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Syntheses, characterization and crystal structures of two structurally similar Schiff bases isonicotinic acid [1-(3-methoxy-2-hydroxyphenyl)methylidene]hydrazide and isonicotinic acid [1-(4-dimethylaminophenyl) methylidene]hydrazide monohydrate

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The Schiff base compounds, isonicotinic acid [1-(3-methoxy-2-hydroxyphenyl) methylidene]hydrazide ($C_{14}H_{13}N_3O_3$, **1**) and isonicotinic acid [1-(4-dimethylaminophenyl) methylidene]hydrazide monohydrate ($C_{15}H_{16}N_4O \cdot H_2O$, **2**) have been synthesized by the condensation of equimolar 3-methoxysalicylaldehyde or 4-dimethylaminobenzaldehyde with isonicotinic acid hydrazide in MeOH or EtOH. The compounds were characterized by elemental analysis, IR, ^{1}HNMR spectra, and single crystal X-ray diffractions. Compound **1** crystallizes in the monoclinic space group P-1 with unit cell dimensions $a = 7.662(1)$ Å, $b = 16.249(2)$, $c = 10.874(2)$ Å, $\beta = 110.426(3)°$, $V = 1268.7(3)$ Å^3, $Z = 4$, $R_1 = 0.0644$, and $wR_2 = 0.1283$. Compound **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions $a = 7.388(1)$ Å, $b = 11.812(1)$ Å, $c = 17.197(2)$ Å, $V = 1500.7(2)$ Å^3, $Z = 4$, $R_1 = 0.0585$, and $wR_2 = 0.1143$. X-ray structure determinations revealed that the molecules of both compounds display *trans* configurations with respect to the C=N double bonds. In the crystal structure of **1**, molecules are linked through N–H $\cdots$ N intermolecular hydrogen bonds, forming layers parallel to the *bc* plane, while in the crystal structure of **2**, molecules are linked through N–H $\cdots$ O, O–H $\cdots$ O, and O–H $\cdots$ N intermolecular hydrogen bonds, forming a network.

KEY WORDS: Schiff base; synthesis; crystal structure; hydrogen bonds.

Introduction

Considerable attention has been paid to the chemistry of aroylhydrazones and their complexes.[1–3] These compounds may serve as potential chelating agents and possess biological activities.[4–6] Schiff bases have been believed to exercise their beneficial therapeutic properties in mammalian cells by inhibiting ribonucleotide reductase in the synthesis of DNA precursors.[7] In this paper, the author reports the syntheses, characterization, and crystal structures of a pair of structurally

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similar Schiff base compounds derived from the condensation of 3-methoxysalicylaldehyde or 4-dimethylaminobenzaldehyde with isonicotinic acid hydrazide in MeOH or in 95% EtOH.

Experimental

Materials and measurements

All chemicals (reagent grade) were commercially available and used without further purification. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were measured with a FT-IR 170-SX (Nicolet) spectrophotometer. The ^{1}HNMR spectra were recorded on Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal reference.

*Synthesis of isonicotinic acid [1-(3-methoxy-2-hydroxyphenyl)methylidene]hydrazide (**1**)*

3-Methoxysalicylaldehyde (152.2 mg, 1.0 mmol) and isonicotinic acid hydrazide (137.1 mg, 1.0 mmol) were dissolved in a MeOH solution (50 cm^3). The mixture was refluxed for about 1 h and cooled to room temperature to give a clear yellow solution. After keeping the solution in air for 8 days, yellow block-shaped crystals of the compound, suitable for X-ray single crystal structural determination, formed at the bottom of the vessel. The crystals were isolated, washed three times with cold MeOH and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yiled 225.7 mg (83.2%). Analysis calculated for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49%; found: C, 61.83; H, 4.93; N, 15.54%. Selected IR data (KBr, cm^{-1}): 3573 (w), 3429 (w), 3066 (w), 2934 (w), 2859 (w), 1654 (s), 1635 (s), 1279 (s), 753 (s). ^{1}HNMR data (CD_3COCD_3, ppm): $\delta = 3.88$ (s, 3H), 6.90 (t, 1H), 7.06 (t, 2H), 7.88 (d, 2H), 8.65 (d, 2H), 8.82 (s, 1H), 11.21 (s, 1H), 11.46 (s, 1H).

