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Synthesis and characterization of some novel schiff base ligands derived from 3- hydroxyquinoxaline-2-carboxaldehyde

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ABSTRACT

*Schiff bases (**1a-1d**) were synthesized by the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde with 2-amino pyridine, 3-amino phenol, 2-amino benzoic acid, phenylalanine by an ecofriendly approach without using any organic solvents. The synthesized Schiff bases were confirmed on the basis of H^1 NMR and IR spectroscopic analysis.*

Keywords: 3-Hydroxyquinoxaline-2-carboxaldehyde, 2-amino pyridine, 3-amino phenol, 2-amino benzoic acid, phenylalanine, Schiff Bases.

INTRODUCTION

Schiff bases are widely used for synthetic purposes both by organic and inorganic chemists. In addition, Schiff bases show numerous biological activities including antibacterial, antifungal, and antitumor and antiherbicidal activities. Such bases are also used as ligands for complex formation with some transition and non-transition metal ions [1].

Quinoxaline [2] also known as 1, 4-benzodizine, benzopardiazine, phenpiazine or benzopyrazine is a heterocyclic compound in which a benzene ring is fused with pyrazine ring. Quinoxaline and its derivatives constitute an important class of nitrogen containing heterocycles. The presence of hetero atoms in their ring and extended π-conjugation causes decrease in columbic repulsion. Derivatives of Quinoxaline are widely used as bridging ligand in both homobimetallic and heterobimetallic complexes. They have wide variety of biological applications [3-10] including in optoelectronic devices [11-12] self extinguishing and flame resistance polymer, flourophores [13-16] photo sensitizers, corrosion inhibitor and electron transport material.

Synthesis of Schiff base is often carried out by the acid catalyzed reaction of aldehydes or ketones with amine in organic medium. In the present work; we report the condensation reaction of 3-hydroxyqiunoxaline 2-carboxaldehyde with various amines simply by stirring. To the best of our knowledge and as per literature survey, the Schiff bases of (**1a-1d**) are unknown and their structures were confirmed by IR, NMR and elemental analysis.

MATERIALS AND METHODS

All the chemicals used were analytical reagent grade and purchased from Spectrochem or Loba. The solvents used were of high purity and distilled in laboratory before use. Thin layer chromatography was carried out on silica gel 60/UV254. Melting points of products were recorded in open capillaries on digital melting point apparatus (optics technology) and were uncorrected.

IR spectra were recorded on Perkin-Elmer FTIR Spectrophotometer in range 4000-500 cm^{-1} using ATR Instrument. Samples were kept directly without KBr pallets. H^1 NMR spectra were obtained on a Perkin-Elmer 300 MHz spectrophotometer using TMS as internal standard in DMSO- d_6 as the solvent.

1. Experimental

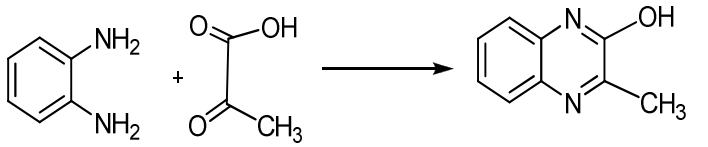
1.1 Synthesis of Schiff base:

The synthesis of Schiff bases involved two main stages namely synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde and the subsequent condensation of this aldehydes with 2-amino pyridine, 3-amino phenol, 2-amino benzoic acid and phenylalanine.

1.1.1 Synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde:

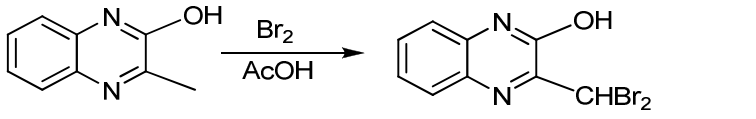
The synthesis of aldehyde involves preparation of 3-hydroxy-2-methylquinoxaline, 3-hydroxy-2-dibromomethyl quinoxaline and subsequent conversion of the latter into the aldehyde.

