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ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2011, **8(1)**, 180-184

Synthesis, Characterization and Use of Schiff Bases as Fluorimetric Analytical Reagents (Part II)

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Received 11 November 2009; Accepted 29 December 2009

Abstract: Many Schiff bases were prepared by condensation reaction of certain aromatic amines with aromatic aldehydes derivatives and then the fluorescence properties of these Schiff bases were examined in acidic and basic media. It is shown that these compounds can be used for fluorimetric monitoring of small pH changes.

Keywords: Schiff bases, Fluorescent indicators, Anthranilic acid, *o*-phenylenediamine.

Introduction

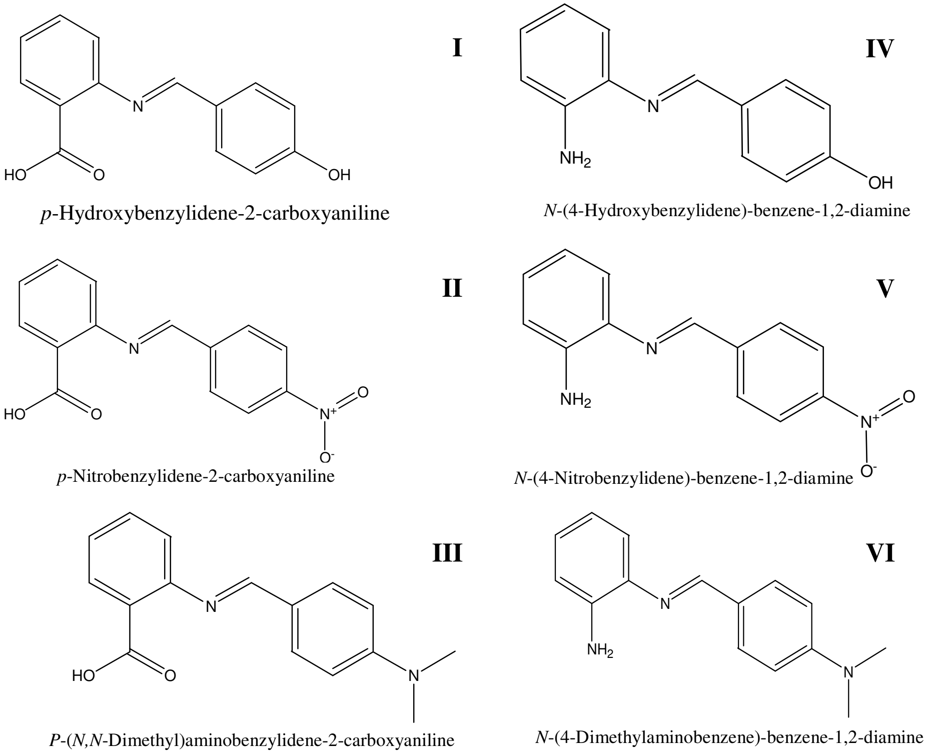
Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, *e.g.*, biological, inorganic and analytical chemistry[1-5]. Application of many new analytical devices requires the presence of organic reagents as essential compounds of the measuring system. They are used, *e.g.*, in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhance selectivity and sensitivity[6-8].

Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properities[9,10].

Schiff bases are widely applicable in analytical determination, using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed (determination of compounds with an amino or carbonyl group); using complex formation reactions (determination of amines, carbonyl compounds and metal ions); or utilizing the variation in their spectroscopic characteristics following changes in pH and solvent (pH of solvent polarity indicators)[11-13].

Unfortunately, most Schiff bases are chemically unstable and show a tendency to be involved in various equilibria, like tautomeric interconversions, hydrolysis, or formation of ionized species[14,15]. Therefore, successful application of Schiff bases requires a careful study of their characteristics.

The Schiff bases prepared are condesation products of aromatic aldehyde derivatives with aromatic mono- and diamines derivatives and presented in (Scheme 1). In this work the spectroscopic characteristics and possibilities of analytical applications of these Schiff bases are presented.



p-Hydroxybenzylidene-2-carboxyaniline

N-(4-Hydroxybenzylidene)-benzene-1,2-diamine

p-Nitrobenzylidene-2-carboxyaniline

N-(4-Nitrobenzylidene)-benzene-1,2-diamine

P-(*N,N*-Dimethyl)aminobenzylidene-2-carboxyaniline

N-(4-Dimethylaminobenzene)-benzene-1,2-diamine

Scheme 1

Experimental

All chemicals and solvents used for synthesis were of reagent grade. All melting points were taken on a melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu 5000 instrument. ^{1}H NMR were run on a Jeol 500 MHz instrument using TMS as internal standard and DMSO as solvent. The spectral analyses were carried out at the NMR laboratory, Alexandaria University, Alexandaria; the elemental analyses at Microanalytical center Cairo University, Cairo, Egypt

