

Note

The synthesis and structure of 1-[3-{(2-hydroxybenzylidene)amino}phenyl]ethanone

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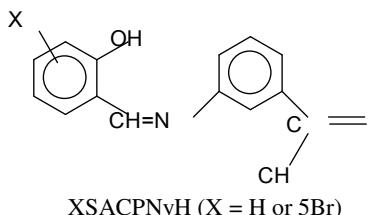
Two Schiff base ligands SACP_NyH **1** and 5BrSACP_NyH **2** are synthesized from the condensation reactions of salicylaldehyde and 5-bromosalicylaldehyde respectively with 3-aminoacetophenone and characterized by elemental analyses, mass, electronic, infrared spectral studies. The molecular structure of **1** is determined by the single crystal X-ray crystallographic study. Space group, monoclinic, $P2_1/n$; $Z = 4$; $a = 14.8717(11)\text{\AA}$, $b = 5.4559(4)\text{\AA}$, $c = 16.7192(12)\text{\AA}$, $\beta = 115.959(3)^\circ$.

Schiff bases are well-known and widely used as ligands in the field of coordination chemistry in general and in the field of transition metal coordination chemistry in particular¹⁻⁴. Some Schiff bases derived from salicylaldehyde or substituted salicylaldehyde are found to generate considerable interest as they show thermochromism and photochromism in the solid state and as proposed molecules showing photochromism are non-planar while molecules showing thermochromism are planar⁵; the concepts being associated with a proton transfer^{6,7}. On the other hand the overall behaviour of such compounds originate from a proton transfer reaction between the phenol-imine and ketoamine tautomers, phenol-imine tautomer predominating in salicyl-adimine Schiff bases in ethanol and in the solid state⁸⁻¹⁰.

Experimental Section

Reagents and techniques

3-aminoacetophenone (Aldrich) and salicylaldehyde (Fluka) were used as purchased. Ethanol was dried over fused CaCl_2 and distilled before use.



Melting points were determined on a Toshniwal apparatus and are uncorrected; microanalysis of C, H and N (Perkin-Elmer 2400 Series II CHN analyzer) and mass spectra (JEOL-D-300 mass spectrometer) were obtained from Central Drug Research Institute, Lucknow, India. Infrared spectra (KBr) and ¹H NMR spectra (in CDCl_3 , TMS as internal standard) were respectively recorded on Perkin-Elmer Paragon 1000 FTIR and Bruker 300 MHz spectrometers. Electronic spectra (in methanol) were recorded on a Shimadzu MPS - 2000 UV-VIS spectrophotometer.

Synthetic procedure

The Schiff base ligands were prepared by the addition of salicylaldehyde (0.61g., 5 mmole) or 5 bromosalicylaldehyde (1.01g., 5 mmole) in 20 mL ethanol to 3 -aminoacetophenone (0.67 g., 5 mmole) dissolved in 20 mL ethanol. The resulting reaction-mixtures were refluxed for 1 hr. On reduction of volume to ~25 mL and keeping cooled at ~5°C, yellow crystalline solid separated out, which was recrystallised from methanol and dried in *vacuo*.

SACP_NyH **1**: Yield: 0.95 g.(80%); m.p., 65°C. EIMS : m/z , 239 ($= \text{M}^+$). ¹H NMR: δ 2.6 (3H, s, CH_3), 6.7 - 8.2 (8H, s, $2\text{C}_6\text{H}_4$), 8.6 (1H, s, $\text{CH}=\text{N}$), 12.8 (H, s, OH). IR(KBr, cm^{-1}) : 1680 (C=O), 1618 (C=N), 1271 (C-O), δ (Ph-ring, out - of - plane deformation), 749. UV (nm): 236 (4.13), 255 (sh), 268 (sh), 340 (3.90). Found: C, 75.40; H, 5.51; N, 5.81. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.30; H, 5.47; N, 5.85%.

