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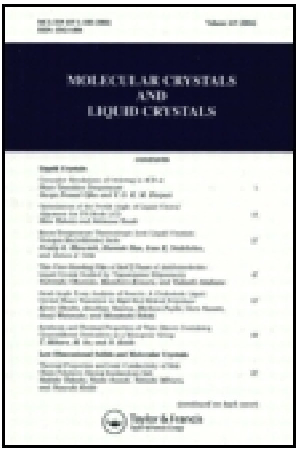

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Formation of Enantiomorphic Crystal From Achiral Molecules - Synthesis and Crystal Structure Determination of Two New Schiff Bases

Sanyog Sharma [a], Amanpreet Kaur [a], Maninder Singh Hundal [a] & Geeta Hundal [a]

[a] Department of Chemistry, UGC Sponsored Centre for Advanced Studies-I, Guru Nanak Dev University, Amritsar, Punjab, India

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Formation of Enantiomorphic Crystal From Achiral Molecules – Synthesis and Crystal Structure Determination of Two New Schiff Bases

SANYOG SHARMA, AMANPREET KAUR, MANINDER SINGH HUNDAL,* AND GEETA HUNDAL*

Department of Chemistry, UGC Sponsored Centre for Advanced Studies-I,
Guru Nanak Dev University, Amritsar, Punjab, India

*Two new Schiff base ligands (**1**) and (**2**), have been synthesized from a reaction between 4-aminomethylpyridine with 3,4- and 2,4-dihydroxybenzaldehyde, respectively. These have been characterized by various spectroscopic techniques and single crystal X-ray diffraction studies. The compound (**2**) crystallizes in a noncentrosymmetric (NCS), chiral space group $P2_12_12_1$ although the molecule itself is not chiral. The intra-molecular H-bonding between the –OH group at C–2 with the* N *of the imine group seems to be responsible for providing a twisted conformation to the molecule which packs ultimately in a chiral space group producing corrugated chains.*

*[Supplemental materials are available for this article. Go to the publisher's online edition of Molecular Crystals and Liquid Crystals to view the free supplemental file: Characterization of Schiff bases by spectroscopic techniques such as NMR, IR, Mass, tables of crystallographic studies and powder pattern comparison for **1** and **2**.]*

Keywords Chiral space group; conformation; corrugated chains; hydrogen bonds; schiff bases

1. Introduction

Schiff bases have attained considerable importance [1–5] due to their wide range of applications in numerous scientific areas such as biological [6–9], analytical [10,11], catalytic [12–14], and nonlinear optical materials [15,16]. The most common NLO behavior is second-harmonic generation (SHG) in which the NLO material doubles the frequency of a laser beam [17]. An understanding of the structure-property relationships associated with the phenomenon is required so as to enhance the SHG capability of materials. One necessary structural prerequisite for SHG is crystallographic noncentrosymmetry (NCS) [18]. The local acentricity of a molecule is a necessary, but not sufficient condition for generating crystallographic NCS as the material may crystallize with the acentric units aligned in an antiparallel manner, resulting in crystallographic centrosymmetry. Therefore, molecular

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*Address correspondence to Maninder Singh Hundal and Geeta Hundal, Department of Chemistry, UGC Sponsored Centre for Advanced Studies-I, Guru Nanak Dev University, Amritsar-143005, Punjab, India. Tel.: 919501114468; 919501114469. E-mail: geetahundal@yahoo.com; hundal_chem@yahoo.com packing has been recognized as the criterion for obtaining NCS. In organic crystals, packing is largely dictated by the space filling characteristics, i.e., intermolecular interactions, functional groups, and the shape/size of the constituent molecules.

