Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# (*E*)-*N*′-(2-Benzyloxybenzylidene)-isonicotinohydrazide methanol solvate monohydrate

**H. S. Naveenkumar,[a] Amirin Sadikun,[a]‡ Pazilah Ibrahim,[a] Madhukar Hemamalini[b] and Hoong-Kun Fun[b]*§**

[a]School of Pharmaceutical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

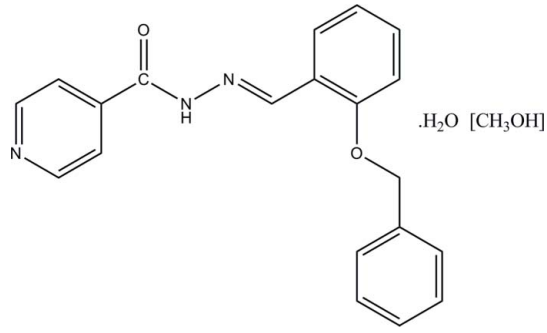
Received 5 May 2010; accepted 10 May 2010

Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.059; $wR$ factor = 0.170; data-to-parameter ratio = 24.1.

The title compound, $C_{20}H_{17}N_3O_2\cdot CH_4O\cdot H_2O$, was synthesized by the condensation reaction of 2-benzyloxybenzaldehyde with isoniazid (isonicotinic acid hydrazide). The tricyclic compound displays a *trans* configuration with respect to the C=N double bond. The central benzene ring makes dihedral angles of 8.83 (7) and 70.39 (8)° with the pyridine ring and the terminal benzene ring, respectively. The dihedral angle between the pyridine ring and the terminal benzene ring is 73.11 (8)°. In the crystal structure, molecules are connected by intermolecular N—H···O, O—H···O, O—H···(N,N) and C—H···O hydrogen bonds, forming a two-dimensional network perpendicular to the *a* axis.

## Related literature

For applications of isoniazid derivatives, see: Janin, 2007; Maccari *et al.* (2005); Slayden & Barry (2000). For the biological activity of Schiff bases, see: Kahwa *et al.* (1986). For related structures, see: Naveenkumar *et al.* (2010*a*, 2010*b*, 2010*c*). For the synthesis of isoniazid derivatives, see: Lourenco *et al.* (2008). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).




## Experimental

### Crystal data

$C_{20}H_{17}N_3O_2\cdot CH_4O\cdot H_2O$
$M_r$ = 381.42
Monoclinic, $P2_1/c$
$a$ = 17.763 (3) Å
$b$ = 12.3888 (18) Å
$c$ = 8.7450 (13) Å
$\beta$ = 98.672 (3)°
$V$ = 1902.4 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 100 K
0.35 × 0.18 × 0.09 mm

### Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.968, $T_{max}$ = 0.992
24474 measured reflections
6515 independent reflections
4012 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.069

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.170
$S$ = 1.00
6515 reflections
270 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.37 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.35 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H1*N2*···O3 | 0.91 (2) | 2.06 (2) | 2.9549 (18) | 169.9 (16) |
| O3—H1*O3*···O1*W* | 0.87 (3) | 1.85 (3) | 2.7165 (19) | 174 (3) |
| O1*W*—H1*W*1···O1$^{i}$ | 0.80 (3) | 2.11 (3) | 2.8713 (18) | 160 (2) |
| O1*W*—H1*W*1···N3$^{i}$ | 0.80 (3) | 2.62 (3) | 3.2119 (19) | 133 (2) |
| O1*W*—H2*W*1···N1$^{ii}$ | 0.87 (3) | 2.05 (3) | 2.898 (2) | 163 (2) |
| C1—H1*A*···O3 | 0.93 | 2.27 | 3.189 (2) | 169 |
| C2—H2*A*···O1$^{iii}$ | 0.93 | 2.48 | 3.229 (2) | 137 |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

This research was supported by Universiti Sains Malaysia (USM) under the Fundamental Research Grant Scheme (203/PFARMASI/671157). HSNK is grateful to Universiti Sains Malaysia for a USM-fellowship. HKF and MH thank the Malaysian Government and Universiti Sains Malaysia for the Research University Golden Goose grant No. 1001/PFIZIK/

‡ Additional correspondence author, e-mail: amirin@usm.my.
§ Thomson Reuters ResearcherID: A-3561-2009.