5BrSACP_NyH **2**: Yield: 1.16g. (73%); m.p., 112°C; EIMS: m/z , 320 ($= \text{M}^++1$). ¹H NMR: δ 2.6 (3H, s, CH_3), 6.8 - 8.4 (7H, s, C_6H_3 , C_6H_4), 8.8 (1H, s, $\text{CH}=\text{N}$), 12.7 (H, s, OH); IR (KBr, cm^{-1}): 1674 (C=O), 1616 (C=N), 1270 (C-O), δ (Ph-ring, out - of - plane deformation), 752. UV(nm): 248 (4.05), 280 (4.10)305 (sh), 358 (3.98). Found: C, 56.24; H, 3.75; N, 4.27. Calcd. for $\text{C}_{15}\text{H}_{12}\text{BrNO}_2$: C, 56.62; H, 3.80; N, 4.40%

Crystallographic data collection and refinement

Suitable crystals for the X-ray diffraction study were obtained from a saturated solution in methanol by slow evaporation of the solvent at RT.

The crystal was mounted on a glass fibre. Preliminary examinations and data collection was performed on a Enraf-Nonius CAD4 diffractometer using graphite monochromatised $\text{MoK}\alpha$ radiation

Table I — Crystal data and structure refinement for **1**

Empirical formula	C ₁₅ H ₁₃ NO ₂
Formula weight	239.26
Temperature	293(2) K
Wavelength	0.71073 Å (MoK _α)
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a, 14.8717(11) Å b, 5.4559(4) Å c, 16.7192(12) Å β, 115.959(3)°
Volume	1219.70(15) Å ³
Z, Calculated density	4, 1.303 Mg/m ³
Absorption coefficient	0.087 mm ⁻¹
F(000)	504
Crystal size	0.30 × 0.30 × 0.20 mm
θ range for data collection	2.71 to 27.34°.
Limiting indices	-19<=h<=19, -6<=k<=7, -21<=l<=21
Reflections collected/unique	13577 / 2737 [R(int) = 0.0273]
Completeness to θ= 27.34	99.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9828 and 0.9744
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	2737 / 0 / 164
Goodness-of-fit on F ²	1.025
Final R indices [I>2σ(I)]	R1 = 0.0409, wR2 = 0.1049
R indices (all data)	R1 = 0.0735, wR2 = 0.1276
Largest diff. peak and hole	0.164 and -0.137 e.Å ⁻³

(λ=0.71073 Å). Cell parameters were calculated from the least-squares fitting of the angular settings of 25 reflections. Three standard reflections monitored at regular intervals during the X-ray exposures indicated no significant decay in the intensities. The structure was solved by direct methods¹¹ and refined¹² by full matrix least squares (programme) procedures on F² using SHELXL- 97. Neutral atom scattering factors and anomalous scattering factors were taken from the International Tables for X-ray Crystallography¹³. All calculations were carried out using programs SHELXS-97 (Ref. 11), SHELXL 97 (Ref. 12) and ORTEP II (Ref. 14). The position of all hydrogen atoms bonded to carbon atoms were calculated and included in the structure factor calculations. The hydrogen atom HO1 was obtained from the difference fourier map.

Results and Discussion

Spectroscopy

Mass spectra of the isolated Schiff bases **1** and **2** gave very similar mass spectral fragmentation patterns and the molecular ion peaks were observed at m/z, 239(M⁺) and at 320(M⁺+1) respectively.

Electronic spectra of the Schiff bases show medium to strong absorption bands in the UV- region of the spectrum. The strong absorption bands observed at 240-270 nm region are possibly due to the π → π* transitions and weak to medium bands observed at 330-370 nm region are possibly due to the η → π* transitions^{15,16}.

