Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N′-(2,3-Dihydroxybenzylidene)-isonicotinohydrazide

Elif Tecer,[a] Necmi Dege,[a] Ayşin Zülfikaroğlu,[b] Nuray Şenyüz[b] and Hümeyra Batı[b]*

[a]Department of Physics, Arts and Sciences Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey, and [b]Department of Chemistry, Arts and Sciences Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey
Correspondence e-mail: elifteceromu@gmail.com

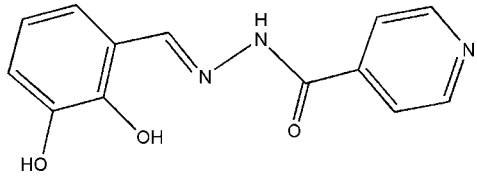
Received 2 November 2010; accepted 22 November 2010

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.084; data-to-parameter ratio = 11.8.

The title compound, $C_{13}H_{11}N_3O_3$, crystallized with two independent molecules in the asymmetric unit. One of the molecules is twisted while the other is almost planar, with dihedral angles of 28.02 (6) and 2.42 (9)°, respectively, between the benzene and pyridine rings. Intramolecular O—H···O and O—H···N hydrogen bonds are present in both molecules. The two independent molecules are linked by pairs of O—H···O hydrogen bonds. The crystal structure is further stabilized by intermolecular N—H···N hydrogen bonds and C—H···N and C—H···O interactions.

Related literature

For the proven therapeutic importance of isonicotinic acid hydrazide, see: Agarwal *et al.* (2005, 2006); Savanini *et al.* (2002). For Schiff base complexes as models for biologically important species, see: Chohan & Sheazi (1999); Abou-Melha (2008). For the antitubercular activity of hydrazones, see: Durgaprasad & Patel (1973); Kriza *et al.* (2010). For hydrogen bonding leading to the dimerization of molecules, see: Avasthi *et al.* (2002). For delocalized double bonds, see: Zülfikaroğlu *et al.* (2009).



Experimental

Crystal data

$C_{13}H_{11}N_3O_3$
M_r = 257.25
Monoclinic, $P2_1/c$
a = 7.7781 (2) Å
b = 30.0719 (8) Å
c = 10.5116 (3) Å
β = 101.551 (2)°
V = 2408.89 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 296 K
0.53 × 0.31 × 0.19 mm

Data collection

Stoe IPDS-II diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.961, T_{max} = 0.984
34859 measured reflections
5118 independent reflections
3512 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.084
S = 1.02
5118 reflections
432 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.10 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···N1	0.96 (2)	1.65 (2)	2.5281 (15)	149.7 (18)
N2—H2*N*···N6^{i}	0.913 (18)	2.051 (17)	2.9407 (17)	164.7 (15)
O2—H2*O*···O1	0.96 (2)	2.20 (2)	2.7022 (14)	111.3 (15)
O2—H2*O*···O4	0.96 (2)	1.97 (2)	2.8605 (15)	153.3 (18)
O4—H4*O*···N4	0.97 (2)	1.65 (2)	2.5441 (15)	151.2 (19)
N5—H5*N*···N3^{ii}	0.900 (18)	2.129 (17)	2.9914 (18)	160.2 (14)
O5—H5*O*···O1	0.91 (2)	1.96 (2)	2.8138 (16)	154 (2)
O5—H5*O*···O4	0.91 (2)	2.25 (2)	2.7171 (16)	111.6 (18)
C10—H10···N6^{i}	0.964 (17)	2.429 (17)	3.369 (2)	164.8 (15)
C11—H11···O6^{iii}	0.953 (18)	2.317 (18)	3.2485 (18)	165.4 (13)
C20—H20···O2^{iv}	0.967 (18)	2.533 (17)	3.4652 (18)	162.0 (13)
C24—H24···O3^{v}	0.949 (18)	2.395 (18)	3.3373 (18)	172.1 (14)

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, -y+1, -z+1$; (iv) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

The authors thanks the Ondokuz Mayıs University Research Fund for financial support of this project.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2224).

