



## Synthesis and Characterization a New Schiff Base with Aliphatic Spacers

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Crystals of a new Schiff base compound with the m.f.  $C_{28}H_{37}N_3O_4$  (**1**), was obtained by the condensation of 4-(quinolin-8-yloxy)butanohydrazide with 2-hydroxy-3,5-dimethylbenzaldehyde and recrystallization of the product from dimethylformamide. The Schiff base (**1**) has been characterized by elemental analysis, IR, <sup>1</sup>H NMR, fluorescence spectra, X-ray single crystal and powder X-ray diffraction measurements. The compound crystallizes in the monoclinic system with the space group P 21/c and Z = 4. The unit cell parameters are a = 25.203 (7), b = 11.292 (3), c = 9.768 (3) Å with  $\beta = 100.01 (7)^\circ$ . The crystal structure reveals that the compound exists as a *trans-trans* conformer in which the benzyl and quinoline group is *trans* with respect to the C=N and C=O bonds. The intermolecular hydrogen bond N-H...O plays a major role in linking the molecules to a zigzag 1-D chain and stabilizes the crystal packing.

**Key Words:** Synthesis, Quinoline derivative, Schiff base, Crystal structure.

### INTRODUCTION

Schiff bases are important family of compounds in medicinal and pharmaceutical field and have been found to play a key role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. They show interesting properties, such as their ability to reversibly bind oxygen<sup>1</sup>, catalytic activity in hydrogenation of olefins<sup>2</sup> and transfer of an amino group<sup>3</sup>, photochromic properties<sup>4</sup> and complexing ability towards toxic metals<sup>5</sup>.

Schiff bases of 8-hydroxyquinoline and its derivatives are one of the most prevalent mixed-donor ligands in coordination chemistry<sup>6-10</sup>. They play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and supramolecular architectures<sup>11-14</sup>. The crystal structure of Schiff bases derived from substituted 2-(quinolin-8-yloxy)butanohydrazide and closely related to the title compound have been reported earlier<sup>15-18</sup>. In this article, we present the synthesis and crystal structure of a new Schiff

base (**1**), which contains oxygen and nitrogen donors and flexible aliphatic spacers (Fig. 1).

### EXPERIMENTAL

Solvents and chemicals obtained from commercial sources were of reagent grade and used without further purification. Melting points were determined on a XRC-1 melting point apparatus and uncorrected. IR spectra were taken on a Thermo Nicolet Avatar 370 FT-IR spectrophotometer (KBr pellets). <sup>1</sup>H NMR spectra was recorded on a Bruker AC 400 spectrometer. Fluorescence spectrum of **1** was characterized at room temperature by a F-4500 fluorescence spectrophotometer (600 nm/min). The crystal structure was determined by a Bruker APEX-II CCD area-detector diffractometer. C, H and N were analyzed using a Carlo-Erba 1106 instrument. Powder X-ray diffraction (PXRD) pattern of the sample was recorded by a PANalytical X' Pert Pro diffractometer using  $CuK\alpha$  radiation. The calculated PXRD pattern was produced using SHELXTL-XPOW program.