811012. MH also thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2796).

## References

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Janin, Y. L. (2007). *Bioorg. Med. Chem.* **15**, 2479–2513.
Kahwa, I. A., Selbin, J., Hsieh, T. C.-Y. & Laine, R. A. (1986). *Inorg. Chim. Acta*, **118**, 179–185.
Lourenco, M. C. S., Ferreira, M. L., de Souza, M. V. N., Peralta, M. A., Vasconcelos, T. R. A. & Henriques, M. G. M. O. (2008). *Eur. J. Med. Chem.* **43**, 1344–1347.
Maccari, R., Ottana, R. & Vigorita, M. G. (2005). *Bioorg. Med. Chem. Lett.* **15**, 2509–2513.
Naveenkumar, H. S., Sadikun, A., Ibrahim, P., Loh, W.-S. & Fun, H.-K. (2010*c*). *Acta Cryst.* E**66**, o1202–o1203.
Naveenkumar, H. S., Sadikun, A., Ibrahim, P., Quah, C. K. & Fun, H.-K. (2010*a*). *Acta Cryst.* E**66**, o291.
Naveenkumar, H. S., Sadikun, A., Ibrahim, P., Yeap, C. S. & Fun, H.-K. (2010*b*). *Acta Cryst.* E**66**, o1235–o1236.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Slayden, R. A. & Barry, C. E. (2000). *Microbes Infect.* **2**, 659–669.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

# supplementary materials

*Acta Cryst.* (2010). E**66**, o1337-o1338 [ **doi:10.1107/S1600536810016958** ]

# (*E*)-*N*'-(2-Benzyloxybenzylidene)isonicotinohydrazide methanol solvate monohydrate

**H. S. Naveenkumar, A. Sadikun, P. Ibrahim, M. Hemamalini and H.-K. Fun**

## Comment

Isoniazid derivatives have been found to possess potential tuberculostatic activity (Janin, 2007; Maccari *et al.*, 2005; Slayden & Barry, 2000). Schiff bases have attracted much attention because of their biological activity (Kahwa *et al.*, 1986). We have recently reported the crystal structures of (*E*)-*N*′-[(*E*)-3-(4-hydroxy- 3-methoxyphenyl)allylidene]isonicotinohydrazide (Naveenkumar *et al.*, 2010*a*), (*E*)-N'-(2,4,5-trimethoxybenzylidene)isonicotinohydrazide dihydrate (Naveenkumar *et al.*, 2010*b*) and (*E*)-*N*′- (2,4,6-trihydroxybenzylidene)isonicotinohydrazide sesquihydrate (Naveenkumar *et al.*, 2010*c*). As a part of our current work on the synthesis of (*E*)-*N*′-substituted isonicotinohydrazide derivatives, in this paper we present the crystal structure of the title compound, (I), Fig.1.

In (I), the molecular structure of the compound displays a trans configuration with respect to the C═N double bond. The central benzene (C8–C13) ring makes dihedral angles of 8.83 (7)° and 70.39 (8)° with the pyridine (N1/C1–C5) ring and the terminal benzene (C15–C20) ring, respectively. The dihedral angle between the pyridine (N1/C1–C5) ring and the terminal benzene (C15–C20) ring is 73.11 (8)°.

In the crystal packing (Fig. 2), molecules are connected by N2—H1N2···O3, O3—H1O3···O1W, O1W—H1W1···O1, O1W—H1W1···N3, O1W—H2W1···N1, C1—H1A···O3 and C2—H2A···O1 (Table 1) hydrogen bonds.

## Experimental

This isoniazid derivative was prepared by a literature procedure (Lourenco *et al.*, 2008) involving the reaction between the 2-benzyloxybenzaldehyde (1.0 eq) and isoniazid (1.0 eq) in ethanol/water. After stirring for 1-3 hours at room temperature, the resulting mixture was concentrated under reduced pressure. The residue, purified by washing with cold ethanol and diethyl ether, afforded the pure derivative. Colorless single crystals suitable for X-ray analysis were obtained by recrystallization from methanol.