References

Abou-Melha, K. S. (2008). *Spectrochim. Acta A*, **70**, 162–170.
Agarwal, R. K., Sharma, D., Singh, L. & Agarwal, H. (2006). *Bioinorg. Chem. Appl.* Article ID 29234, 9 pp.
Agarwal, R. K., Singh, L., Sharma, D. K. & Singh, R. (2005). *Turk. J. Chem.* **29**, 309–316.
Avasthi, K., Rawat, D. S., Chandra, T., Sharon, A. & Maulik, P. R. (2002). *Acta Cryst.* C**58**, o311–o313.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Chohan, Z. H. & Sheazi, S. K. A. (1999). *Synth. React. Inorg. Met. Org. Chem.* **29**, 105–118.
Durgaprasad, G. & Patel, C. C. (1973). *Indian J. Chem. Sect. A*, **11**, 1300–1305.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kriza, A., Ababei, L. V., Cioatera, N., Rau, I. & Stanica, N. (2010). *J. Serb. Chem.* 75, 229–242

Savanini, L., Chiasserini, L., Gaeta, A. & Pellerano, C. (2002). *Bioorg. Med. Chem.* **10**, 2193–2198.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst*. D**65**, 148–155.
Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.
Zülfikaroğlu, A., Yüksektepe, Ç., Bati, H., Çalışkan, N. & Büyükgüngör, O. (2009). *J. Struct. Chem.* **50**, 1166–1170

supplementary materials

Acta Cryst. (2010). E**66**, o3369-o3370 [**doi:10.1107/S1600536810048701**]

N'-(2,3-Dihydroxybenzylidene)isonicotinohydrazide

E. Tecer, N. Dege, A. Zülfikaroglu, N. Senyüz and H. Bati

Comment

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde. Also, Schiff bases are a functional group that contains a carbon-nitrogen (C=N) double bond (an imine group). These bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species (Abou-Melha 2008; Chohan *et al.*, 1999). The remarkable biological activity of acid hydrazides R—CO—NH—NH_2, a class of Schiff base, their corresponding aroylhydrazones, R—CO—NH—N=CH—*R*' and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest in the past. Isonicotinic acid hydrazide (INH) is a drug of proven therapeutic importance and is used against a wide spectrum of bacterial ailments, *e.g.*, tuberculosis (Agarwal *et al.*, 2005, Savanini *et al.*, 2002). Hydrazones derived from the condensation of isonicotinic acid hydrazide with pyridine aldehydes have been found to show better antitubercular activity than INH (Kriza *et al.*, 2010, Agarwal *et al.*,2006, Durgaprasad *et al.*,1973).

The molecular structure of the two independent molecules (a and b) of the title compound are shown in Fig. 1. The title molecule comprises three functional groups: pyridine, phenyl and hydrazone. Both molecules, a and b, have the *E* configuration at the central C=N bond (Fig. 1). One of the molecules (b) is twisted while the other (a) is planar, with the dihedral angles between the phenyl and pyridine rings being 28.02 (6)° and 2.42 (9)° in molecules (b) and (a), respectively. Because of this different conformation molecules (a) and (b) have different hydrogen bonding patterns. Molecule (a) is influenced by the O—H···N, O—H···O intramolecular hydrogen bonds and C—H···O intramolecular interactions, and the intermolecular N—H···N, O—H···O, C—H···O and C—H···N hydrogen bonds (Table 1). Molecule (b) is influenced by O—H···N and O—H···O intramolecular hydrogen bonds and N—H···N, O—H···O and two C—H···O intermolecular hydrogen bonds (Table 1).

The N1—N2 (molecule a) and N4—N5 (molecule b) bond distances of 1.3726 (15) Å and 1.3679 (16) Å, respectively, are appreciably shorter than a typical N—N single bond, such as that found in free 2,4-dinitrophenylhydrazone, i.e. 1.405 (6) Å; this suggests the existence of a delocalized double bond system (Zülfikaroğlu *et al.*, 2009). The N1═C7 (molecule a) and N4═ C20 (molecule b) bond distances of 1.2782 (18) Å and 1.276 (2) Å, respectively, are typical for a double bond. For both molecules, the central torsion angles are C7—N1—N2—C8 at 177.63 (14)° (molecule a) and C21—N5—N4—C20 at 174.77 (14)° (molecule b). Also, the torsion angles N4—C20—C14—C15 and C23—C22—C21—N5 in the molecule (*b*) are 2.16 (22)° and 22.12 (20)°, respectively.