1.1.1.1 Preparation of 3-methylquinoxaline-2-ol: Pyruvic acid (8.8 gm, 0.1 mol) was added with constant stirring to a solution of orthophenylenediamine (10.8 g, 0.1 mol) in 250 ml of distilled water. After completion of the reaction as indicated by TLC; the precipitated pale yellow colored solid was filtered, washed with water and dried. The crude product was recrystallised from 50% absolute ethanol. Yield: (90%, 14.4 g): Color: pale yellow; no sharp melting point. The compound decomposes within the range 212-225 ^oC accompanied by change in color pale yellow to light brown.



3-methylquinoxalin-2-ol

1.1.1.2 Preparation of 3(bromomethyl) quinoxalin-2-ol: To a solution of 3-methyl quinoxaline 2-ol (13.6 gm 0.1mol) in glacial acetic acid (200 ml), 10% (v/v) bromine in glacial acetic acid (110 ml) was added dropwise with constant stirring. The mixture was then exposed to sun light for 1 hrs with occasional stirring and then poured into water and precipitated dibromo compound was filtered off, washed with water and dried. The crude product was purified by recrystallisation 50% absolute ethanol. Yield: (92%, 29.3 g): Color: pale yellow; no sharp melting point but decomposes within the range 210-222 with a color changing from pale yellow to light brown.

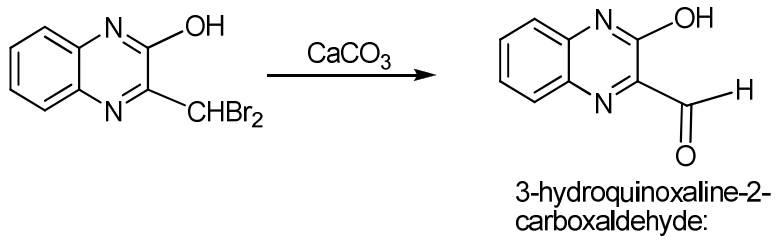


3(bromomethyl) quinoxalin-2-ol

1.1.1.3 Preparation of 3-hydroxyquinoxaline-2-carboxaldehyde:

The dibromo compound (5 g, 0.01 mol) was thoroughly mixed with precipitated calcium carbonate (20 g) using mortar and pestle. The ensuing mixture was refluxed with distilled water (500 ml) for 3 hrs Occasional shaking and the aldehyde remaining in the solution was collected by filtration. The yellow colored aqueous solution thus obtained was stable and could be used for the preparation of Schiff base. The aldehyde was obtained as a fine yellow powder by concentrating the aqueous solution on rotary evaporator, extracting the aldehyde with ether, drying the ether extract with anhydrous sodium sulphate and removal of ether with rotary evaporator.

Color: yellow; no sharp melting point. The aldehyde decomposes within the range 108-130^{o} C and the color is changed from yellow to light brown. The yellow solid is not stable and changes its color to light brown in air indicating oxidation/decomposition of the aldehyde. However the aqueous solution of the aldehyde is stable. Therefore, it would be better to use the aldehyde solution for the synthesis of Schiff base.

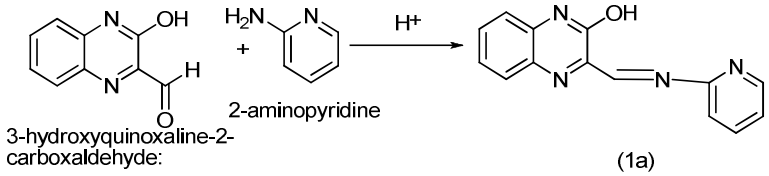


1.1.2 Preparation of 3-[(pyridine-2-ylimino) methyl] quinoxalin-2-ol :(1a)

The aldehyde solution was made 0.025 molar with respect to HCl. Aq. Solution of 2-aminopyridine (0.94 gm 0.001 mol) was added to this drop by drop while solution was stirred. The amino pyridine solution was added till the precipitation of the Schiff base was complete. The yellow compound thus obtained was filtered, washed with ethanol and dried in *vacuo* over anhydrous calcium chloride (Yield: 50-60%, M.P.: 254^{0}C).