## Refinement

Atoms H1N2, H1O3, H1W1 and H2W1 were located in a difference Fourier map and refined freely. The remaining H atoms were positioned geometrically [C–H = 0.93–0.97 Å] and were refined using a riding model, with $U_{iso}$(H) = 1.2 or 1.5$U_{eq}$(C).

**Figures**

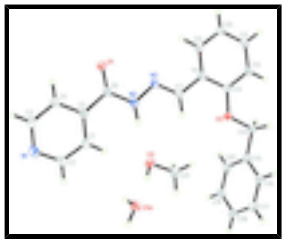


Fig. 1. The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

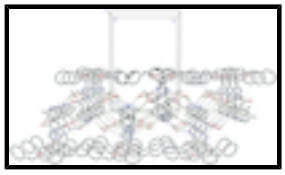


Fig. 2. The crystal packing of the title compound, showing the hydrogen-bonding (dashed lines) network.

**(*E*)-*N*'-(2-Benzyloxybenzylidene)isonicotinohydrazide methanol solvate monohydrate**

*Crystal data*

| | |
|---|---|
| $C_{20}H_{17}N_3O_2 \cdot CH_4O \cdot H_2O$ | $F(000) = 808$ |
| $M_r = 381.42$ | $D_x = 1.332$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 3013 reflections |
| $a = 17.763$ (3) Å | $\theta = 2.3$–$30.0°$ |
| $b = 12.3888$ (18) Å | $\mu = 0.09$ mm$^{-1}$ |
| $c = 8.7450$ (13) Å | $T = 100$ K |
| $\beta = 98.672$ (3)° | Plate, colourless |
| $V = 1902.4$ (5) Å$^3$ | 0.35 × 0.18 × 0.09 mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker APEXII DUO CCD area-detector diffractometer | 6515 independent reflections |
| Radiation source: fine-focus sealed tube | 4012 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.069$ |
| φ and ω scans | $\theta_{max} = 32.0°$, $\theta_{min} = 2.0°$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2009) | $h = -26 \rightarrow 26$ |
| $T_{min} = 0.968$, $T_{max} = 0.992$ | $k = -17 \rightarrow 18$ |
| 24474 measured reflections | $l = -13 \rightarrow 12$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.059$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.170$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.00$ | $w = 1/[\sigma^2(F_o^2) + (0.0887P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 6515 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 270 parameters | $\Delta\rho_{max} = 0.37$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.35$ e Å$^{-3}$ |

*Special details*

**Experimental**. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

**Geometry**. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.12066 (6) | 0.05407 (9) | 0.36337 (14) | 0.0250 (3) |
| O2 | 0.36364 (6) | 0.37324 (8) | 0.80611 (13) | 0.0211 (2) |
| N1 | −0.05513 (8) | 0.28776 (12) | 0.00600 (16) | 0.0258 (3) |
| N2 | 0.17041 (7) | 0.21885 (11) | 0.43066 (15) | 0.0194 (3) |
| N3 | 0.22141 (7) | 0.17181 (10) | 0.54646 (15) | 0.0196 (3) |
| C1 | 0.04882 (9) | 0.31412 (13) | 0.2126 (2) | 0.0241 (3) |
| H1A | 0.0791 | 0.3622 | 0.2765 | 0.029* |
| C2 | −0.00980 (9) | 0.35168 (14) | 0.1031 (2) | 0.0270 (4) |
| H2A | −0.0181 | 0.4258 | 0.0966 | 0.032* |
| C3 | −0.04163 (10) | 0.18181 (14) | 0.0186 (2) | 0.0284 (4) |
| H3A | −0.0721 | 0.1356 | −0.0480 | 0.034* |
| C4 | 0.01531 (9) | 0.13683 (13) | 0.1257 (2) | 0.0256 (3) |
| H4A | 0.0223 | 0.0624 | 0.1304 | 0.031* |
| C5 | 0.06174 (8) | 0.20416 (12) | 0.22571 (17) | 0.0191 (3) |
| C6 | 0.12010 (8) | 0.15226 (12) | 0.34544 (18) | 0.0194 (3) |
| C7 | 0.26917 (8) | 0.23667 (12) | 0.62477 (18) | 0.0192 (3) |
| H7A | 0.2676 | 0.3101 | 0.6022 | 0.023* |
| C8 | 0.32580 (8) | 0.19465 (12) | 0.74905 (17) | 0.0176 (3) |
| C9 | 0.33274 (8) | 0.08431 (12) | 0.78078 (18) | 0.0200 (3) |
| H9A | 0.3004 | 0.0360 | 0.7218 | 0.024* |
| C10 | 0.38701 (9) | 0.04540 (12) | 0.89869 (19) | 0.0216 (3) |