*Synthesis of isonicotinic acid [1-(4-dimethylaminophenyl)methylidene]hydrazide monohydrate (**2**)*

Compound **2** was prepared by a similar procedure as described for **1**, with 3-methoxysalicylaldehyde replaced by 4-dimethylaminobenzaldehyde (149.2 mg, 1.0 mmol), and with MeOH replaced by 95% EtOH. Yellow block-shaped crystals of **2** were formed after evaporating the solvent for 5 days. The crystals were isolated, washed three times with cold EtOH and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yiled 196.8 mg (87.2%). Analysis calculated for $C_{15}H_{18}N_4O_2$: C, 62.92; H, 6.34; N, 19.57%; found: C, 62.71; H, 6.27; N, 19.72%. Selected IR data (KBr, cm^{-1}): 3612 (m), 3327 (w), 3067 (w), 2933 (w), 2861 (w), 1655 (s), 1632 (s), 755 (s). ^{1}HNMR data (CD_3COCD_3, ppm): $\delta = 3.10$ (s, 6H), 6.78 (d, 2H), 7.61 (d, 2H), 7.82 (d, 2H), 8.34 (s, 1H), 8.74 (d, 2H), 10.88 (s, 1H).

Crystallography

X-ray diffraction intensities were collected using a Bruker SMART Apex 1000 CCD area detector equipped with graphite-monochromated Mo-*Ka* radiation ($\lambda = 0.71073$ Å) at 298(2) K. Absorption corrections were applied by SADABS program.[8] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL version 5.1.[9] All non-hydrogen atoms were refined anisotropically. Atom H2 in **1** and atoms H2A, H2B and H2C in **2** were located in difference Fourier maps and refined isotropically, with the U_{iso}(H) value fixed at 0.08 Å^2 and the N–H distances restrained to 0.90(1) Å, O–H distances restrained to 0.85(1) Å, and $H \cdots H$ restrained to 1.37(2) Å. The other H atoms were placed in idealized positions and constrained to ride on their parent atoms. The details of the crystallographic data are summarized in Table 1. Selected bond lengths

Table 1. Crystal Data and Refinement Parameters for the Compounds **1** and **2**

Compound	**1**	**2**
CCDC	615072	620235
Molecular formula	$C_{14}H_{13}N_3O_3$	$C_{15}H_{18}N_4O_2$
Molecular weight	271.27	286.33
Crystal system	Monoclinic	Orthorhombic
Space group	P-1	$P2_12_12_1$
Temperature (K)	298(2)	298(2)
a (Å)	7.662(1)	7.388(1)
b (Å))	16.249(2)	11.812(1)
c (Å)	10.874(2)	17.197(2)
β (°)	110.426(3)	90.00
V (Å^3)	1268.7(3)	1500.7(2)
Z	4	4
D_{calc} (g cm^{-3})	1.420	1.267
Crystal dimensions (mm); colour	0.20 × 0.18 × 0.13; yellow	0.22 × 0.17 × 0.13; yellow
Absorption coefficient (mm^{-1})	0.103	0.087
Radiation (λ)	MoKα (0.71073 Å)	MoKα (0.71073 Å)
T_{min}/T_{max}	0.980/0.987	0.981/0.989
Reflections measured	10745	12320
Range/indices (h, k, l)	$-9, 9$; $-21, 21$; $-13, 13$	$-9, 9$; $-14, 14$; $-21, 21$
θ limit (°)	2.36–27.50	2.09–26.50
Total no. of unique data	2877 ($R_{int} = 0.0629$)	1805 ($R_{int} = 0.0657$)
No. of observed data, $I > 2\sigma(I)$	1615	1302
No. of variables	186	204
No. of restraints	1	4
Goodness of fit on F^2	1.019	1.099
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0644, 0.1283	0.0585, 0.1143
R_1, wR_2 (all data)^a	0.1265, 0.1532	0.0889, 0.1256

$^aR_1 = \Sigma||Fo| - |Fc||/\Sigma|F_o|$, $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$.

and angles are summarized in Table 2. Hydrogen bonding interactions are listed in Table 3.