The infrared spectrum of the Schiff bases showed medium to strong absorption bands at 1625 cm⁻¹ assignable to (C=N) vibrations^{17,18}. Medium but sharp bands were observed at ~1285 cm⁻¹ (C-O) (phenolic) bands¹⁹. The CH₂-rocking vibration provided bands at 850 cm⁻¹. Reasonably sharp bands were observed for “out-of-plane” C-H deformation of the phenyl ring at ~760 cm⁻¹. Besides there were bands at ~3380 and ~3320 cm⁻¹ corresponded to (O-H) vibrations and the weakening of these absorptions suggested the presence of intermolecularly hydrogen bonded -OH groups (hydrogen bonded to imine nitrogen atom) and was found to be in agreement with the crystal structure analysis performed on **1**.

The ¹H NMR spectrum of **1** and **2** showed respectively the presence of singlets at δ, 12.80 ppm (s,H), 12.70 ppm (s,H) and at δ, 8.60 ppm (s,H), 8.80 ppm (s,H) assigned as the phenolic -OH and (-CH=N-) protons along with a multiplett in the range δ, 6.70 - 8.20 ppm (m, 8H) and 6.8 - 8.4 (m,7H) assignable to phenyl ring protons and a singlet at δ, ~2.6 ppm for the methyl ring protons.

Crystallography

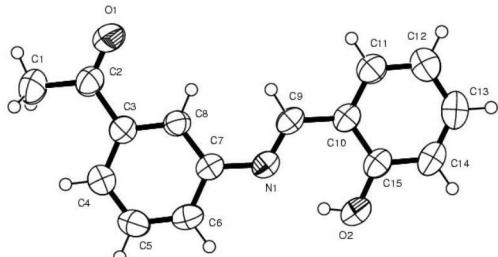
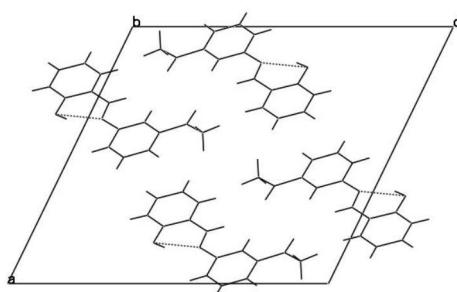
Crystal data collection, structure solution and refinement details are given in **Table I**. A selection of bond lengths and angles is given in **Table II**. The molecular structure of **1** including the atom numbering scheme is presented in **Figure 1** and **Figure 2** illustrates the stereoview of the unit cell of **1**.

The crystal structure of the compound SACPN_xH is reported^{10,20} to adopt phenol-imine tautomeric form with intramolecular O-H....N hydrogen bonding. The syntheses and spectroscopic studies of **1** and **2** along with the crystal structure determination of the title compound **1** is reported which is found to exist in enol form with a short O(2) - H(2) distance of 0.82 Å,

Table II—Bond lengths [\AA] and angles [$^\circ$] for **1**

C(1)-C(2)	1.492(2)	C(2)-O(1)	1.211(2)
C(2)-C(3)	1.492(2)	C(3)-C(4)	1.387(2)
C(4)-C(5)	1.375(2)	C(5)-C(6)	1.375(2)
C(6)-C(7)	1.389(2)	C(7)-C(8)	1.385(2)
C(7)-N(1)	1.416(1)	C(9)-N(1)	1.277(1)
C(9)-C(10)	1.443(2)	C(10)-C(11)	1.393(2)
C(10)-C(15)	1.406(2)	C(11)-C(12)	1.373(2)
C(12)-C(13)	1.382(3)	C(13)-C(14)	1.366(2)
C(14)-C(15)	1.388(2)	C(15)-O(2)	1.342(1)
O(2)-H(2)	0.8200		
O(1)-C(2)-C(3)	120.6(2)	O(1)-C(2)-C(1)	119.9(2)
C(3)-C(2)-C(1)	119.6(2)	C(4)-C(3)-C(8)	119.7(2)
C(4)-C(3)-C(2)	122.2(2)	C(8)-C(3)-C(2)	118.1(1)
C(5)-C(4)-C(3)	119.8(2)	C(6)-C(5)-C(4)	120.3(2)
C(5)-C(6)-C(7)	120.9(1)	C(8)-C(7)-C(6)	118.7(1)
C(8)-C(7)-N(1)	124.9(1)	C(6)-C(7)-N(1)	116.5(1)
C(7)-C(8)-C(3)	120.7(1)	N(1)-C(9)-C(10)	122.2(1)
C(11)-C(10)-C(15)	118.7(1)	C(11)-C(10)-C(9)	119.8(1)
C(15)-C(10)-C(9)	121.6(1)	C(12)-C(11)-C(10)	121.4(2)
C(11)-C(12)-C(13)	119.1(2)	C(14)-C(13)-C(12)	121.3(2)
C(13)-C(14)-C(15)	120.3(2)	O(2)-C(15)-C(14)	119.1(2)
O(2)-C(15)-C(10)	121.4(1)	C(14)-C(15)-C(10)	119.5(2)
C(9)-N(1)-C(7)	121.72(13)		