| | | | | |
|---|---|---|---|---|
| H10A | 0.3906 | −0.0282 | 0.9193 | 0.026* |
| C11 | 0.43586 (8) | 0.11734 (13) | 0.98564 (19) | 0.0216 (3) |
| H11A | 0.4724 | 0.0914 | 1.0644 | 0.026* |
| C12 | 0.43089 (8) | 0.22761 (12) | 0.95664 (18) | 0.0198 (3) |
| H12A | 0.4644 | 0.2751 | 1.0145 | 0.024* |
| C13 | 0.37506 (8) | 0.26656 (11) | 0.83943 (17) | 0.0179 (3) |
| C14 | 0.40996 (9) | 0.45051 (12) | 0.90037 (19) | 0.0212 (3) |
| H14A | 0.4624 | 0.4457 | 0.8825 | 0.025* |
| H14B | 0.4084 | 0.4369 | 1.0091 | 0.025* |
| C15 | 0.37824 (9) | 0.55991 (12) | 0.85576 (17) | 0.0201 (3) |
| C16 | 0.41662 (9) | 0.63173 (13) | 0.77156 (19) | 0.0240 (3) |
| H16A | 0.4638 | 0.6129 | 0.7455 | 0.029* |
| C17 | 0.38469 (10) | 0.73098 (13) | 0.7266 (2) | 0.0291 (4) |
| H17A | 0.4104 | 0.7784 | 0.6702 | 0.035* |
| C18 | 0.31456 (10) | 0.75978 (13) | 0.7654 (2) | 0.0287 (4) |
| H18A | 0.2932 | 0.8263 | 0.7349 | 0.034* |
| C19 | 0.27639 (10) | 0.68912 (14) | 0.8500 (2) | 0.0278 (4) |
| H19A | 0.2295 | 0.7086 | 0.8768 | 0.033* |
| C20 | 0.30781 (9) | 0.58952 (13) | 0.89466 (19) | 0.0245 (3) |
| H20A | 0.2818 | 0.5423 | 0.9508 | 0.029* |
| O3 | 0.17234 (7) | 0.45730 (9) | 0.42445 (15) | 0.0268 (3) |
| C21 | 0.21264 (10) | 0.52275 (14) | 0.5437 (2) | 0.0269 (3) |
| H21A | 0.2657 | 0.5039 | 0.5583 | 0.040* |
| H21B | 0.1926 | 0.5110 | 0.6383 | 0.040* |
| H21C | 0.2068 | 0.5974 | 0.5149 | 0.040* |
| O1W | 0.16524 (7) | 0.56017 (11) | 0.14832 (15) | 0.0261 (3) |
| H1N2 | 0.1707 (11) | 0.2913 (16) | 0.416 (2) | 0.027 (5)* |
| H1O3 | 0.1722 (13) | 0.4936 (19) | 0.339 (3) | 0.051 (7)* |
| H1W1 | 0.1606 (14) | 0.518 (2) | 0.079 (3) | 0.052 (7)* |
| H2W1 | 0.1375 (15) | 0.616 (2) | 0.115 (3) | 0.056 (7)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0287 (6) | 0.0175 (5) | 0.0262 (6) | −0.0017 (4) | −0.0046 (5) | 0.0026 (5) |
| O2 | 0.0244 (5) | 0.0139 (5) | 0.0223 (5) | −0.0010 (4) | −0.0054 (4) | −0.0011 (4) |
| N1 | 0.0228 (6) | 0.0274 (7) | 0.0257 (7) | 0.0022 (5) | −0.0009 (6) | 0.0010 (6) |
| N2 | 0.0213 (6) | 0.0161 (6) | 0.0187 (6) | −0.0002 (5) | −0.0032 (5) | 0.0025 (5) |
| N3 | 0.0188 (6) | 0.0188 (6) | 0.0199 (6) | 0.0012 (4) | −0.0016 (5) | 0.0024 (5) |
| C1 | 0.0232 (7) | 0.0209 (7) | 0.0259 (8) | −0.0017 (6) | −0.0038 (6) | −0.0008 (7) |
| C2 | 0.0259 (8) | 0.0224 (8) | 0.0309 (9) | 0.0036 (6) | −0.0012 (7) | 0.0024 (7) |
| C3 | 0.0274 (8) | 0.0283 (9) | 0.0259 (8) | −0.0019 (6) | −0.0078 (7) | −0.0013 (7) |
| C4 | 0.0275 (8) | 0.0196 (8) | 0.0269 (8) | −0.0007 (6) | −0.0045 (7) | −0.0009 (7) |
| C5 | 0.0181 (6) | 0.0209 (7) | 0.0179 (7) | −0.0005 (5) | 0.0012 (6) | 0.0020 (6) |
| C6 | 0.0203 (7) | 0.0200 (7) | 0.0173 (7) | −0.0019 (5) | 0.0011 (6) | 0.0000 (6) |
| C7 | 0.0207 (7) | 0.0156 (7) | 0.0202 (7) | −0.0008 (5) | −0.0008 (6) | 0.0008 (6) |
| C8 | 0.0181 (6) | 0.0165 (7) | 0.0177 (7) | 0.0006 (5) | 0.0005 (5) | 0.0012 (6) |