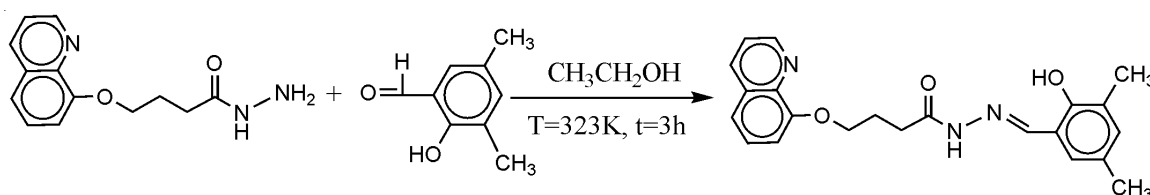


Fig. 1. Synthesis scheme of **1**

**Synthesis of 1:** The title Schiff base was synthesized by condensing 2-hydroxy-3, 5-dimethylbenzaldehyde (0.60 g, 4.0 mmol) with 4-(quinolin-8-yloxy)butanohydrazide (0.98 g, 4.0 mmol) in ethanol (100 mL). The solution was refluxed for 3 h. The solvent was removed and crystals of the compound **1** were recrystallized from dimethyl formamide (yield 50 %), m.p. 170-172 °C. Anal. calcd. (%) for C<sub>28</sub>H<sub>37</sub>N<sub>3</sub>O<sub>4</sub> (479.61): C, 70.06; H, 7.71; N, 8.76. Found (%): C, 69.67; H, 7.75; N, 8.74. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 9.98 (s, 1H, Ar-OH), 9.48 (s, 1H, -CO-NH-), 8.92 (m, 1H, quinoliziny-H), 8.62 (s, 1H, -N=CH-), 7.52-8.31 (m, 5H, *J* = 4.10 Hz, quinoliziny-H), 7.04-8.19 (m, 2H, Ar-H), 4.36-4.48 (t, *J* = 6.50, 5.64 Hz, 2H, -O-CH<sub>2</sub>-), 3.05 (t, *J* = 7.20 Hz, 2H, -CH<sub>2</sub>-CO-), 2.15-2.67 (m, *J* = 7.10 Hz, 2H, -C-CH<sub>2</sub>-C; 6H Ar-CH<sub>3</sub>), 2.15-2.34 (s, 6H Ar-CH<sub>3</sub>). Selected IR data (KBr, ν<sub>max</sub>, cm<sup>-1</sup>), 3513 (O-H), 3008 (N-H), 1710 (C=O), 1631, 1601 (C=N + C=C), 1256 (C-O), 793, 751 (C-H) stretching frequency, respectively.

**Single crystal structure determination:** A colourless prism of dimensions 0.20 mm × 0.18 mm × 0.10 mm was used for data collection with a Bruker SMART CCD APEX-II area-detector diffractometer with graphite monochromated Mo-K<sub>α</sub> radiation (λ = 0.71073 Å) operating at 50 kV and 200 mA. Intensity data were collected up to a θ<sub>max</sub> of 27.72° by the ω/2θ scan method. The raw frame data were integrated with the SAINT program<sup>19</sup> and absorption corrections were applied by using the SADABS program<sup>20</sup>. The structure was solved by direct methods procedures as implemented in SHELXS97<sup>21</sup> program. The positions of all the non-hydrogen atoms were included in the full-matrix least-squares refinement using SHELXL97 program. All H atoms were placed in idealized positions (C-H = 0.93-0.97 Å, N-H = 0.86 Å, O-H = 0.82-0.86 Å) and refined as riding atoms with U<sub>iso</sub>(H) = 1.2 U<sub>eq</sub>(C, N) and with U<sub>iso</sub>(H) = 1.5 U<sub>eq</sub>(O). The quinoline ring is disordered over two sites along C8-C9-N1 and the occupancy is refined a 0.63:0.37 ratio. All quinoline ring 1,2-related atoms were restrained to 1.39 ± 0.01 Å and 1,3-related atoms to 2.35 ± 0.01 Å. Crystallographic details for the structure determination are presented in Table-1. Selected bond lengths and bond angles of Schiff base (**1**) are listed in Table-2.

TABLE-1  
CRYSTALLOGRAPHIC DATA FOR COMPOUND **1**

Empirical formula	C <sub>28</sub> H <sub>37</sub> N <sub>3</sub> O <sub>4</sub>
Formula weight	479.61
Temperature (K)	295(2)
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Unit cell parameters	a = 25.203(7), b = 11.292(3), c = 9.768(3) Å α = 90, β = 100.010(7), γ = 90°
V (Å <sup>3</sup> )	2737.6(13)
Z	4
D <sub>calc</sub> (g/cm <sup>3</sup> )	1.164
μ (mm <sup>-1</sup> )	0.078
F(000)	1032
Crystal size (mm)	0.20 × 0.18 × 0.10
θ Range (°)	2.44-27.72
Limiting indices h/k/l (max, min)	-26, 30/ -13, 13/ -9, 11
Reflections collected	14613
Independent reflections (R <sub>int</sub> )	2958 (0.0517)
Absorption correction	SADABS
Completeness to θ	99.3 %
Max. and min. transmission	0.9922 and 0.9846
Refinement method	Full-matrix least squares on F <sup>2</sup>
Data/restraints/parameters	2958/0/ 387
Goodness-of-fit on F <sup>2</sup>	1.02
R indices [I > 2σ (I)]	R <sub>1</sub> = 0.0879, wR <sub>2</sub> = 0.2370
R indices (all data)	R <sub>1</sub> = 0.1342, wR <sub>2</sub> = 0.2736
Largest diff. peak and hole (e/Å <sup>3</sup> )	0.463 and -0.431