The Schiff bases (**I-VI**) were prepared according to the reported methods[16,17]. The procedure is as follows: A solution of the amine derivative (0.01 mol) in absolute ethanol (10 mL) was slowly added to a solution of the aldehyde derivative (0.01 mol) in absolute ethanol (10 mL). After stirring the reaction mixture for 2 h (compounds **I, II** and **III**), and for 5 h at 60-70 °C and cooling (compounds **IV, V** and **VI**), a precipitate was formed which collected by filtration then washed several times with cold ethanol and recrystallised from ethanol.

p-Hydroxybenzylidene-2-carboxyaniline **I** was prepared from anthranilic acid and *p*-hydroxybenzaldehyde; pale orange; m.p. 229.5-230 °C; 1.6 g (70%) yield. IR (KBr, cm^{-1}) ν = 3500 (OH), 2900 (C-H), 1715 (C=O), 1615 (C=N), 1490 (C=C), 1280,1170(C-O); ^{1}H NMR (500 MHz, DMSO); δ (ppm): 6.41-7.66 (8H, m, Ar-H), 8.3 (1H, s, CH=N), 9.70 (1H, s, Ar-OH), 11.00 (1H, s, COOH); $C_{14}H_{11}NO_3$ (241.2): calcd. C 69.65%, H 4.56%, N 5.80%; found C 68.92%, H 4.52%, N 5.77%.

p-Nitrobenzylidene-2-carboxyaniline (**II**) was prepared from anthranilic acid and *p*-nitrobenzaldehyde; yellow-white; m.p. 172-174 °C; 1.7 g (62%) yield. IR (KBr, cm^{-1}) ν = 3500 (OH), 2900 (C-H), 1720 (C=O), 1610 (C=N), 1480 (C=C), 1495, 1320 (N=O), 1285,1170(C-O); ^{1}HNMR (500 MHz, DMSO); δ (ppm): 6.35-8.28 (8H, m, Ar-H), 8.30 (1H, s, CH=N),10.11 (1H, s, COOH); $C_{14}H_{10}N_2O_4$ (270.2): calcd. C 62.17%, H 3.70%, N 10.36%; found C 61.88%, H 3.65%, N 10.03%.

*p-(N,N-*Dimethyl)aminobenzylidene-2-carboxyaniline (**III)** was prepared from anthranilic acid and *p*-(*N,N*-dimethylamino)benzaldehyde; pale green; m.p. 198 °C; 2.0 g (75%) yield. IR (KBr, cm^{-1}) **ν =** 3500 (OH), 2910 (C-H), 1725 (C=O), 1615 (C=N), 1355 (C-N), 1475 (C=C)1280,1170(C-O); ^{1}H NMR (500 MHz, DMSO); δ (ppm): 2.89 (6H, s, N-$(CH_3)_2$), 6.41-7.62 (8H, m, Ar-H), 8.29 (1H, s, CH=N), 9.57 (1H, s, Ar-OH); $C_{16}H_{16}N_2O_2$ (268.2): calcd. C 71.58%, H 5.96%, N 10.43%; found C 70.42%, H 5.81%, N 9.33%.

*N-(4-*Hydroxybezylidene)-benzene-1,2-diamine (**IV)** was prepared from *o*-phenylenediamine and *p*-hydroxybenzaldehyde; cotton pale brown; m.p. 148 °C; 1.3 g (64%) yield. IR (KBr, cm^{-1}) ν = 3400,3300 (N-H), 3000 (O-H), 3010 (C-H), 1600 (C=N), 1445 (C=C), 1360 (C-N); ^{1}HNMR (500 MHz, DMSO); δ (ppm): 5.00 (2H, s, -NH_2), 6.41-7.70 (8H, m, Ar-H), 8.38 (1H, s, CH=N), 10.47 (1H, s, Ar-OH); $C_{13}H_{12}N_2O$ (212.2): calcd. C 73.51%, H 5.65%, N 13.19%; found C 73.01%, H 5.42%, N 12.87%.

*N-(4-*Nitrobezylidene)-benzene-1,2-diamine (**V**) was prepared from *o*-phenylenediamine and p-nitrobenzaldehyde; pale brown; m.p. 317-318 °C; 1.9 g (81%) yield. IR (KBr, cm^{-1}) ν = 3400,3300 (N-H), 3010 (C-H), 1615 (C=N), 1440 (C=C), 1365 (C-N), 1510, 1330 (N=O); ^{1}H NMR (500 MHz, DMSO); δ (ppm): 5.00 (2H, s, -NH_2), 6.40-8.1 (8H, m, Ar-H), 8.38 (1H, s, CH=N); $C_{13}H_{11}N_3O_2$ (241.2): calcd. C 64.67%, H 4.56%, N 17.41%; found C 63.28%, H 4.22%, N 15.96%.