Interestingly, in the crystal the hydrogen bonding (O2—H2O···O4 and O5—H5O···O1) leads to the dimerization of the molecules (Avasthi *et al.*, 2002) (Table 1), as shown in Fig. 2, and finally to the formation of a layer-like structure (Fig. 3).

Experimental

Isonicotinic acid hydrazide (1.4 g, 10 mmol) was dissolved in 15 ml of absolute ethanol. To this solution 2,3-dihydroxy benzaldehyde (1.38 g, dissolved in 10 ml absolute ethanol) was added. The reaction mixture was refluxed for 5 h and then cooled to room temperature, giving a clear yellow solution. After keeping the solution in air for 10 days, yellow crystals of the title compound, suitable for X-ray diffraction analysis, were obtained. The crystals were isolated washed with cold absolute ethanol and dried in air. Yield 79%. Anal. Calcd. for $C_{13}H_{11}N_3O_3$: C 60.70, H 4.31, N 16.33%. Found: C 60.64, H 4.39, N 16.39%. Spectroscopic and other synthetic details are given in the archived CIF.

Refinement

All the H-atoms were located in difference Fourier maps and were freely refined.

Figures

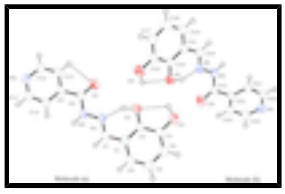


Fig. 1. A view of the asymmetric unit of the title compound, showing the molecular structure and atom-numbering scheme of the two independent molecules (a and b). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed lines show possible hydrogen bonding (see Table 1 for details).

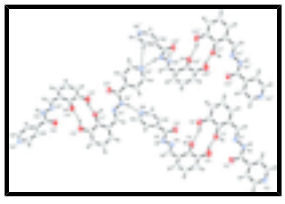


Fig. 2. A diagram showing the dimerization of molecules of the title compound through O–H···O, N–H···N and C–H···N hydrogen bonding [Hydrogen bonds are shown as dashed lines - see Table 1 for details; Symmetry codes: (i) -x, 1/2+y, 1/2-z; (ii) x, y, -1+z].

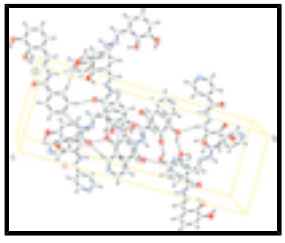


Fig. 3. Crystal-packing diagram for the title compound, showing the layered structure formed due to the strong intermolecular hydrogen bonds (dashed lines; see Table 1 for details).

N'-(2,3-Dihydroxybenzylidene)isonicotinohydrazide

Crystal data

$C_{13}H_{11}N_3O_3$	$F(000) = 1072$
$M_r = 257.25$	$D_x = 1.419$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 29970 reflections
$a = 7.7781$ (2) Å	$\theta = 1.4$–$27.3°$
$b = 30.0719$ (8) Å	$\mu = 0.10$ mm^{-1}
$c = 10.5116$ (3) Å	$T = 296$ K

β = 101.551 (2)°	Prism, yellow
V = 2408.89 (11) Å^3	0.53 × 0.31 × 0.19 mm
Z = 8	

Data collection

Stoe IPDS-II diffractometer	5118 independent reflections
Radiation source: fine-focus sealed tube	3512 reflections with $I > 2\sigma(I)$
plane graphite	R_{int} = 0.049
w–scan rotation	θ_{max} = 26.8°, θ_{min} = 1.4°
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)	h = −9→9
T_{min} = 0.961, T_{max} = 0.984	k = −37→37
34859 measured reflections	l = −13→13