## RESULTS AND DISCUSSION

**Crystal structure description of 1:** The molecular structure of the present compound with atom numbering scheme and its intermolecular hydrogen bonds are shown in Figs. 2 and 3, respectively. Selected bond lengths, bond angles, torsion angles and intermolecular hydrogen bonds are listed in Tables 2 and 3, respectively. The X-ray single crystal structure diffraction analysis of **1** reveals that it crystallizes in monoclinic crystal system and P 2<sub>1</sub>/c space group with the asymmetric unit of one crystallographically independent organic molecule and one water solvent. As shown in Fig. 2, the conformation

TABLE-2  
SELECTED BOND DISTANCES (Å), BOND AND TORSION ANGLES (°) FOR **1**

Bond distances			
O(1)-C(8)	1.380(5)	N(1)-C(9)	1.384(5)
O(1)-C(10)	1.436(4)	N(2)-C(13)	1.365(4)
O(2)-C(13)	1.217(4)	N(2)-N(3)	1.370(4)
O(3)-C(16)	1.371(4)	N(3)-C(14)	1.279(4)
N(1)-C(1)	1.396(18)	C(14)-C(15)	1.458(5)
Bond angles			
N(3)-N(2)-C(13)	119.0(3)	O(2)-C(13)-N(2)	121.2(3)
C(14)-N(3)-N(2)	118.7(3)	O(2)-C(13)-C(12)	124.5(3)
O(1)-C(8)-C(7)	131.5(6)	N(2)-C(13)-C(12)	114.2(3)
O(1)-C(8)-C(9)	116.5(4)	N(3)-C(14)-C(15)	120.8(3)
O(1)-C(10)-C(11)	108.5(3)	C(11)-C(12)-C(11)	114.6(3)
Torsion angles			
C(8)-O(1)-C(10)-C(11)	-175.4(3)	C(13)-N(2)-N(3)-C(14)	-178.0(3)
O(1)-C(10)-C(11)-C(12)	177.7(3)	N(2)-N(3)-C(14)-C(15)	173.0(3)
C(10)-C(11)-C(12)-C(13)	-174.0(3)	N(3)-N(2)-C(13)-O(2)	7.0(5)
C(11)-C(12)-C(13)-N(2)	-163.1(3)	C(11)-C(12)-C(13)-O(2)	19.3(5)
N(3)-N(2)-C(13)-C(12)	-170.7(3)	O(3)-C(16)-C(17)-C(18)	-177.6(3)

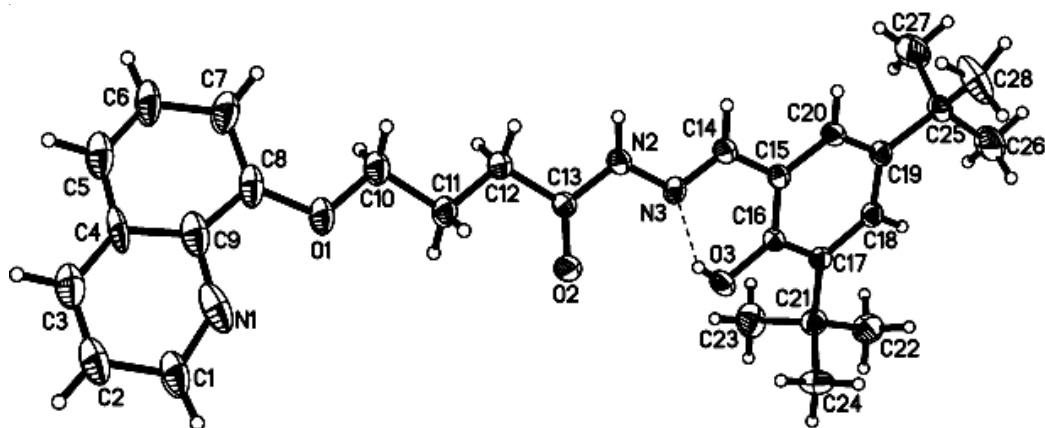


Fig. 2. Molecular structure of **1** at 30 % probability thermal ellipsoids. Intramolecular hydrogen bonds are shown as dashed lines and the water solvent omitted for clarity