Symmetry transformations used to generate equivalent atoms

**Figure 1**—Molecular structure of **1****Figure 2**—Stereoview of the unitcell of **1****Table III**—Torsion angles [$^\circ$] for **1**

O(1)-C(2)-C(3)-C(4)	174.66(17)
C(1)-C(2)-C(3)-C(4)	-6.4(2)
O(1)-C(2)-C(3)-C(8)	-5.3(2)
C(1)-C(2)-C(3)-C(8)	173.59(16)
C(8)-C(3)-C(4)-C(5)	0.0(2)
C(2)-C(3)-C(4)-C(5)	-179.97(15)
C(3)-C(4)-C(5)-C(6)	-0.1(2)
C(4)-C(5)-C(6)-C(7)	-0.5(2)
C(5)-C(6)-C(7)-C(8)	1.2(2)
C(5)-C(6)-C(7)-N(1)	-176.95(13)
C(6)-C(7)-C(8)-C(3)	-1.3(2)
N(1)-C(7)-C(8)-C(3)	176.66(13)
C(4)-C(3)-C(8)-C(7)	0.7(2)
C(2)-C(3)-C(8)-C(7)	-179.28(14)
N(1)-C(9)-C(10)-C(11)	-179.52(14)
N(1)-C(9)-C(10)-C(15)	-0.4(2)
C(15)-C(10)-C(11)-C(12)	-0.3(2)
C(9)-C(10)-C(11)-C(12)	178.85(14)
C(10)-C(11)-C(12)-C(13)	0.2(2)
C(11)-C(12)-C(13)-C(14)	0.0(3)
C(12)-C(13)-C(14)-C(15)	-0.1(3)
C(13)-C(14)-C(15)-O(2)	179.87(15)
C(13)-C(14)-C(15)-C(10)	0.0(2)
C(11)-C(10)-C(15)-O(2)	-179.67(13)
C(9)-C(10)-C(15)-O(2)	1.2(2)
C(11)-C(10)-C(15)-C(14)	0.2(2)
C(9)-C(10)-C(15)-C(14)	-178.96(14)
C(10)-C(9)-N(1)-C(7)	-178.04(12)
C(8)-C(7)-N(1)-C(9)	3.5(2)
C(6)-C(7)-N(1)-C(9)	-178.49(13)

Symmetry transformations used to generate equivalent atoms

Table IV—Hydrogen bonds for **1** [\AA and $^\circ$]

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
O(2)-H(2)...N(1)	0.82	1.88	2.6051(17)	147.3

Symmetry transformations used to generate equivalent atoms

the O(2) - N(1) distance of 2.6051(17) \AA is however found to be close to those already reported²¹⁻²³.

All bond lengths and bond angles are found to be normal (**Table II**) and all the H atoms are found and refined (C - H, 0.93-0.96 \AA).

Schiff bases may show thermochromism or photochromism-thermochromic properties are expected for **1** (**Tables III** and **IV**) due to planarity of the molecule.

Acknowledgement

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Supplementary materials

Further details of structure analysis may be obtained from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK by quoting the depository number CCDC-668456, e-mail:deposit@ccdc.cam.ac.uk.

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