

2-Hydroxy-3-methoxybenzaldehyde  
(pyridine-2-carbonyl)hydrazoneMing-Li Liu, Jian-Min Dou,\*  
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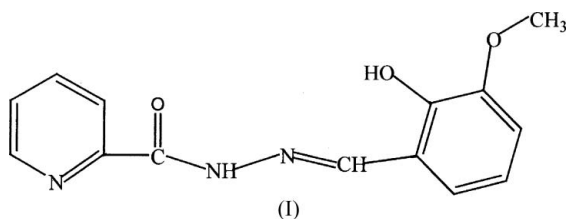
## Key indicators

Single-crystal X-ray study  
 $T = 298$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.043  
 $wR$  factor = 0.129  
Data-to-parameter ratio = 10.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The approximately planar molecule of the title compound,  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_3$ , is in an *E* configuration with respect to the  $\text{C}=\text{N}$  bond, with a  $\text{C}-\text{C}=\text{N}-\text{N}$  torsion angle of  $-177.3$  ( $2$ )°. There is an intramolecular hydrogen bond involving the hydrazone N atom and the hydroxyl O atom on the benzene ring. Intermolecular  $\text{C}-\text{H}\cdots\text{O}$  weak interactions are also formed between two adjacent methoxy groups, linking two molecules into a coplanar dimer. These dimers are further assembled into a zigzag framework along the [010] axis, using intermolecular short  $\text{C}-\text{H}\cdots\text{O}$  and long  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, resulting in a two-dimensional supramolecular crystal structure.

## Comment

The chemistry of aroylhydrazones continues to attract much attention due to their coordination ability to metal ions (Singh *et al.*, 1982; Salem, 1998) and their biological activity (Singh *et al.*, 1982; Carcelli *et al.*, 1995). In particular, aroylhydrazones containing a pyridine ring present high sensitivity and selectivity to some metals and have therefore been applied as analytical reagents (Singh *et al.*, 1982; Iki *et al.*, 1994, 1997; Babaiah *et al.*, 1996). Such compounds as *N'*-salicylidene-3-pyridinecarbohydrazide, 2-[1-(salicyloylhydrazono)ethyl]pyridinium chloride dihydrate and 2-(2-hydroxybenzylidene)-1-(2-picoloyl)hydrazine have been synthesized and characterized by X-ray diffraction (Abboud *et al.*, 1997; Wang *et al.*, 1998; Galić *et al.*, 2001). We now report on another compound, (I), whose structure was determined by X-ray diffraction.

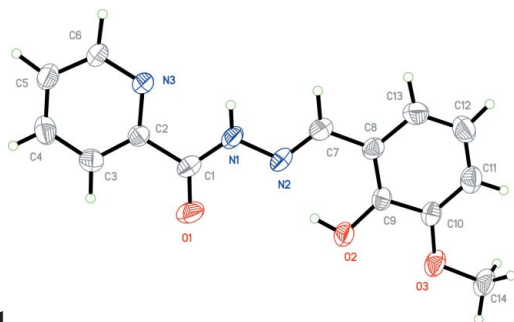


The molecular structure of the title compound is shown in Fig. 1. This compound contains two aromatic rings linked through a monoacylhydrazone group. An *E* configuration with respect to the  $\text{C}=\text{N}$  bond is shown by the molecule, with a  $\text{C}-\text{C}=\text{N}-\text{N}$  torsion angle of  $-177.3$  ( $2$ )°. Bond lengths  $\text{C1}=\text{O1}$  and  $\text{C7}=\text{N2}$  are 1.221 (3) and 1.281 (3) Å, respectively, in agreement with double-bond character, whereas bonds  $\text{C1}-\text{N1}$ ,  $\text{C8}-\text{C7}$ ,  $\text{C9}-\text{O2}$  and  $\text{C10}-\text{O3}$  are typical single bonds (Table 1). Bond lengths observed in (I) are in agreement with values found in the related compounds, *N'*-salicylidene-3-pyridinecarbohydrazide (Galić *et al.*, 2001) and isonicotinic acid(2-hydroxy-3-methoxybenzylidene)hydrazide (Yu *et al.*,

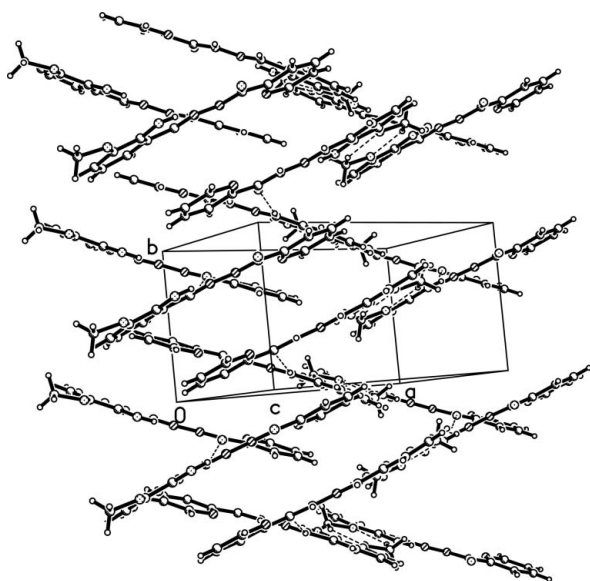
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**Figure 1**  
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**  
The crystal packing of (I).