Table 2. Bond Distances (Å) and Angles (°) for the Compounds **1** and **2**

	1		
Bond distances			
N1–N2	1.372(3)	N1–C8	1.280(3)
N2–C9	1.356(3)	O3–C9	1.212(3)
Bond angles			
C3–O2–C7	117.4(2)	C8–N1–N2	118.0(2)
C9–N2–N1	117.5(2)	O3–C9–N2	123.7(2)
N2–C9–C10	114.9(2)		
	2		
Bond distances			
O1–C11	1.227(4)	N2–C11	1.336(4)
N2–N3	1.389(4)	N3–C10	1.286(4)
Bond angles			
O1–C11–N2	124.6(3)	C10–N3–N2	114.4(3)
C11–N2–N3	119.4(3)		

Results and discussion

The compounds were obtained in excellent yields as air stable yellow block-shaped crystals

Table 3. Distances (Å) and Angles (°) Involving Hydrogen Bonding of the Compounds **1** and **2**

D–H···A	D(D–H) (Å)	D(H···A) (Å)	D(D···A) (Å)	Angle (D–H···A) (°)
1				
N2–H2···N3$^{\#1}$	0.897(10)	2.173(12)	3.060(3)	170(3)
O1–H1···N1	0.82	1.87	2.588(3)	146
2				
N2–H2A···O2$^{\#2}$	0.897(10)	1.867(13)	2.754(4)	169(3)
O2–H2C···O1$^{\#3}$	0.842(10)	1.99(2)	2.738(4)	147(4)
O2–H2B···N1$^{\#4}$	0.849(10)	1.996(12)	2.839(5)	172(4)

Note. Symmetry transformations used to generate the equivalent atoms: #1 x, $1/2 - y$, $1/2 + z$; #2 $1 - x$, $-1/2 + y$, $1/2 - z$; #3 $-1 + x$, $1 + y$, z; #4 $3/2 - x$, $1 - y$, $1/2 + z$.

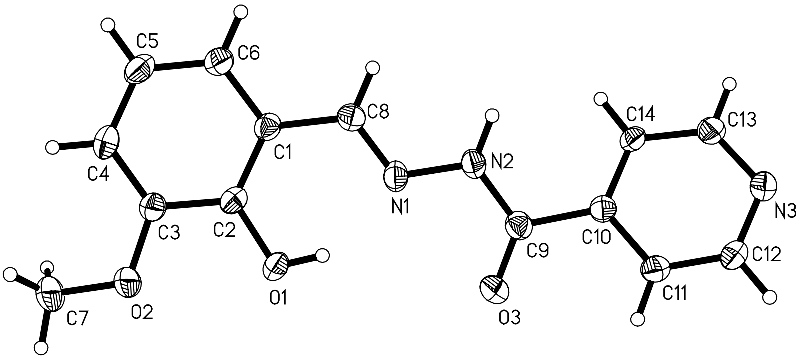

Fig. 1. Molecular structure of the compound. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii; numbering according to Table 2.

from the MeOH or 95% EtOH solution. They gave satisfactory elemental analyses corresponding to the formulae $C_{14}H_{13}N_3O_3$ for **1** and $C_{15}H_{18}N_4O_2$ for **2**. The crystals of the compounds are soluble in MeOH, EtOH and MeCN, but insoluble in water and Et_2O.

Crystal structure description

Figures 1 and 2 give perspective views of the compounds with the atomic labeling systems. All the bond lengths in the compounds are within normal ranges,[10] and comparable to those of the similar compounds.[4–6] The C8=N1 bond length of 1.280(3) Å in **1** and the C10=N3 bond length of 1.286(4) Å in **2** confirm them as double bonds. The C9–N2 bond (1.356(3) Å) and the N1–N2 bond (1.372(3) Å) in **1** and the C11–N2 bond (1.336(4) Å) and the N2–N3 bond (1.389(4) Å) in **2** are relatively short, suggesting some degree of delocalization in each of the acetohydrazide systems. The dihedral angle between the pyridine ring and the benzene ring is 15.6(2)° in **1**, which is much less than that of 48.0(3)° in **2**, which might due to the formation of the intramolecular O1–H1 · · · N1 hydrogen bonding in **1**. The same pattern can be observed in the similar compounds cited.

In the crystal structure of **1**, molecules are linked through N–H · · · N intermolecular

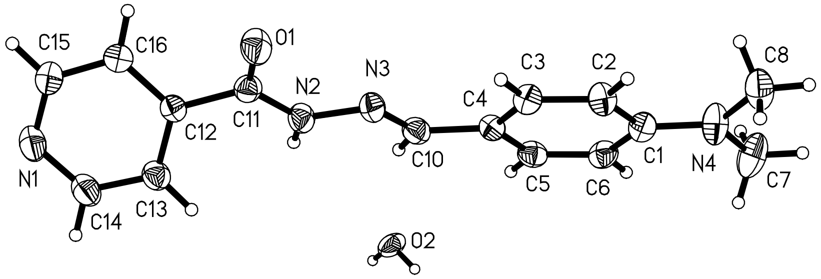

Fig. 2. Molecular structure of the compound. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii; numbering according to Table 2.