Aiming to design small organic molecules for NLO studies, we report here synthesis, spectral characterization, and single crystal analyses of two Schiff-base ligands (**1**) and (**2**), obtained from a reaction between 4-aminomethylpyridine with 3,4- and 2,4-dihydroxybenzaldehyde, respectively. With the help of X-ray crystal structures it is demonstrated that a change of position of one of the –OH groups from C–3 to C–2 results in changing the space group from centrosymmetric Pbca to NCS $P2_12_12_1$. Although both the molecules are achiral in nature with nonplanar structures, the packing forces guide one of them, i.e., (**2**) to crystallize in a chiral space group whereas (**1**) packs in a centrosymmetric space group Pbca. Space filling characteristics have been seen to be responsible for the above [19,20].

2. Experimental

2.1. Materials and Instrumentation

4-aminomethylpyridine, 3,4-dihydroxybenzaldehyde, and 2,4-dihydroxybenzaldehyde were obtained from Aldrich and were used without any further purification. NMR spectra were recorded in DMSO-d_6 with TMS as an internal reference, on a 300 MHz JEOL NMR spectrometer. The IR spectra were recorded using KBr pellets with a Varian FT-IR spectrometer. Single crystal structural X-ray diffraction was carried out on a Bruker's Apex-II CCD diffractometer using Mo Kα ($\lambda = 0.71069$) at room temperature. C, H, and N were carried out with a thermoelectron FLASHEA1112 analyzer. Mass spectra were recorded on a Bruker's microTOF-QII spectrophotometer.

2.2. Synthesis of Schiff Bases

2.2.1. Synthesis of (Z)-4-(((pyridin-4-ylmethyl)imino)methyl)benzene-1,2-diol (1). To the ethanolic solution (20 ml) of the 4-aminomethylpyridine (0.108 g, 1 mmol) was added ethanolic solution (30 ml) of 3,4-dihydroxybenzaldehyde (0.138 g, 1 mmol) dropwise through dropping funnel with continuous stirring. The reaction mixture was then stirred for 4 h at room temperature. After completion of reaction, solvent was evaporated and product was recrystallized from methanol. Pure product is solid and light orange. Yield = 62%. Melting point = 157°C–158°C. IR (KBr, cm^{-1}) 3508, 2886, 1602, 1450, 1296, 1176, 874. ^{1}H NMR (300 MHz, DMSO-d_6, 298K): $\delta = 4.71$ (s, 2H, CH_2), 6.79 (d, 1H, J = 8.1 Ar), 7.03 (d, 1H, J = 8.1, Ar), 7.27 (s, 1H, Ar), 7.32 (d, 2H, J = 5.4, Ar), 8.29 (s, 1H, CH=N), 8.51 (d, 2H, J = 5.4, Ar), 9.35 (s, 2H, OH). ^{13}C NMR (75 MHz, DMSO-d_6, 298K): $\delta = 62.5$ (CH_2), 114.2 (Ar), 115.7 (Ar), 121.8 (Ar), 122.3 (Ar), 123.2 (Ar), 124.4(Ar), 148.9 (Ar), 149.5 (C—OH), 149.6 (C—OH), 149.9 (Ar), 163.1 (CH=N). Elemental analysis calculated for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27%. Found: C, 68.04; H, 5.34; N, 12.12%. ESI MS: m/e = 228.30 [M^+].

2.2.2. Synthesis of (Z)-4-(((pyridin-4-ylmethyl)imino)methyl)benzene-1,3-diol (2). Compound **2** was prepared by the same method as that of compound **1** except that 2,4-dihydroxybenzaldehyde was taken instead of 3,4-dihydroxybenzaldehyde. Pure product is solid and dark orange. Yield = 77%. Melting point 155°C–157°C. IR (KBr, cm^{-1}) 3510, 2930, 1638, 1418, 1324, 1234, 1168, 1008, 816, 634, 486. ^{1}H NMR (300 MHz, DMSO-d_6, 298K): $\delta = 4.76$ (s, 2H, CH_2), 6.22 (d, 1H, $J = 2.1$, Ar), 6.33 (d, 1H, $J = 8.5$, Ar), 7.28 (s, 1H, Ar), 7.32 (d, 2H, $J = 5.7$, Ar), 8.54 (s, 1H, CH=N), 8.56 (s, 2H, Ar), 10.10 (s, 1H, OH), 13.55 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6, 298K): $\delta = 59.9$ (CH_2), 102.4 (Ar), 107.3 (Ar), 111.3 (Ar), 122.6 (Ar), 133.6 (Ar), 147.9 (Ar), 149.8 (Ar), 161.8 (C—OH), 163.5 (C—OH), 166.9 (CH=N). Elemental analysis calculated for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27%. Found: C, 68.34; H, 5.28; N, 12.25%. ESI MS m/e: 229.09 $[M + H]^+$.