| C9 | 0.0205 (7) | 0.0174 (7) | 0.0213 (7) | −0.0007 (5) | 0.0006 (6) | −0.0015 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C10 | 0.0231 (7) | 0.0163 (7) | 0.0249 (8) | 0.0022 (5) | 0.0020 (6) | 0.0035 (6) |
| C11 | 0.0195 (7) | 0.0233 (8) | 0.0208 (7) | 0.0039 (5) | −0.0006 (6) | 0.0025 (6) |
| C12 | 0.0178 (6) | 0.0209 (7) | 0.0195 (7) | 0.0003 (5) | −0.0010 (6) | −0.0012 (6) |
| C13 | 0.0197 (6) | 0.0152 (7) | 0.0190 (7) | 0.0011 (5) | 0.0032 (6) | −0.0001 (6) |
| C14 | 0.0225 (7) | 0.0170 (7) | 0.0222 (7) | −0.0024 (5) | −0.0032 (6) | −0.0014 (6) |
| C15 | 0.0252 (7) | 0.0170 (7) | 0.0165 (7) | −0.0015 (5) | −0.0022 (6) | −0.0019 (6) |
| C16 | 0.0245 (7) | 0.0228 (8) | 0.0234 (8) | −0.0026 (6) | −0.0003 (6) | −0.0005 (7) |
| C17 | 0.0339 (9) | 0.0220 (8) | 0.0294 (9) | −0.0054 (6) | −0.0013 (7) | 0.0039 (7) |
| C18 | 0.0361 (9) | 0.0174 (8) | 0.0294 (9) | 0.0018 (6) | −0.0053 (8) | −0.0013 (7) |
| C19 | 0.0300 (8) | 0.0251 (8) | 0.0270 (8) | 0.0051 (6) | 0.0003 (7) | −0.0035 (7) |
| C20 | 0.0291 (8) | 0.0222 (8) | 0.0220 (8) | −0.0002 (6) | 0.0032 (7) | −0.0003 (7) |
| O3 | 0.0307 (6) | 0.0224 (6) | 0.0244 (6) | −0.0056 (4) | −0.0052 (5) | 0.0018 (5) |
| C21 | 0.0288 (8) | 0.0243 (8) | 0.0262 (8) | −0.0023 (6) | 0.0000 (7) | −0.0033 (7) |
| O1W | 0.0298 (6) | 0.0224 (6) | 0.0231 (6) | 0.0033 (5) | −0.0058 (5) | −0.0012 (5) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C6 | 1.2263 (18) | C11—C12 | 1.390 (2) |
| O2—C13 | 1.3619 (17) | C11—H11A | 0.9300 |
| O2—C14 | 1.4382 (18) | C12—C13 | 1.400 (2) |
| N1—C3 | 1.336 (2) | C12—H12A | 0.9300 |
| N1—C2 | 1.338 (2) | C14—C15 | 1.497 (2) |
| N2—C6 | 1.3542 (19) | C14—H14A | 0.9700 |
| N2—N3 | 1.3817 (18) | C14—H14B | 0.9700 |
| N2—H1N2 | 0.91 (2) | C15—C20 | 1.394 (2) |
| N3—C7 | 1.2881 (19) | C15—C16 | 1.397 (2) |
| C1—C5 | 1.383 (2) | C16—C17 | 1.386 (2) |
| C1—C2 | 1.385 (2) | C16—H16A | 0.9300 |
| C1—H1A | 0.9300 | C17—C18 | 1.386 (3) |
| C2—H2A | 0.9300 | C17—H17A | 0.9300 |
| C3—C4 | 1.387 (2) | C18—C19 | 1.387 (2) |
| C3—H3A | 0.9300 | C18—H18A | 0.9300 |
| C4—C5 | 1.387 (2) | C19—C20 | 1.386 (2) |
| C4—H4A | 0.9300 | C19—H19A | 0.9300 |
| C5—C6 | 1.502 (2) | C20—H20A | 0.9300 |
| C7—C8 | 1.461 (2) | O3—C21 | 1.426 (2) |
| C7—H7A | 0.9300 | O3—H1O3 | 0.88 (2) |
| C8—C9 | 1.397 (2) | C21—H21A | 0.9600 |
| C8—C13 | 1.406 (2) | C21—H21B | 0.9600 |
| C9—C10 | 1.388 (2) | C21—H21C | 0.9600 |
| C9—H9A | 0.9300 | O1W—H1W1 | 0.80 (3) |
| C10—C11 | 1.388 (2) | O1W—H2W1 | 0.88 (3) |
| C10—H10A | 0.9300 | | |
| C13—O2—C14 | 117.99 (12) | C11—C12—C13 | 119.40 (14) |
| C3—N1—C2 | 116.47 (15) | C11—C12—H12A | 120.3 |
| C6—N2—N3 | 116.85 (13) | C13—C12—H12A | 120.3 |
| C6—N2—H1N2 | 123.0 (12) | O2—C13—C12 | 123.87 (14) |
| N3—N2—H1N2 | 120.1 (12) | O2—C13—C8 | 115.77 (13) |
| C7—N3—N2 | 115.66 (13) | C12—C13—C8 | 120.35 (13) |