Anal.Cald.For$C_{14}H_{10}N_4O$(250.25)C(67.19%)H(4.03%)N(22.39%)O(6.39%)IR:3537,3351,3097,2836,1673,1599,1487,1435,1069,770 cm^{-1}. NMR δ p.p.m.: (300 MHz, DMSO-d_6, 297K)δ=5.86 to 8.00(ArH, m, 8H), 10.87(HC=N, s, 1H), 12.53(OH, s, 1H).

Scheme 1a:

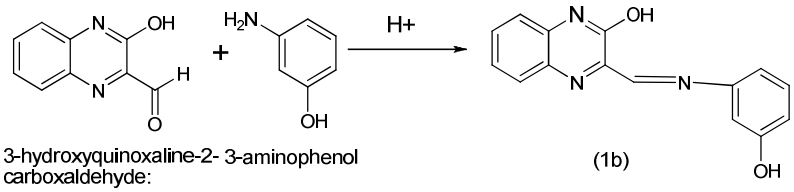


1.1.3 Preparation of 3-((3-hydroxyphenyl Imino)methyl)quinoxalin-2-ol:(1b)

The aldehyde solution was made 0.025 molar with respect to HCl. Ethanolic Solution of 3-aminophenol (1.09 gm 0.001 mol) was added to this dropwise with constant stirring. The amino pyridine solution was added till the precipitation of the Schiff base was complete. The yellow compound thus obtained was filtered, washed with ethanol and dried in *vacuo* over anhydrous calcium chloride (Yield: 50-65%, M.p: 250^{0}C).

Anal. Cald. For $C_{16}H_{12}N_3O_2$ (264.78) C (72.72%) H (4.58%) N (10.60%) O (12.11%) IR: 3362, 3170, 2918, 1658, 1613, 1495, 1191, 753 cm^{-1} NMR δ ppm: (300 MHz, DMSO-d_6, 297 K) δ=6.04 (Ph-OH, s, 1H), 6.21 to 7.98(ArH, m, 8H), 8.97(HC=N, s, 1H), 12.58(OH, s, 1H).

Scheme 1b:

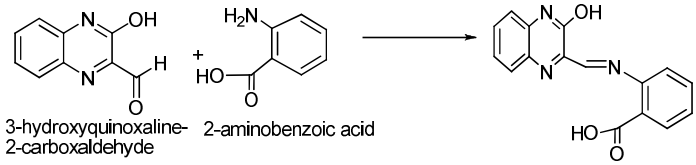


1.1.4 Preparation of 2-{(*E*)-[(3-hydroxyquinoxalin-2-yl)methylidene]amino} benzoic acid: (1c)

The aldehyde solution was concentrated to half amount and ethanolic solution of 2-amino benzoic acid (1.37 gm 0.001 mol) was added to this drop wise while the solution was stirred. The solution was added till the precipitation of Schiff base was complete. The yellow compound thus obtained was filtered, washed with ethanol and dried in *vacuo* over anhydrous $CaCl_2$ (Yield: 60-70%, Melting point: 258^{0}C).

Anal.Cald.For $C_{16}H_{11}N_3O_3$ (293.27) C (65.53%) H (3.78%) N (14.33%) O (16.37%) IR: broad band 2700-3300, 2836, 1660, 1604, 1495, 1250, 1046, 740 cm^{-1} NMR δ ppm: (300 MHz, DMSO-d_6, 297K) δ=6.5 to 7.94 (m, 9H), 10.20 (COOH, s, 1H), 12.50 (ArOH, s, 1H).

Scheme 1c:



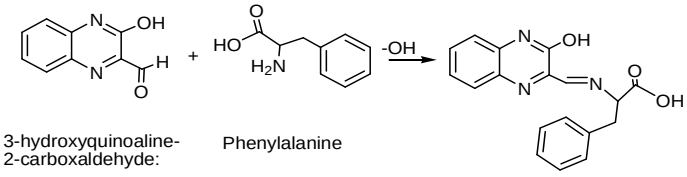
(1c)

1.1.5 Preparation of 2-{(*E*)-[(3-hydroxyquinoxalin-2-yl)methylidene] amino}-3-phenylpropanoic acid: (1d)

The aldehyde solution was concentrated to half amount and phenylalanine (1.65 gm 0.001 mol) made 0.002 M with respect to NaOH this solution was added to aldehyde while the solution was stirred. The phenylalanine solution was added till the precipitation of Schiff base was completed. The yellow compound thus obtained was filtered, washed with absolute ethanol and dried in vacuo over anhydrous $CaCl_2$ (Yield: 60-70%, Melting point: 258^0C).