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.038	All H-atom parameters refined
$wR(F^2)$ = 0.084	$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.005P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.001
5118 reflections	$\Delta\rho_{max}$ = 0.14 e Å^{-3}
432 parameters	$\Delta\rho_{min}$ = −0.10 e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0038 (6)

Special details

Experimental. Elemental analyses were performed using standard methods at TUBİTAK (The Turkish Scientific Research Centre). The IR spectrum was recorded on a Vertex 80v sample Compartment RT-DLaTGS spectrophotometer operating within 4000–500 cm^{-1}. ^{1}H NMR spectra were obtained on BRUKER DPX-400, 400 MHz High Performance Digital FT-NMR spectrometer using deuterated as solvent.

Spectroscopic characterization of the title compound: The structure was verified by means of IR, ^{1}H NMR (DMSO), UV-VIS spectral data and elemental analyses. In the ^{1}H NMR spectra of I the azomethine proton appears as a singlet at 8.68 p.p.m.. A single resonance for the proton in –NHN= group is observed at 12.51 p.p.m.. Chemical shifts of the protons on the pyridine ring exhibit two sets of signals in 8.93–8.67 p.p.m. as a doublet and in 8.02–7.74 p.p.m. as doublet, too. The phenyl protons of 1 resonate at 7.07–6.70 p.p.m.. The protons of the phenolic OH are observed at 11.14 p.p.m. and 9.59 p.p.m. as singlets. The IR spectrum of the I shows a weak band at 3520 cm^{-1} assigned to ν OH of the phenolic group. The deformation vibration, δ of the phenolic OH groups appears at 1272 cm^{-1}. The NH stretching absorption appears as strong band 3392 cm^{-1}. Another important band occurs at 1680 cm^{-1} attributed to ν(C=0)

(carbonyl) mode. Azomethine ν(C=N) absorption band appear at 1561 cm^{-1}. The medium intensity band at 1061 cm^{-1} is ascribed to ν(N—N) vibration.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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}
C1	0.34616 (19)	0.51866 (5)	0.32097 (13)	0.0431 (3)
C2	0.35373 (19)	0.56269 (5)	0.36519 (13)	0.0419 (3)
C3	0.4074 (2)	0.59653 (5)	0.29149 (14)	0.0462 (3)
C4	0.4506 (2)	0.58674 (6)	0.17444 (16)	0.0581 (4)
C5	0.4439 (3)	0.54342 (6)	0.12981 (17)	0.0640 (5)
C6	0.3938 (2)	0.50971 (6)	0.20279 (16)	0.0568 (4)
C7	0.2901 (2)	0.48325 (5)	0.39706 (14)	0.0453 (3)
C8	0.14430 (19)	0.47313 (4)	0.68980 (14)	0.0444 (3)
C9	0.08913 (19)	0.43654 (4)	0.77030 (13)	0.0420 (3)
C10	0.0715 (2)	0.39237 (5)	0.73485 (15)	0.0534 (4)
C11	0.0135 (2)	0.36246 (5)	0.81626 (15)	0.0540 (4)
C12	−0.0071 (3)	0.41568 (5)	0.96253 (16)	0.0599 (4)
C13	0.0503 (2)	0.44791 (5)	0.88844 (15)	0.0547 (4)
C14	0.4163 (2)	0.72836 (5)	0.73128 (14)	0.0449 (3)
C15	0.41093 (19)	0.68485 (4)	0.68380 (13)	0.0422 (3)
C16	0.5024 (2)	0.65111 (5)	0.76002 (14)	0.0480 (4)
C17	0.5992 (2)	0.66094 (6)	0.88134 (16)	0.0566 (4)
C18	0.6080 (3)	0.70385 (6)	0.92819 (17)	0.0643 (5)
C19	0.5175 (2)	0.73716 (6)	0.85442 (16)	0.0585 (4)
C20	0.3177 (2)	0.76380 (5)	0.65502 (15)	0.0484 (4)
C21	0.0455 (2)	0.77429 (5)	0.34901 (14)	0.0464 (4)
C22	−0.0175 (2)	0.81153 (4)	0.25675 (14)	0.0435 (3)
C23	0.0552 (2)	0.85359 (5)	0.26961 (15)	0.0464 (3)
C24	−0.0049 (2)	0.88488 (5)	0.17529 (15)	0.0525 (4)
C25	−0.1971 (3)	0.83591 (6)	0.05928 (17)	0.0614 (4)
C26	−0.1452 (2)	0.80275 (5)	0.14845 (16)	0.0558 (4)
N1	0.24130 (16)	0.49326 (4)	0.50259 (11)	0.0446 (3)
N2	0.18813 (17)	0.46034 (4)	0.57653 (12)	0.0458 (3)
N3	−0.02774 (18)	0.37320 (4)	0.92838 (12)	0.0526 (3)
N4	0.22153 (17)	0.75411 (4)	0.54531 (11)	0.0472 (3)
N5	0.13318 (18)	0.78684 (4)	0.46848 (12)	0.0494 (3)
N6	−0.12988 (19)	0.87675 (4)	0.07101 (12)	0.0563 (3)
O1	0.30926 (15)	0.57472 (3)	0.47939 (9)	0.0522 (3)

