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Synthesis, Characterization and Use of Schiff Bases as Fluorimetric Analytical Reagents

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

Keyword: Schiff bases, Fluorescent indicators, 1-Naphthylamine, 4-Amino-1-naphthalenesulfonic acid.

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 chemistry¹⁻⁵. 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 sensitivity⁶⁻⁸.

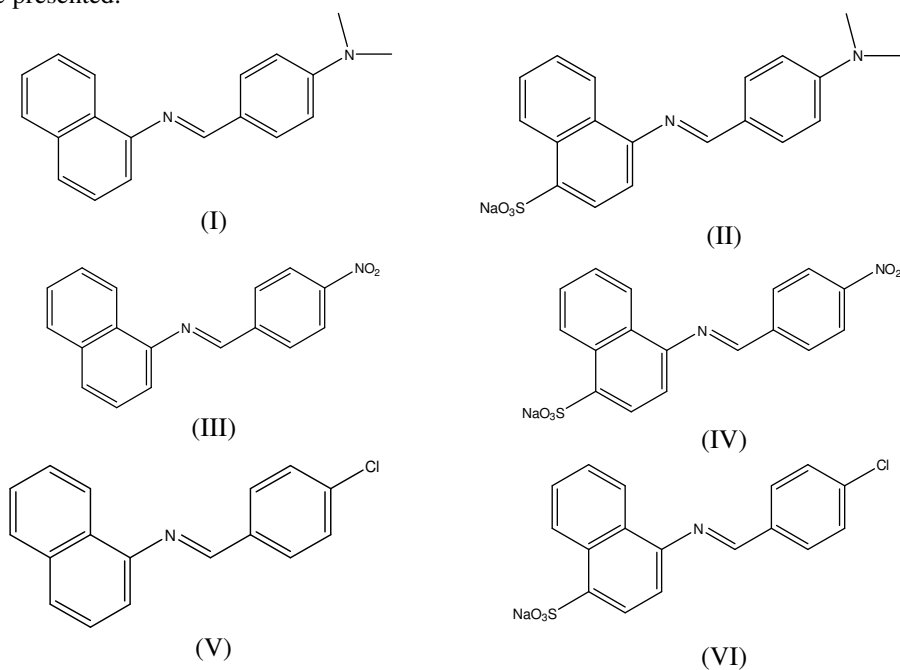
Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties^{9,10}.

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)^{1,11-13}.

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 condensation 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.



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. ¹HNMR 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, Alexandria University, Alexandria; 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), (with 0.01 mol NaOH for compounds IV-VI), 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 5-10 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.

N-(4-(*N,N*-Dimethylamino)benzylidene)naphthalen-1-amine (I) was prepared from 1-naphthylamine and *p*-(*N,N*-dimethylamino)benzaldehyde; yellow; m.p. 112-114 °C; 2.1 g (76 %) yield. IR (KBr, cm⁻¹) ν = 3050 (=C-N), 3020 (=C-H), 2900 (C-H), 1600 (C=N), 1480 (C=C), 1300 (C-N); ¹HNMR (500 MHz, DMSO); δ (ppm): 2.84 (6H, s, -NMe₂), 6.63-7.71 (11H, m, Ar-H), 8.32 (1H, s, CH=N); C₁₉H₁₈N₂ (274.3): calcd. C 83 %, H 6.5 %, N 10.2 %; found C 82.8 %, H 6.45 %, N 10.03 %.

N-(4-Nitrobenzylidene)naphthalen-1-amine (II) was prepared from 1-naphthylamine and *p*-nitrobenzaldehyde; dark yellow; m.p. 164-165 °C; 2.3 g (85 %) yield. IR (KBr, cm⁻¹) ν = 3020 (=C-H), 1600 (C=N), 1480 (C=C), 1510, 1330 (N=O); ¹HNMR (500 MHz, DMSO); δ (ppm): 7.26-8.27 (11H, m, Ar-H), 8.86 (1H, s, CH=N); C₁₇H₁₂N₂O₂ (276.3): calcd. C 74 %, H 4.3 %, N 10.1 %; found C 72.9 %, H 4.25, N 9.77 %.

N-(4-Chlorobenzylidene)naphthalen-1-amine (III) was prepared from 1-naphthylamine and *p*-chlorobenzaldehyde; pale yellow; m.p. 103-105 °C; 2.08 g (78 %) yield. IR (KBr, cm⁻¹) ν = 3020 (=C-H), 1620 (C=N), 1480 (C=C), 1100-1035 (C-Cl); ¹HNMR (500 MHz, DMSO); δ (ppm): 7.1-7.9 (11H, m, Ar-H), 8.64 (1H, s, CH=N); C₁₇H₁₂NCl (265.7): calcd. C 77 %, H 4.5 %, N 5.3 %; found C 76.5 %, H 4.49 %, N 5.26 %.