2.3. X-ray Data Collection and Structure Determination

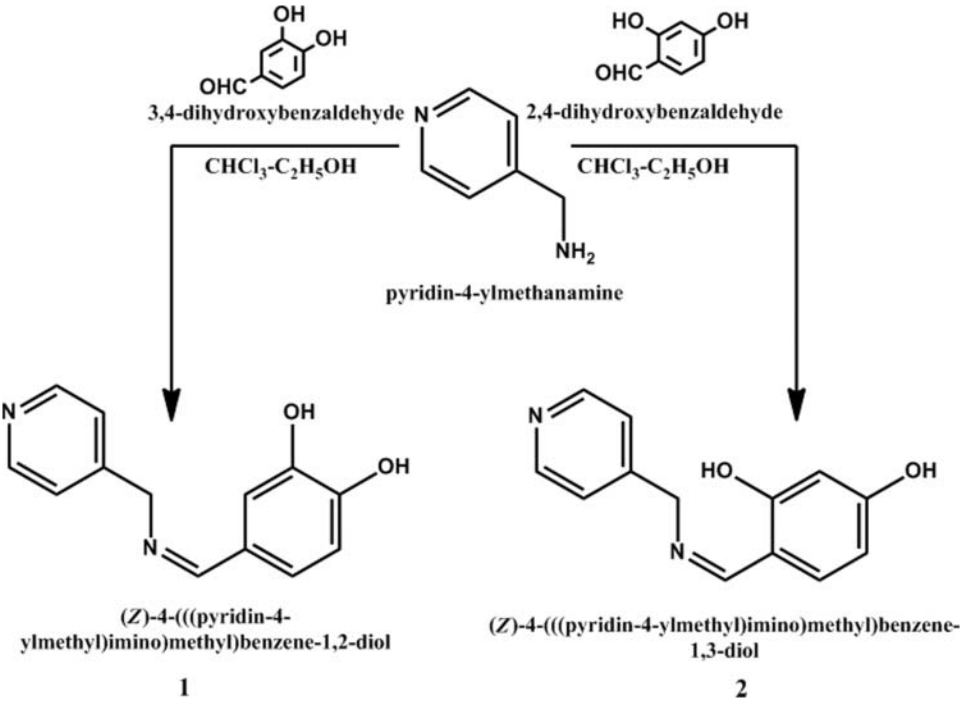
The crystals of (**1**) and (**2**) were grown by slow evaporation of methanolic solutions of compounds. X-ray data of both the complexes were collected on a Bruker's Apex-II CCD diffractometer using Mo Kα ($\lambda = 0.71069$ Å) at room temperature. A total of 15,843 reflections were measured for (**1**) out of which 3042 were independent and 2003 were observed [$I \geq 2\ \sigma(I)$] for theta 29°. Crystal for (**2**) showed poor diffraction at high theta values therefore 3600 reflections were measured out of which 1515 were independent and 1243 were observed [$I \geq 2\ \sigma(I)$] up to theta 22.8°. The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. The structures were solved by direct methods in orthorhombic Pbca and $P2_12_12_1$ space group, respectively using SIR-92 [21] and refined by full-matrix least squares refinement methods based on F^{-2}, using SHELX-97 [22]. The hydrogens of the –OH groups were located from the difference Fourier synthesis and were refined isotropically with Uiso values 1.2 times that of their carrier oxygen atoms, with restraints on the O—H distance. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of the phenylene and methylene carbons and 1.5 times of the methyl carbons. All calculations were performed using Wingx [23] package. The important crystal and refinement parameters are given in Table 1.