Anal.Cald.For $C_{18}H_{15}N_3O_3$ (321.33) C (67.28%) H (4.71%) N (13.08%) O (14.94 IR: broad band 2500-3500, 2843, 1659, 1604, 1496,1235, 1023, 730 cm-1 NMR δ ppm: (300 MHz, DMSO-d_6, 297K) δ = 2.8 (CH, t, 1H), 3.1 (CH, d, 2H), 7.30 -7.90(ArH, m, 9H), 8.40 (HC=N, s, 1H),11.3 (COOH, s, 1H), 12.50 (Ph-OH, s, 1H).

Scheme (1d):



(1d)

RESULTS AND DISCUSSION

2.1 IR spectra:

The IR spectra of Schiff bases under study are recorded in solid state selected bands of diagnostic importance are collected in Table1.

Table 1: Selected bands of diagnostic importance from the IR spectra

Compound number				Assignment
1a	1b	1c	1d	
3351	3362	……	…….	ν (OH) free
……	…	3300	3500	ν (OH) bonded
2836	2918	2836	2843	ν (N=CH) asym
…	…	2700-3300	2500-3500	ν (COOH) broad
1673	1658	1660	1659	ν (C=N) Schiff
1599	1613	1604	1604	ν (C=N) ring
1487	1495	1495	1496	δ (OH)
1240	1235	1250	1235	δ (N=CH)
1069	1191	1046	1023	γ(CH=N)

The spectra of Schiff base 1a, 1b having OH groups free display band at 3351, 3362 cm-1. Hydrogen bonded OH group in 1c, 1d show band at 3300, 3500 cm^{-1}. Acidic group in 1c, 1d show broad band between 2500-3500 cm-1 due to H bonding. The azomethine hydrogen gives bands at 2836-2918 cm^{-1}[γ (N=CH)]. [γ (C=N)] band observed 1658-1673 cm-1 position of band varies with molecular structure. The spectra of compounds 1a-1d exhibit sharp band at 1599-1613 cm^{-1} corresponding to [γ(C=N)] in quinoxaline ring. [δ (OH)] of quinoxaline ring show sharp band at 1487-1496 cm^{-1}. The spectra of all compounds show medium to sharp bands within the 870-630 cm^{-1} range due to out of plane deformation of aromatic C-H groups.

2.2 H^1 NMR spectra:

The signals observed in the ^1H NMR spectra of the Schiff bases under study are summarized in Table 2. The spectra exhibit a multiplet at 5.86-8.00 ppm for the hydrogens of the aromatic rings. The azomethine hydrogen (-CH=N-) leads to a singlet of integration intensity equivalent to one hydrogen at 7.94 -10.87 ppm. The spectra of 1d display signals at 2.8 and 3.1 ppm for CH and CH_2 respectively. OH group of quinoxaline ring obtained at 12.50-12.58 ppm. Hydrogen of COOH group in 1c and 1d display at 10.20 -11.3 ppm.

Table 2: Data from H^1 NMR spectra of Schiff base 1a-1d

Compound number				Assignment
1a	1b	1c	1d	
-------	--------	-------	2.8	CH
-------	--------	--------	3.1	CH_2
--------	6.04	--------	-------	Ph-OH
5.86 –8.00	6.21 -7.98	6.5 -7.94	7.3 -7.9	C-H(Ar)
10.87	8.97	7.94	8.4	N=C-H
12.53	12.58	12.5	12.5	Ar-OH
--------	----------	10.2	11.3	COO-H

CONCLUSION

In conclusion, we have developed convenient procedures for the synthesis of Schiff bases of 3-hydroxyquinoxaline 2-carboxaldehyde without refluxing condition. The yields were excellent and reactions were fast. And synthesized Schiff bases were not synthesized and not any literature available.

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