Sodium-4-(4-(*N,N*-dimethylamino)benzylideneamino)naphthalene-1-sulfonate (IV) was prepared from 4-amino-1-naphthalenesulfonic acid and *p*-(*N,N*-dimethylamino)benzaldehyde; green-yellow; m.p. > 370 °C; 3.6 g (96 %) yield. IR (KBr, cm⁻¹) ν = 3600-3100, 1250-1150 (S=O), 3020 (=C-H), 1600 (C=N), 1480 (C=C), 1310 (C-N), 650 (S-O); ¹HNMR (500 MHz, DMSO); δ (ppm): 2.89 (6H, s, -NMe₂) 6.68-8.50 (10H, m, Ar-H), 8.37 (1H, s, CH=N). C₁₉H₁₇N₂O₃SNa (377.4): calcd. C 60 %, H 4.5 %, N 7.4%; found C 59.6 %, 4.43 %, N 7.33 %.

Sodium-4-(4-nitrobenzylideneamino)naphthalene-1-sulfonate (V) was prepared from 4-amino-1-naphthalenesulfonic acid and *p*-nitrobenzaldehyde; dark brown; m.p. > 370 °C; 2.3 g (63 %) yield. IR (KBr, cm⁻¹) ν = 3600-3100, 1250-1150 (S=O), 3030 (=C-H), 1600 (C=N), 1460 (C=C), 1510, 1350 (N=O), 650 (S-O); ¹HNMR (500 MHz, DMSO); δ (ppm): 7.20-8.61 (10H, m, Ar-H), 8.68 (1H, s, CH=N) C₁₇H₁₁N₂O₅SNa (379.3): calcd. C 54 %, H 2.9 %, N 7.4 %; found C 53.5 %, H 2.8 %, N 7.2 %.

Sodium-4-(4-chlorobenzylideneamino)naphthalene-1-sulfonate (VI) was prepared from 4-amino-1-naphthalenesulfonic acid and *p*-chlorobenzaldehyde; grey; m.p. > 370 °C; 1.8 g (51 %) yield. IR (KBr, cm⁻¹) ν = 3600-3100, 1250-1150 (S=O), 3020 (=C-H), 1620 (C=N), 1470 (C=C), 1100-1035 (C-Cl), 650 (S-O); ¹HNMR (500 MHz, DMSO); δ (ppm): 7.17-8.62 (10H, m, Ar-H), 8.65 (1H, s, CH=N); C₁₇H₁₁NO₃ClSNa (368.8): calcd. C 55 %, H 3 %, N 3.8 %; found C 54.9 %, H 2.98 %, N 3.7 %.

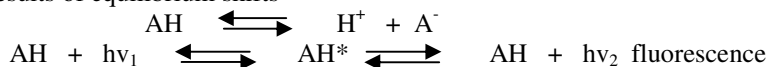
Results and Discussion

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



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	1.0-2.0	Non-fl. to pale blue	0.5 % solution in ehtanol
	2.0-3.5	Blue	
	3.5-5.3	Bright blue	
	5.3-6.0	Blue	
	6.0-14	Non-fl.	
II	1.0-3.4	Non-fl. to blue	0.5 % solution in ehtanol
	3.4-4.2	Blue	
	4.2-5.2	Pale blue	
	5.2-14	Non-fl.	
III	1.0-3.5	Non-fl. to blue	0.5 % solution in ehtanol
	3.5-4.7	Blue	
	4.7-5.2	Pale blue	
IV	5.2-14	Non-fl.	Solution of compound in water
	1-7	Orange-yellow	
V	7-13	Green-yellow	Solution of compound in water
	1-2	Pale green-yellow	
	2-12	Bright green-yellow	
VI	12-13	Pale green-yellow	Solution of compound in water
	1-2	Pale green-yellow	
	2-12	Bright green-yellow	
	12-13	Pale green-yellow	

*Most of the colours are based on visual observations.

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

Table 2. Acid-base fluorescent aromatic amine¹⁹

Aromatic amine	pH Range	Colour Change	Indicator Solution
1-naphthylamine	3.4-4.8	Non-fl. to blue	0.5 % solution in ethanol
4-amino-1-naphthalenesulfonic acid	3-4	Non-fl. to blue	Solution of compound in water
	10-12	Blue to yellow-green	compound in water

Most Schiff bases prepared in this work through condensation of 1-naphthylamine and 4-amino-1-naphthalenesulfonic acid with the corresponding aldehyde derivatives show fluorescent properties in acid-base medium as shown in Table 1. Compound I showed characteristic colour change at pH range 3.5-5.3 while in strong acid media (low pH) or strong base media (high pH) shows no or weak fluorescence. Compounds II and III seems to

be not very useful as fluorescent indicators because they exhibit no or weak fluorescence at either high or low pH. Compounds IV, V, and VI show very clearly the influence of pH on the fluorescence properties, as well as proved that these compounds are excellent indicators due to the colour change over a wide pH range, there is another favoring condition that the experiment, were carried out in aqueous solution. The results obtained from the Schiff bases were quite different from the results obtained from examining the fluorescence properties of the starting materials (Table 2).

Conclusions

The fluorescence of these compounds pH dependent and can be used for monitoring pH. This fact open 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 application as special sensors.

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