3. Results and Discussion

The Schiff bases **1** and **2** (Scheme 1) were synthesized by the condensation reaction of equimolar quantities of 4-aminomethylpyridine with 3,4-dihydroxybenzaldehyde and 2,4-dihydroxybenzaldehyde respectively, in ethanol. The air stable orange products of Schiff Bases are soluble in methanol, ethanol, DMF, and DMSO. The elemental analyses are in good agreement with chemical formulae proposed for the compounds. All the compounds are characterized by ^{1}H, ^{13}C, IR, Mass spectroscopy, powder diffractogram, and also by X-ray spectroscopy. (Fig. S1–S14).

3.1. IR and NMR Spectroscopic Studies

The IR bands at 1602 cm^{-1} for **1** and at 1638 cm^{-1} for **2** are characteristic of stretching vibrations of imine (CH=N) bonds of Schiff bases. The broad bands at 3508 cm^{-1} for **1** and 3510 cm^{-1} for **2** shows the presence of –OH groups. In ^{1}H NMR, the signals at δ 8.29 for **1** and at δ 8.54 ppm for **2** indicate formation of imine (CH=N) group. The signals at δ 9.35 for **1** and at δ 10.10 and 13.55 ppm for **2** correspond to OH groups. The chemical shift of one OH group is typical for the resonance-assisted hydrogen bonded proton of O—H···N [24]. This intramolecular H-bonding between phenolic O and N of imine group in **2** is also confirmed by its crystal structure (Fig. 1). The aromatic protons of **1** resonate in the region ranges from δ 6.78 to δ 7.33 and a doublet at δ 8.51 ppm for aromatic protons in



Scheme 1. Synthetic route to the Schiff Base **l** and **2**.

the neighboring position of N atom of pyridine ring. For **2** aromatic protons appear in the region *δ* 6.22 to *δ* 7.33 and *δ* 8.55 ppm, the latter corresponding to the proton adjacent to N atom of pyridine ring. In ^{13}C NMR spectrum signals at *δ* 62.4 ppm for **1** and at *δ* 59.9 ppm for **2** indicate methylene carbon resonances. The signals at *δ* 163.1 for **1** and at *δ* 166.9 for **2** confirm the formation of imine (CH=N) group. The aromatic region resonates in the region ranging from *δ* 114.1 to *δ* 149.9 ppm for **1** and from *δ* 102.4 to *δ* 149.8 ppm for **2**.

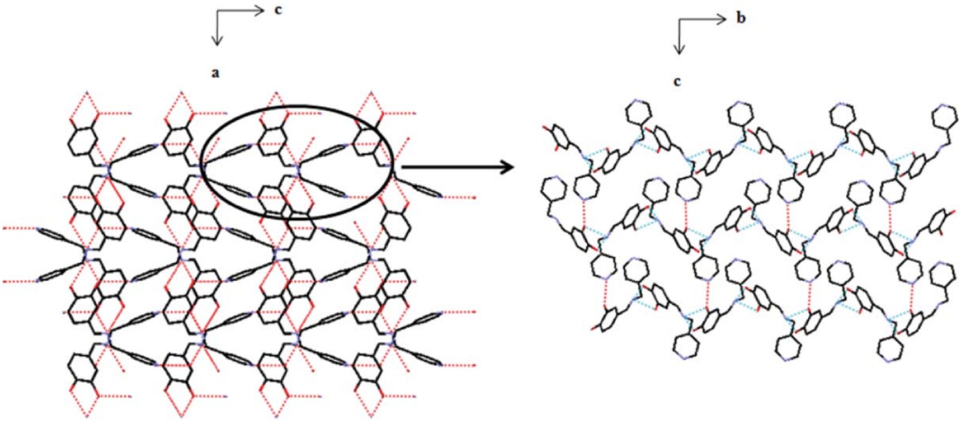


Figure 1. Showing the formation of a 3D network in (**1**) due to H-bonding interactions. Hydrogens have been removed for clarity. In the blown up figure dots represent the H-bonding propagating the chains along *b* and *c* axis.