O2	0.41509 (17)	0.63953 (3)	0.33438 (11)	0.0598 (3)
O3	0.14895 (16)	0.51167 (3)	0.72583 (10)	0.0587 (3)
O4	0.31740 (15)	0.67309 (3)	0.56449 (9)	0.0512 (3)
O5	0.49762 (18)	0.60853 (4)	0.71623 (12)	0.0666 (3)
O6	0.02582 (17)	0.73564 (3)	0.31578 (10)	0.0636 (3)
H1O	0.276 (3)	0.5475 (7)	0.5152 (19)	0.090 (6)*
H2N	0.180 (2)	0.4320 (6)	0.5448 (15)	0.057 (5)*
H2O	0.375 (3)	0.6411 (7)	0.415 (2)	0.099 (7)*
H4	0.486 (2)	0.6103 (6)	0.1235 (15)	0.061 (5)*
H4O	0.260 (3)	0.7006 (8)	0.531 (2)	0.095 (7)*
H5	0.472 (2)	0.5371 (6)	0.0478 (18)	0.077 (5)*
H5N	0.128 (2)	0.8148 (6)	0.4980 (16)	0.059 (5)*
H5O	0.427 (3)	0.6065 (8)	0.636 (2)	0.106 (8)*
H6	0.390 (2)	0.4797 (6)	0.1748 (15)	0.060 (5)*
H7	0.294 (2)	0.4536 (5)	0.3685 (14)	0.051 (4)*
H10	0.096 (2)	0.3824 (6)	0.6532 (17)	0.066 (5)*
H11	0.003 (2)	0.3318 (6)	0.7931 (15)	0.061 (5)*
H12	−0.034 (2)	0.4237 (6)	1.0435 (18)	0.074 (5)*
H13	0.060 (2)	0.4793 (6)	0.9133 (16)	0.068 (5)*
H17	0.661 (2)	0.6365 (6)	0.9290 (16)	0.064 (5)*
H18	0.679 (2)	0.7098 (6)	1.0143 (18)	0.073 (5)*
H19	0.522 (2)	0.7674 (6)	0.8835 (16)	0.071 (5)*
H20	0.325 (2)	0.7937 (6)	0.6894 (15)	0.060 (5)*
H23	0.151 (2)	0.8611 (5)	0.3421 (15)	0.052 (4)*
H24	0.043 (2)	0.9140 (6)	0.1819 (16)	0.064 (5)*
H25	−0.286 (3)	0.8311 (6)	−0.0207 (19)	0.082 (6)*
H26	−0.199 (2)	0.7732 (6)	0.1373 (16)	0.064 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0451 (8)	0.0384 (7)	0.0454 (7)	0.0024 (6)	0.0085 (6)	0.0008 (6)
C2	0.0449 (8)	0.0393 (7)	0.0405 (7)	0.0000 (6)	0.0060 (6)	0.0019 (6)
C3	0.0504 (9)	0.0391 (8)	0.0478 (8)	0.0000 (6)	0.0071 (7)	0.0057 (6)
C4	0.0643 (11)	0.0556 (10)	0.0587 (10)	0.0014 (8)	0.0227 (8)	0.0135 (8)
C5	0.0803 (13)	0.0641 (11)	0.0557 (9)	0.0077 (9)	0.0331 (9)	0.0021 (8)
C6	0.0709 (11)	0.0454 (9)	0.0583 (9)	0.0057 (8)	0.0228 (8)	−0.0051 (7)
C7	0.0523 (9)	0.0330 (8)	0.0504 (8)	0.0006 (6)	0.0096 (7)	−0.0012 (6)
C8	0.0508 (9)	0.0330 (7)	0.0490 (8)	0.0004 (6)	0.0086 (7)	0.0007 (6)
C9	0.0443 (8)	0.0353 (7)	0.0457 (7)	0.0011 (6)	0.0078 (6)	0.0011 (6)
C10	0.0756 (11)	0.0383 (8)	0.0504 (9)	−0.0048 (8)	0.0228 (8)	−0.0033 (7)
C11	0.0726 (11)	0.0340 (8)	0.0569 (9)	−0.0064 (7)	0.0165 (8)	−0.0012 (7)
C12	0.0894 (13)	0.0462 (9)	0.0480 (9)	−0.0041 (9)	0.0228 (9)	−0.0016 (7)
C13	0.0771 (12)	0.0376 (8)	0.0521 (9)	−0.0036 (8)	0.0190 (8)	−0.0030 (7)
C14	0.0509 (9)	0.0400 (8)	0.0460 (8)	−0.0012 (7)	0.0151 (7)	−0.0035 (6)
C15	0.0480 (8)	0.0393 (8)	0.0402 (7)	−0.0011 (6)	0.0113 (6)	−0.0011 (6)
C16	0.0543 (9)	0.0399 (8)	0.0498 (8)	0.0008 (7)	0.0106 (7)	−0.0004 (6)
C17	0.0580 (11)	0.0562 (10)	0.0529 (9)	0.0070 (8)	0.0044 (8)	0.0055 (8)