| | | | |
|---|---|---|---|
| C5—C1—C2 | 119.11 (15) | O2—C14—C15 | 107.03 (12) |
| C5—C1—H1A | 120.4 | O2—C14—H14A | 110.3 |
| C2—C1—H1A | 120.4 | C15—C14—H14A | 110.3 |
| N1—C2—C1 | 123.90 (15) | O2—C14—H14B | 110.3 |
| N1—C2—H2A | 118.0 | C15—C14—H14B | 110.3 |
| C1—C2—H2A | 118.0 | H14A—C14—H14B | 108.6 |
| N1—C3—C4 | 123.64 (16) | C20—C15—C16 | 119.24 (14) |
| N1—C3—H3A | 118.2 | C20—C15—C14 | 119.41 (14) |
| C4—C3—H3A | 118.2 | C16—C15—C14 | 121.32 (14) |
| C5—C4—C3 | 119.19 (15) | C17—C16—C15 | 120.22 (15) |
| C5—C4—H4A | 120.4 | C17—C16—H16A | 119.9 |
| C3—C4—H4A | 120.4 | C15—C16—H16A | 119.9 |
| C1—C5—C4 | 117.68 (14) | C16—C17—C18 | 120.22 (16) |
| C1—C5—C6 | 124.60 (14) | C16—C17—H17A | 119.9 |
| C4—C5—C6 | 117.66 (14) | C18—C17—H17A | 119.9 |
| O1—C6—N2 | 122.82 (14) | C17—C18—C19 | 119.84 (15) |
| O1—C6—C5 | 120.34 (14) | C17—C18—H18A | 120.1 |
| N2—C6—C5 | 116.84 (13) | C19—C18—H18A | 120.1 |
| N3—C7—C8 | 119.84 (13) | C20—C19—C18 | 120.24 (16) |
| N3—C7—H7A | 120.1 | C20—C19—H19A | 119.9 |
| C8—C7—H7A | 120.1 | C18—C19—H19A | 119.9 |
| C9—C8—C13 | 118.68 (13) | C19—C20—C15 | 120.24 (15) |
| C9—C8—C7 | 121.79 (13) | C19—C20—H20A | 119.9 |
| C13—C8—C7 | 119.53 (13) | C15—C20—H20A | 119.9 |
| C10—C9—C8 | 121.22 (14) | C21—O3—H1O3 | 105.8 (16) |
| C10—C9—H9A | 119.4 | O3—C21—H21A | 109.5 |
| C8—C9—H9A | 119.4 | O3—C21—H21B | 109.5 |
| C9—C10—C11 | 119.40 (14) | H21A—C21—H21B | 109.5 |
| C9—C10—H10A | 120.3 | O3—C21—H21C | 109.5 |
| C11—C10—H10A | 120.3 | H21A—C21—H21C | 109.5 |
| C10—C11—C12 | 120.93 (14) | H21B—C21—H21C | 109.5 |
| C10—C11—H11A | 119.5 | H1W1—O1W—H2W1 | 107 (2) |
| C12—C11—H11A | 119.5 | | |
| C6—N2—N3—C7 | 179.30 (13) | C9—C10—C11—C12 | 0.3 (2) |
| C3—N1—C2—C1 | 0.1 (2) | C10—C11—C12—C13 | 0.9 (2) |
| C5—C1—C2—N1 | −0.8 (3) | C14—O2—C13—C12 | −2.2 (2) |
| C2—N1—C3—C4 | 0.5 (2) | C14—O2—C13—C8 | 176.90 (12) |
| N1—C3—C4—C5 | −0.4 (3) | C11—C12—C13—O2 | 177.34 (13) |
| C2—C1—C5—C4 | 0.9 (2) | C11—C12—C13—C8 | −1.7 (2) |
| C2—C1—C5—C6 | −176.15 (14) | C9—C8—C13—O2 | −177.83 (12) |
| C3—C4—C5—C1 | −0.3 (2) | C7—C8—C13—O2 | 2.38 (19) |
| C3—C4—C5—C6 | 176.90 (14) | C9—C8—C13—C12 | 1.3 (2) |
| N3—N2—C6—O1 | −3.1 (2) | C7—C8—C13—C12 | −178.47 (13) |
| N3—N2—C6—C5 | 176.55 (12) | C13—O2—C14—C15 | −171.52 (12) |
| C1—C5—C6—O1 | 169.54 (15) | O2—C14—C15—C20 | 69.93 (18) |
| C4—C5—C6—O1 | −7.5 (2) | O2—C14—C15—C16 | −107.99 (16) |
| C1—C5—C6—N2 | −10.1 (2) | C20—C15—C16—C17 | −0.4 (2) |
| C4—C5—C6—N2 | 172.90 (14) | C14—C15—C16—C17 | 177.56 (15) |
| N2—N3—C7—C8 | −179.56 (12) | C15—C16—C17—C18 | 0.2 (3) |