Table 1. Crystal data and structure refinement for compounds **1** and **2**

Identification code	**1**	**2**
Empirical formula	$C_{13}H_{12}N_2O_2$	$C_{13}H_{12}N_2O_2$
Formula weight	228.25	228.25
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	$P2_12_12_1$
Unit cell dimensions	$a = 14.1187(11)$Å	$a = 6.2131(6)$ Å
	$\alpha = 90°$	$\alpha = 90°$
	$b = 10.2843(8)$Å	$b = 7.4853(8)$ Å
	$\beta = 90°$	$\beta = 90°$
	$c = 15.9120(14)$Å	$c = 24.020(2)$ Å
	$\gamma = 90°$	$\gamma = 90°$
Volume	2310.4(3) Å^3	1117.07(19) Å^3
Z	8	4
Density	1.312 Mg/m^3	1.357 Mg/m^3
Absorption coefficient	0.090 mm^{-1}	0.094 mm^{-1}
F(000)	960	480
Crystal size	0.20 × 0.15 × 0.05 mm^3	0.18 × 0.16 × 0.13 mm^3
Theta range for data collection	2.56 to 28.97°	2.85 to 22.81°
Index ranges	$-13 < = h < = 19$, $-13 < = k < = 14$, $-21 < = l < = 21$	$-5 < = h < = 6$, $-8 < = k < = 7$, $-25 < = l < = 26$
Reflections collected	15,843	3600
Independent reflections	3042 [R(int) = 0.0314]	1515[R(int) = 0.0234]
Completeness to theta (%)	28.97°, 99.5%	22.81°, 99.8%
Absorption correction	Semi-empirical 0.7458 and 0.6649	Semi–empirical 0.7448 & 0.6431
Maximum and minimum transmission		
Data/restraints/parameters	3042/2/160	1515/2/160
Goodness-of-fit on F2	1.012	1.038
Final R indices [$I > 2$ sigma(I)]	R1 = 0.0411, wR2 = 0.0967	R1 = 0.0327, wR2 = 0.0693
Final R indices (all reflections)	R1 = 0.0758, wR2 = 0.1146	R1 = 0.0467, wR2 = 0.0760
Largest diff. peak and hole	0.202 and −0.185 e.Å^{-3}	0.091 & −0.131 e.Å^{-3}
CCDC number	895,159	895,160

The signals at δ 149.5, δ 149.6 for **1** and at δ 161.8, δ 163.4 for **2** show the presence of OH groups.

3.2. Thermogravimetric Analysis

In the present thermal study of Schiff base **1** and **2**, weight loss was measured from the ambient temperature to 800°C. In Fig. 2(A) TGA curve shows that compound **1** was stable

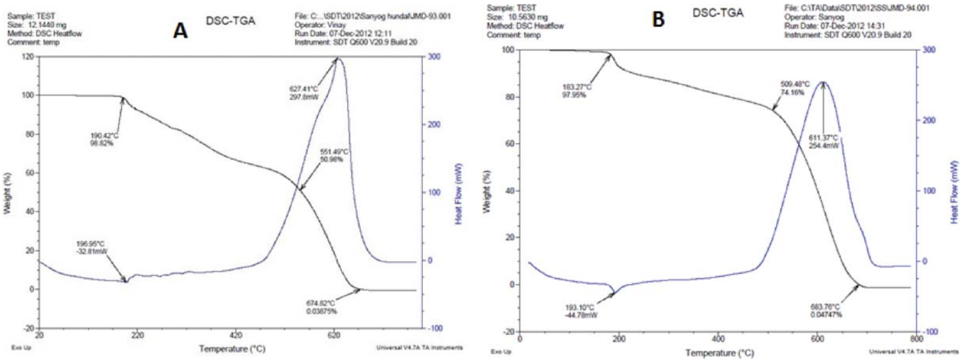


Figure 2. DSC-TGA of compound **1** and **2**.