C18	0.0656 (11)	0.0689 (12)	0.0523 (10)	0.0003 (9)	−0.0028 (9)	−0.0103 (9)
C19	0.0667 (11)	0.0513 (10)	0.0561 (9)	−0.0041 (8)	0.0087 (8)	−0.0145 (8)
C20	0.0622 (10)	0.0353 (8)	0.0509 (9)	0.0000 (7)	0.0188 (8)	−0.0049 (7)
C21	0.0629 (10)	0.0325 (7)	0.0479 (8)	0.0024 (7)	0.0208 (7)	−0.0017 (6)
C22	0.0539 (9)	0.0339 (7)	0.0467 (8)	0.0035 (6)	0.0195 (7)	−0.0021 (6)
C23	0.0599 (10)	0.0353 (8)	0.0463 (8)	0.0003 (7)	0.0165 (8)	−0.0019 (6)
C24	0.0754 (11)	0.0338 (8)	0.0520 (9)	−0.0014 (8)	0.0213 (8)	−0.0002 (7)
C25	0.0696 (12)	0.0520 (10)	0.0585 (10)	−0.0008 (8)	0.0028 (9)	0.0043 (8)
C26	0.0663 (11)	0.0400 (9)	0.0599 (10)	−0.0082 (8)	0.0096 (8)	−0.0003 (7)
N1	0.0524 (7)	0.0340 (6)	0.0469 (7)	−0.0034 (5)	0.0092 (6)	0.0050 (5)
N2	0.0602 (8)	0.0308 (6)	0.0474 (7)	−0.0044 (6)	0.0133 (6)	0.0021 (5)
N3	0.0655 (9)	0.0425 (7)	0.0501 (7)	−0.0038 (6)	0.0123 (6)	0.0053 (6)
N4	0.0638 (8)	0.0335 (6)	0.0472 (7)	0.0073 (6)	0.0179 (6)	0.0023 (5)
N5	0.0726 (9)	0.0303 (6)	0.0463 (7)	0.0102 (6)	0.0141 (6)	0.0002 (5)
N6	0.0732 (9)	0.0437 (7)	0.0533 (8)	0.0070 (7)	0.0156 (7)	0.0053 (6)
O1	0.0784 (8)	0.0367 (6)	0.0438 (5)	−0.0078 (5)	0.0173 (5)	−0.0032 (4)
O2	0.0840 (8)	0.0379 (6)	0.0586 (7)	−0.0085 (5)	0.0171 (6)	0.0042 (5)
O3	0.0850 (8)	0.0314 (5)	0.0626 (6)	−0.0013 (5)	0.0219 (6)	−0.0019 (5)
O4	0.0701 (7)	0.0362 (5)	0.0437 (5)	0.0066 (5)	0.0029 (5)	−0.0044 (4)
O5	0.0877 (9)	0.0389 (6)	0.0653 (8)	0.0103 (6)	−0.0038 (7)	−0.0001 (5)
O6	0.0994 (9)	0.0308 (6)	0.0602 (7)	0.0008 (6)	0.0149 (6)	−0.0044 (5)