| | | | |
|---|---|---|---|
| N3—C7—C8—C9 | 3.6 (2) | C16—C17—C18—C19 | 0.2 (3) |
| N3—C7—C8—C13 | −176.60 (13) | C17—C18—C19—C20 | −0.5 (3) |
| C13—C8—C9—C10 | −0.1 (2) | C18—C19—C20—C15 | 0.4 (3) |
| C7—C8—C9—C10 | 179.69 (14) | C16—C15—C20—C19 | 0.1 (2) |
| C8—C9—C10—C11 | −0.7 (2) | C14—C15—C20—C19 | −177.91 (15) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H1N2···O3 | 0.91 (2) | 2.06 (2) | 2.9549 (18) | 169.9 (16) |
| O3—H1O3···O1W | 0.87 (3) | 1.85 (3) | 2.7165 (19) | 174 (3) |
| O1W—H1W1···O1$^{i}$ | 0.80 (3) | 2.11 (3) | 2.8713 (18) | 160 (2) |
| O1W—H1W1···N3$^{i}$ | 0.80 (3) | 2.62 (3) | 3.2119 (19) | 133 (2) |
| O1W—H2W1···N1$^{ii}$ | 0.87 (3) | 2.05 (3) | 2.898 (2) | 163 (2) |
| C1—H1A···O3 | 0.93 | 2.27 | 3.189 (2) | 169. |
| C2—H2A···O1$^{iii}$ | 0.93 | 2.48 | 3.229 (2) | 137. |