up to 185.32°C, and above this temperature shows weight loss 50.98% at 551.49°C and 0.0385% at 674.82°C. DSC curve for the compound shows a small endothermic peak at 196.95°C and a sharp exothermic peak with a maximum temperature at 627.41°C which shows decomposition of the compound. Figure 2(B) shows TGA curve for compound **2** which is stable up to 178.57°C and then shows weight loss 97.95%, 74.16%, and 0.04747% at 183.27°C, 509.48°C, and 683.76°C respectively. DSC curve of compound **2** shows one endothermic peak at 193.10°C and an exothermic peak at 611.37°C.

3.3. Single Crystal X-ray Diffraction Studies

3.3.1. X-ray Structure Description of Compound 1. ORTEP diagram of compound **1** is shown in Fig. 3. All the bond lengths and angles are normal. Pyridine ring is almost perpendicular to the phenyl ring (dihedral angle between the two rings being 82.6(1)°. The torsion angles about the imine bond C9—C8—N1—C7 and C8—N1—C7—C4 are −125.3(1)° and

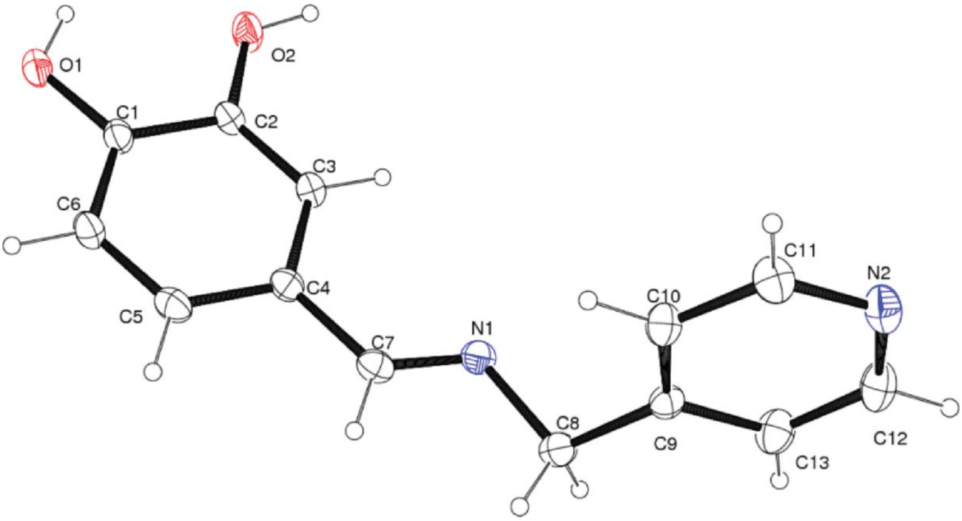


Figure 3. ORTEP diagram of (**1**) and the labeling scheme used.

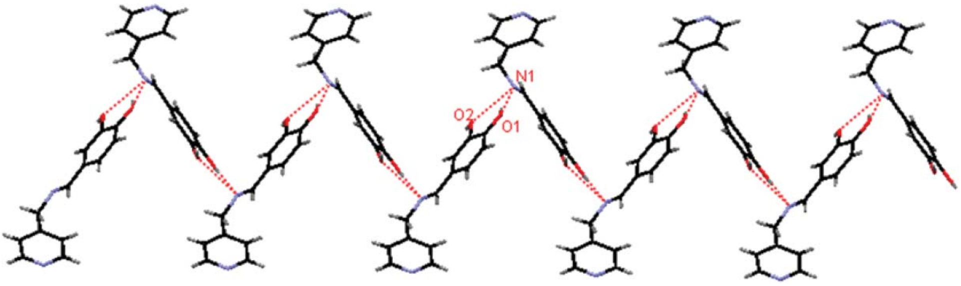


Figure 4. Showing the formation of a zig-zag chain along the *b* axis of (**1**).