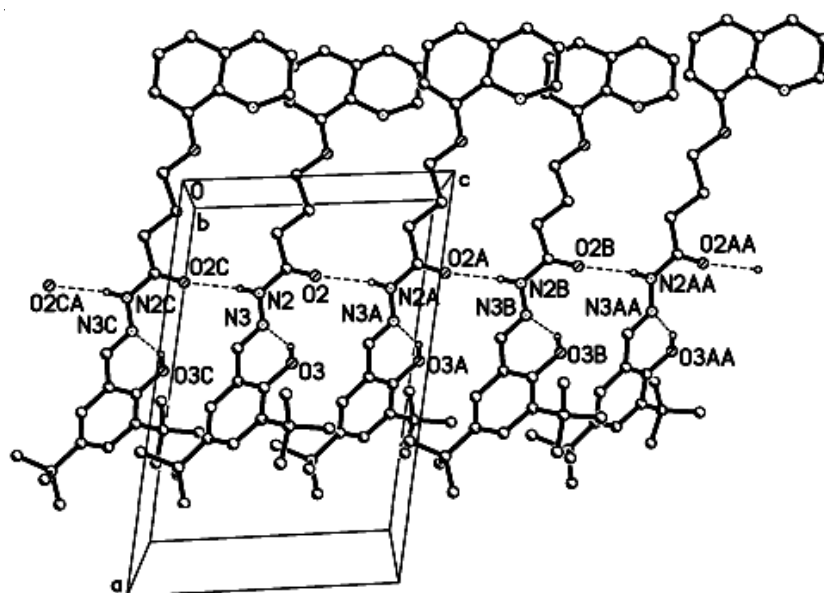


Fig. 3. A segment of the one dimensional zigzag chain structure of **1** along c axis. H atoms, except for those involved in hydrogen bonds, are not included

TABLE-3  
HYDROGEN BOND DISTANCES (Å) AND BOND ANGLE (°)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)H(2)...O(2) <sup>i</sup>	0.86	2.10	2.876(4)	149
O(3)-H(3)...N(3)	0.82	1.84	2.572(4)	147
O(4)-H(29)...N(1) <sup>ii</sup>	0.85	2.61	3.046(12)	113
O(4)-H(30)...O(4) <sup>iii</sup>	0.85	1.97	2.402(16)	110
C(23)-H(23A)...O(3)	0.96	2.39	3.024(5)	123
C(24)-H(24C)...O(3)	0.96	2.32	2.974(5)	125

Symmetry code: (i)  $x, 1/2 - y, -1/2 + z$ ; (ii)  $1 + x, y, z, z$ ; (iii)  $-x, 1/2 + y, 3/2 - z$ .

along the bond sequence (C8-O1-C10-C11-C12-C13-N2-N3-C14-C15) linking the benzene and quinoline rings, which have a mean inter-plane dihedral angle of 43.2 (4)°, is *trans-trans-trans-trans-trans-trans-trans* [torsion angles (°): C8-O1-C10-C11, -175.4 (3); O1-C10-C11-C12, 177.7 (3); C10-C11-C12-C13, -174.0 (3); C11-C12-C13-N2, -163.1 (3); C12-C13-N2-N3, -170.7 (3); C13-N2-N3-C14, -178.0 (3); N2-N3-C14-C15, 173.0 (3)]. According to the crystal structure, the compound exist in the thione form with benzene and quinoline moieties are *trans* with respect to the C14-N3 bond whereas *cis* with respect to the C13-O2 bond. The C14-N3 and C13-O2 bond

length of 1.279 (4) and 1.217 (4) Å, respectively, indicate the presence of a typical C=N and C=O double bonds. The C=N-N angle of 118.7 (3)° is significantly smaller than the ideal value of 120° expected for sp<sup>2</sup> hybridized N atoms. This is probably a consequence of repulsion between the nitrogen lone pairs and the adjacent N atom<sup>22</sup>. The C13-N2 (1.365 (4) Å) is shorter than the normal C-N single bond indicating significant *p*-charge delocalization along the OCNNC moiety. The N1-N2 bond distance of 1.370 (4) Å is in agreement with those observed in Schiff bases derived from substituted 2-(quinolin-8-yloxy)-butanehydrazide<sup>15-18</sup>.

In the crystal structure (Fig. 3, Table-3), the intramolecular O-H...N hydrogen bond produces a S(6) ring motifs and an intermolecular hydrogen contact [N2-H2...O2<sup>ii</sup>: N5-H5 = 0.86 Å, H2...N2 = 2.10 Å, N2...O2 = 2.876 (4) Å, N5-H5...N1 = 149°; symmetry code: #1  $x, 1/2 - y, -1/2 + z$ ] plays a major role in linking the molecules to a zigzag 1-D infinite chain along the c axis in the unit cell. These chains are interwoven together through the other class hydrogen bond of C-H...O and are further aggregated *via* weak  $\pi$ ... $\pi$  stacking interactions into parallel sheets and stabilize the packing.