2005). These values suggest that the aroylhydrazone moiety in (I) exists in the ketoamino form.

The molecule of the title compound is almost planar. Three relevant dihedral angles indicative of a slight deviation from planarity are:  $7.60(12)^\circ$  between the benzene and pyridine rings;  $5.06(13)^\circ$  between the benzene ring and the central hydrazone linkage (O1/C1/N1/N2/C7);  $5.25(12)^\circ$  between the pyridine ring and the central hydrazone linkage. The intramolecular hydrogen bond involving the hydroxy group bonded to the benzene ring and atom N2 of the hydrazone chain stabilizes this configuration. Moreover, a search of the Cambridge Structural Database (CSD; Version 5.18; Allen, 2002) for unsubstituted salicylideneamines in the enolimino form revealed 165 fragments in 123 structures, with structures invariably almost planar and including an intramolecular O—H $\cdots$ N hydrogen bond.

Atoms C14 and O3 of the methoxy group in one molecule act as donor and acceptor to form a weak intermolecular hydrogen bond (Table 2). As a result, a stable six-membered ring is built with two symmetry-related molecules linked into a planar dimer. These dimers are further hydrogen bonded: each dimer provides one carbonyl O atom, which interacts with NH and CH groups of the hydrazone group of a neigh-

bouring molecule, giving a zigzag framework along the [010] axis (Fig. 2). It is worth noting that the C7 $\cdots$ O1<sup>ii</sup> separation is significantly shorter than the N1 $\cdots$ O1<sup>ii</sup> separation [symmetry code: (ii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ].

## Experimental

A solution of pyridinehydrazone (10.0 mmol, 1.371 g) in methanol (15 ml) was mixed with *o*-vanillin (14.0 mmol, 2.134 g) in methanol (25 ml) and stirred for 2 h at *ca* 323 K. The yellow precipitate was filtered off and crystallized from methanol–DMF (1:1 *v/v*), yielding crystals suitable for X-ray diffraction (m.p. 448–450 K). FT–IR spectrum: 3432, 3272, 2923, 2850, 1669, 1607, 775, 729, 707  $\text{cm}^{-1}$ .

### Crystal data

$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_3$	$D_x = 1.358 \text{ Mg m}^{-3}$
$M_r = 271.27$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1287 reflections
$a = 16.534(5) \text{ \AA}$	$\theta = 2.6\text{--}20.6^\circ$
$b = 7.538(2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 11.228(3) \text{ \AA}$	$T = 298(2) \text{ K}$
$\beta = 108.554(5)^\circ$	Block, yellow
$V = 1326.6(7) \text{ \AA}^3$	$0.43 \times 0.38 \times 0.21 \text{ mm}$
$Z = 4$	

### Data collection

Siemens SMART CCD area-detector diffractometer	2322 independent reflections
$\varphi$ and $\omega$ scans	1261 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.052$
$T_{\text{min}} = 0.959, T_{\text{max}} = 0.980$	$\theta_{\text{max}} = 25.0^\circ$
6656 measured reflections	$h = -19 \rightarrow 19$
	$k = -7 \rightarrow 8$
	$l = -13 \rightarrow 12$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.0418P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.129$	$(\Delta\rho)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
2322 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
233 parameters	
All H-atom parameters refined	

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

N1—C1	1.345 (3)	O2—C9	1.353 (3)
N1—N2	1.378 (3)	O3—C10	1.371 (3)
N2—C7	1.281 (3)	O3—C14	1.420 (3)
O1—C1	1.221 (3)		
C1—N1—N2	120.3 (2)	O1—C1—N1	124.0 (2)
C7—N2—N1	116.7 (2)	O1—C1—C2	122.7 (3)
C10—O3—C14	117.9 (3)	N1—C1—C2	113.3 (2)
N2—N1—C1—C2	$-177.2(2)$	N1—N2—C7—C8	$-177.3(2)$

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C7—H6 $\cdots$ O1 <sup>i</sup>	1.00 (3)	2.29 (3)	3.213 (3)	153 (2)
O2—H7 $\cdots$ N2	0.89 (2)	1.81 (2)	2.618 (2)	149 (3)
N1—H1 $\cdots$ O1 <sup>i</sup>	0.84 (3)	2.66 (3)	3.402 (3)	148 (2)
C14—H11 $\cdots$ O3 <sup>ii</sup>	1.00 (3)	2.41 (3)	3.264 (5)	142 (2)

Symmetry codes: (i)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z$ .

All H atoms were located in a difference Fourier map and freely refined isotropically [ C–H = 0.91 (3)–1.02(3) Å].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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