*N-(4-(N,N-*Dimethylaminobezylidene)-benzene-1,2-diamine (**VI**) was prepared from *o*-phenylenediamine and *p*-(*N,N*-dimethylbenzaldehyde; yellow; m.p. 141-142 °C; 0.4 g (16 %) yield. IR (KBr, cm^{-1}) ν = 3460,3370 (N-H), 2900, 2800 (C-H), 1600 (C=N), 1440 (C=C), 1360 (C-N); ^{1}HNMR (500 MHz, DMSO); δ (ppm): 2.86 (6H, s, -N-$(CH_3)_2$), 4.97 (2H, s, -NH_2), 6.40-7.66 (8H, m, Ar-H), 8.31 (1H, s, CH=N); $C_{15}H_{17}N_3$ (239.2): calcd. C75.25%, H 7.10%, N 17.55%; found C 74.90%, H 6.58%, N 17.04%.

Results and Discussion

Fluorescence studies

Fluorescent indicators[18,19] have many applications and are generally employed in cases where colorimetric indicators are difficult to observe or lack sensitivity. Such cases are found in dark, turbid or coloured solutions or titrations in which a precipitate is formed. A flash of light from a fluorescent indicator is much easier to see or measure than the appearance of a weak colour. Fluorescent colours under UV light are often easier to observe than a weak change in colour in an ordinary colour indicator.

Determination with fluorescent indicators may be carried out in a dark room or the use of a view box provided with an entry door. UV light (Herolab, 254 nm, NU-4 KL) was used as a source of radiation. For pH measurements, pH-meter (Mettler-Toledo, MP 220) was used. The change of fluorescent intensity or colour of a compound caused by a change in pH may be the results of equilibrium shifts

$$AH \leftrightarrows H^+ + A^-$$

$$AH + h\nu_1 \leftrightarrows AH^* \rightleftarrows AH + h\nu_2 \text{ fluorescence}$$

The use of fluorescent indicators in titration of coloured solutions is probably the most prominent of the indicator applications. Table 1 below shows the change in colours according to the pH change:

Table 1. Acid-base fluorescent Schiff bases

Schiff base	pH Range	Flourescent Colour Change*	Indicator Solution
I	1.5-2.7	non-fl. to pale blue	0.1 % solution
	2.7-6.5	bright blue	in 50 % ethanol
	6.5-12.5	dark blue	
	12.5-14	pale blue to blue-green	
II	0.8-1.4	non-fl.	0.1 % solution
	1.5-2.7	pale blue	in 50 % ethanol
	2.7-6.0	bright blue	
	6.0-12.6	dark blue	
	12.6-14	pale blue to blue-green	
III	0.95-1.4	pale blue	0.1 % solution
	1.45-2.0	dark blue	in 50 % ethanol
	2.0-6.0	bright blue	
	6.0-12.5	dark blue	
	12.5-14	pale blue to blue-green	
IV	1-9.2	pale blue	0.2 % solution
	9.2-14	bright blue	in 70 % ethanol
V	1-14	non-fl.	0.2 % solution
			in 70 % ethanol
VI	1.0-6.0	pale blue	0.2 % solution
	6.0-14	dark blue	in 70 % ethanol

**Most of the colours are based on visual observations*

Whereas, the effect of pH on the statring materials (aromatic amines), listed in the Table 2.

Table 2. Acid-base fluorescent aromatic amine[19]

Aromatic amine	pH	Colour Change	Indicator Solution
Anthranilic acid	1.5-3.0	non-fl. to light blue	0.1 % solution
	4.5-6.0	light blue to dark blue	in 50 % ethanol
	12.5-14	dark blue to non-fl.	
o-Phenylenediamine	3.1-4.4	green to non-fl.	0.2 % solution
			in 70 % ethanol

Conclusion

Most Schiff bases prepared in this work through condensation of anthranilic acid and *o*-phenylenediamine with the corresponding aldehyde derivatives show fluorescent properties, therefore, they can be used as fluorescent indicators.

Compounds **I-III** showed characteristic colour change on pH range 1-6 (acidic medium) as well as in basic medium. Compounds **IV** and **VI** also showed colour change over a wide pH range. Compound **V** prove to be not suitable and showed non-fluorescence property. The fluorescence of these compounds is pH dependent and can be used for monitoring pH. This fact opens an attractive possibility of application in optical sensors where pH sensitivity is required over limited pH range.

Future efforts will be carried out on other types of Schiff bases and study of their applications as optical sensors.

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