**IR spectra:** The IR spectrum of Schiff base (**1**) shows  $\nu(\text{C}=\text{N})$  at  $1631\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{O})$  peak at around  $1710\text{ cm}^{-1}$  and  $\nu(\text{N}-\text{H})$  at around  $3008\text{ cm}^{-1}$ , indicative of Schiff base's feature peaks. A strong ( $\text{H}_2\text{O}$ ) band at about  $3513\text{ cm}^{-1}$  is observed in Schiff base (**1**) and assigned to  $\nu(\text{O}-\text{H})$  stretching vibration. Also, the IR spectra of Schiff base (**1**) clearly demonstrated the C-O-C and C-C-O stretching vibrations at about  $1256$ ,  $1189$  and  $1110\text{ cm}^{-1}$ .

**Fluorescence properties:** The solid state fluorescent spectra of the Schiff base is shown in Fig. 4. Compound **1** emits strong fluorescence with the maximum wavelength centered at *ca.* 497, 521 and 538 nm upon photoexcitation at 340 nm at room temperature, which would likely originate from the  $\pi-\pi^*$  and  $n-\pi^*$  transitions on the basis of the emission of  $-\text{C}=\text{O}$ ,  $-\text{C}=\text{N}$  and  $-\text{C}=\text{C}$  components. Also, the observed strong fluorescence is perhaps due to the presence of multiform hydrogen bonds,  $\pi\cdots\pi$  and  $\text{C}-\text{H}\cdots\pi$  interactions in the crystal packing.

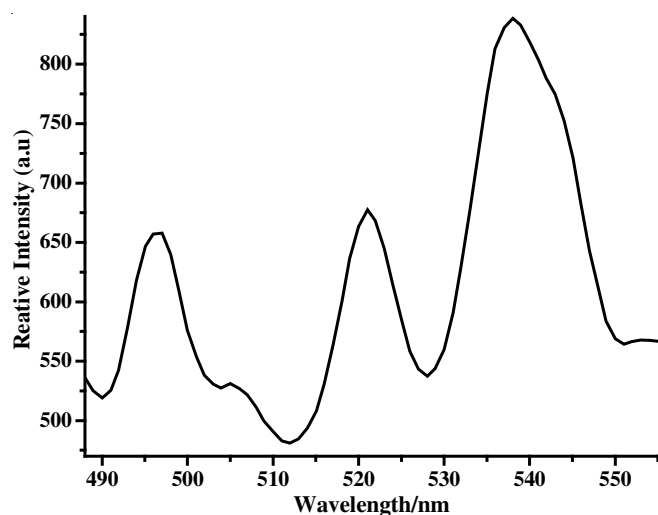


Fig. 4. Emission spectrum of Schiff base **1** (solid,  $\lambda_{\text{ex}} = 340\text{ nm}$ ) in the solid state at room temperature

**Powder X-ray diffraction (PXRD):** As shown in Fig. 5, the phase purity of the bulk samples was established by the observed powder X-ray diffraction (PXRD) patterns.

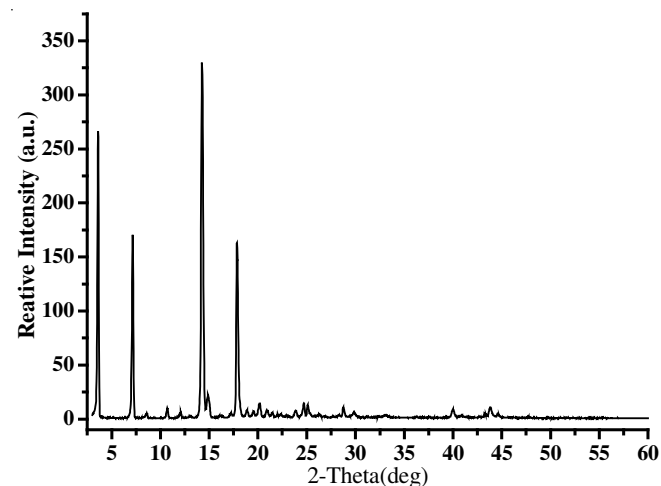


Fig. 5. Experimental powder XRD patterns of **1**

**Supplementary data:** CCDC-824335 contains the supplementary crystallographic data for this article. This data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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