogen bond in the enol form of the molecules and keto-enol tautomeric equilibrium can become the following types, C–O–H···N; C–O···H···N; C–O$^-$ $^+$H–N; C=O···H···N; C=O···H–N in different compounds. ^{1}H NMR chemical shift (δ, ppm) of O–H bond of the compound **3** is 13.31, while the chemical shift of the first one is 12.36 and the second one is 12.83 (this peak is very small, which means that the compound **2** is almost entirely in the keto form). An IR band of **3** assignable to the stretching of O–H bond is found to be broadened at the frequency of 3446 cm^{-1} implies that the H atom of the O–H group has a tendency to the N atom in N=C *via* O–H···N→O$^-$···H–N$^+$ intramolecular hydrogen bonding. Thus ^{1}H NMR and IR data show that there is a strong hydrogen bonding between –OH and N=C functional group and the compound **3** has an intramolecular H bond, so acidity has increased. The chlorine atom of the compound **2** raises the acidity, thus the chemical shift of this compound is higher than that of the compound **1**.

The first three ligand contain oxygen and nitrogen donor atoms and they may be tetradentate, while the other two can be bidentate with nitrogen donor atom. Coordination behaviours of these ligands are being tested and will be reported in due course.

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