Symmetry codes: (i) *x*, −*y*+1/2, *z*−1/2; (ii) −*x*, −*y*+1, −*z*; (iii) −*x*, *y*+1/2, −*z*+1/2.

**Fig. 1**

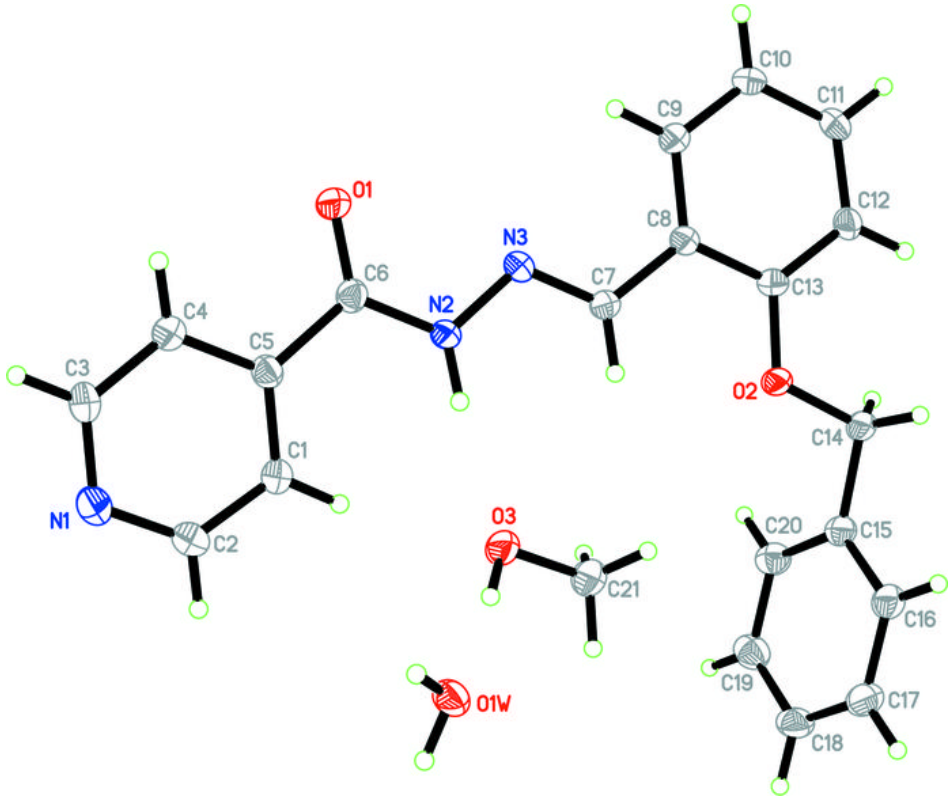

C10
C11
C9
C12
O1
C8
N3
C6
C7
C13
C4
N2
C5
C3
O2
C14
C1
N1
C2
O3
C20
C15
C21
C16
C19
C17
O1W
C18

**Fig. 2**