−178.5(1)°, respectively. There is strong inter-mlecular H-bonding between the two –OH groups and the imine and pyridine N atoms. Both the phenolic oxygen O1 and O2 are behaving as H-bond donors to the imine nitrogen N1 while O2 is also H-bonded to pyridine nitrogen N2 and behaving as a double H-bond donor (Table 2).

The crystal packing gives rise to centrosymmetric, zig-zag chains along the b axis due to O—H· · ·imine H-bonding interactions (Fig. 4). Such chains are held to each other due to O2· · ·N (pyridine) Hydrogen bonds which extends the packing perpendicularly along the *c* axis (Fig. 1). This self-assembled 3D network is further supported by weak C—H· · ·O and C—H· · ·N type of H-bonding interactions (Table 2).

3.3.2. X-ray Structure Description of Compound 2. An ORTEP diagram of the final structure of (**2**) has been shown in Fig. 5. All the bond lengths and angles are normal. The torsion angles about the imine bond C9—C8—N1—C7 and C8—N1—C7—C4 are −134.9(2)° and −176.2(2)°, respectively. The former angle is about 10° more than in (**1**) thus the Py ring is relatively more toward a *trans* conformation viz-a-viz the phenyl ring, in the solid-state structure of (**2**). This results in a decrease in the dihedral angle between the two which is

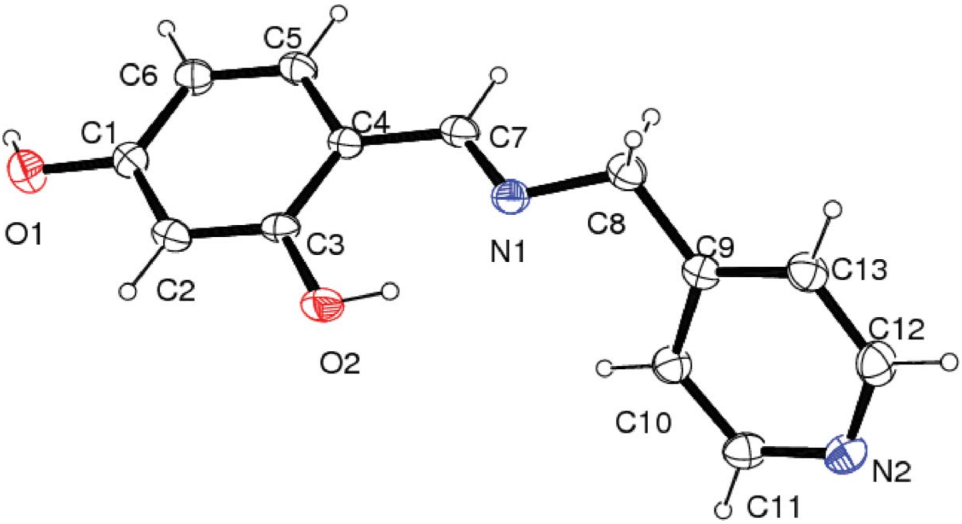


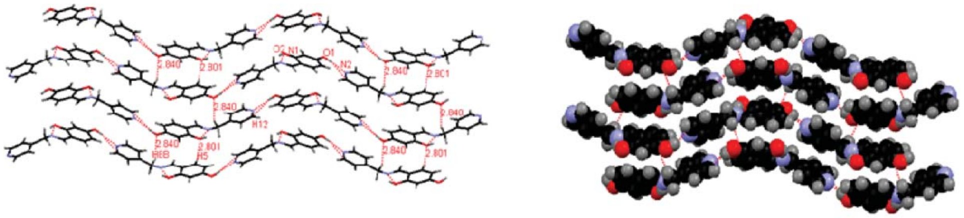
Figure 5. ORTEP diagram of (**2**) showing the labeling scheme used.