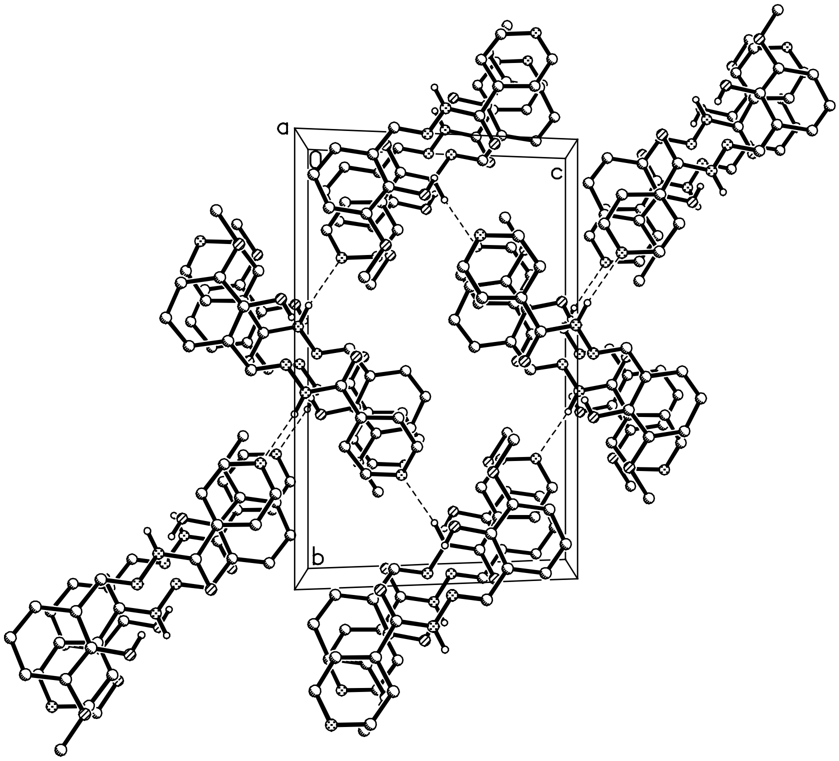

Fig. 3. Molecular packing of the compound, viewed along the *a* axis. Intermolecular hydrogen bonds are shown as dashed lines.

hydrogen bonds, forming layers parallel to the *bc* plane, as shown by Fig. 3. In the crystal structure of **2**, molecules are linked through N–H$\cdots$O, O–H$\cdots$O, and O–H$\cdots$N intermolecular hydrogen bonds, forming a network, as shown by Fig. 4.

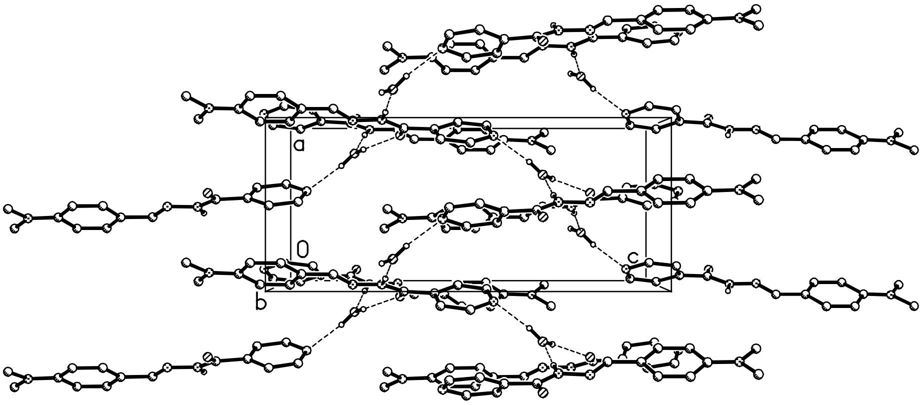

Fig. 4. Molecular packing of the compound, viewed along the *b* axis. Intermolecular hydrogen bonds are shown as dashed lines.

Supplementary material CCDC-615072 and 620235 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdccam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223–336033 or e-mail: deposit@ccdc.cam.ac.uk.

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