Table 2. Showing important H-bonding interactions (Å)

X—H···Y	X···Y	H···Y	<X—H···Y
(1)			
O1—H1···O2	2.715(2)	2.34	107
C3—H3···O1^{1}	3.569(2)	2.75	148
C8—H8A···O2^{1}	3.523(2)	2.99	115
C5—H5···N2^{2}	3.671(2)	2.84	149
C6—H6···O1^{3}	3.413(2)	2.57	151
C10—H10···O1^{4}	3.641(2)	2.96	132
C10—H10···O2^{4}	3.817(2)	2.99	149
C7—H7···O2^{4}	3.443(2)	2.99	112
O1—H1···N1^{5}	2.812(2)	1.99	163
O2—H2···N2^{6}	2.704(2)	1.88	166
(1) $-x + 2, +y - 1/2, -z + 1/2$ (2) $x, -y + 1/2, + z + 1/2$ (3) $-x + 2, -y + 1, -z + 1$ (4) $x + 1/2, +y, -z + 1/2$ () $-x + 2, +y + 1/2, -z + 1/2$ (6) $x - 1/2, -y + 1/2, -z$			
(2)			
O2—H2···N1	2.618(2)	1.87	148
C5—H5···O1^{1}	3.573(3)	2.97	124
C8—H8A···O2^{1}	3.249(3)	2.74	113
C8—H8B···O2^{1}	3.249(3)	2.87	104
C8—H8B···O1^{2}	3.743(3)	2.84	155
C5—H5···O2^{2}	3.690(3)	2.80	160
O1—H1···N2^{3}	2.760(3)	1.91	178
O1—H1···C12^{3}	3.483(3)	2.75	152
C6—H6···N2^{3}	3.570(3)	2.98	123
C11—H11···N2^{4}	3.590(3)	2.86	136
C10—H10···O1^{5}	3.650(3)	2.79	155
(1) $x - 1, +y, +z$ (2) $-x + 1, +y - 1/2, -z + 1/2$ (3) $-x + 1/2 + 1, -y + 1, +z + 1/2$ (4) $x + 1/2, -y + 1/2, -z$ (5) $-x + 2, +y - 1/2, -z + 1/2$			

now 57.7(1)° unlike that found for (**1**) and the two rings are almost in a *gauche* conformation. It may be a consequence of the strong intramolecular H-bonding between phenolic O2 and the imine N1 (Table 2) which is absent in (**1**). The second phenolic oxygen O1 is H-bonded to the Py N2 atom and C12. These H-bonding interactions, coupled with the twist between the pyridine and phenyl rings gives rise to the formation of corrugated chains running parallel to the *c* axis as shown in Fig. 6. The packing is also responsible for the formation of enantiomorphic crystal (space group $P2_12_12_1$) from the achiral molecules. On the other hand, despite near orthogonal disposition of two rings in (**1**) the dipole–dipole interactions induce the formation of centrosymmetric assemblies of the molecules.

The corrugated chains in (**2**) are further held to each other due to various (Table 2) C—H···O and C—H···N kind of interactions (some of them have been shown in Fig. 5) and various C—H···π interactions to show the stacking down the *a* axis. The main C—H···π interactions are C2—H2A···π (3.657Å C2···centroid of symmetry related phenyl ring in the parallel chain), C5—H5···π (3.564 Å, C5···centroid of symmetry related phenyl ring in the parallel chain), C12—H12···π (3.650 Å C12···centroid of symmetry related pyridine ring, C8—H8··· π (3.693Å, C8··· centroid of symmetry related pyridine ring).



a

b

Figure 6. Showing (a) corrugated chain parallel to the *c* axis being viewed down the *a* axis (b) space filled representation of the corrugated chains (atom size is 0.53 times that of the van der Waals radii) of (**2**).

4. Conclusions

Two small Schiff bases have been synthesized and characterized by spectroscopic and X-ray crystal structure determination. It has been seen that a change in position of the hydroxyl group from C-3 in (**1**) to C-2 in (**2**) has significant effect on the crystal packing and the self-assembly of the molecules. The intramolecular H-bonding between the *ortho* —OH group and the imine group in (**2**) is responsible for reducing the dihedral angle between the two rings from ~90° (in (**1**)) to ~58°. It triggers the change in conformation between the molecular and crystal structures of the two similar Schiff bases.

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