Geometric parameters (Å, °)

C1—C6	1.392 (2)	C15—C16	1.396 (2)
C1—C2	1.4005 (19)	C16—O5	1.3589 (18)
C1—C7	1.450 (2)	C16—C17	1.377 (2)
C2—O1	1.3630 (17)	C17—C18	1.378 (2)
C2—C3	1.3925 (19)	C17—H17	0.961 (18)
C3—O2	1.3669 (18)	C18—C19	1.372 (3)
C3—C4	1.371 (2)	C18—H18	0.979 (19)
C4—C5	1.382 (2)	C19—H19	0.958 (19)
C4—H4	0.961 (17)	C20—N4	1.276 (2)
C5—C6	1.374 (2)	C20—H20	0.967 (17)
C5—H5	0.951 (19)	C21—O6	1.2145 (17)
C6—H6	0.949 (17)	C21—N5	1.3571 (19)
C7—N1	1.2782 (18)	C21—C22	1.498 (2)
C7—H7	0.943 (16)	C22—C26	1.378 (2)
C8—O3	1.2174 (16)	C22—C23	1.381 (2)
C8—N2	1.3582 (18)	C23—C24	1.379 (2)
C8—C9	1.5023 (19)	C23—H23	0.979 (16)
C9—C13	1.379 (2)	C24—N6	1.334 (2)
C9—C10	1.379 (2)	C24—H24	0.950 (18)
C10—C11	1.378 (2)	C25—N6	1.331 (2)
C10—H10	0.964 (17)	C25—C26	1.373 (2)
C11—N3	1.322 (2)	C25—H25	0.99 (2)
C11—H11	0.952 (17)	C26—H26	0.977 (18)
C12—N3	1.328 (2)	N1—N2	1.3726 (15)
C12—C13	1.373 (2)	N2—H2N	0.912 (17)

C12—H12	0.946 (18)	N4—N5	1.3679 (16)
C13—H13	0.977 (18)	N5—H5N	0.901 (17)
C14—C15	1.3981 (19)	O1—H1O	0.96 (2)
C14—C19	1.399 (2)	O2—H2O	0.96 (2)
C14—C20	1.456 (2)	O4—H4O	0.97 (2)
C15—O4	1.3644 (17)	O5—H5O	0.91 (2)
C6—C1—C2	118.56 (13)	O5—C16—C15	120.95 (13)
C6—C1—C7	120.89 (14)	C17—C16—C15	119.80 (14)
C2—C1—C7	120.56 (13)	C16—C17—C18	120.71 (16)
O1—C2—C3	116.93 (12)	C16—C17—H17	116.3 (10)
O1—C2—C1	122.82 (12)	C18—C17—H17	123.0 (10)
C3—C2—C1	120.24 (13)	C19—C18—C17	119.92 (16)
O2—C3—C4	119.77 (13)	C19—C18—H18	121.4 (11)
O2—C3—C2	120.41 (13)	C17—C18—H18	118.7 (11)
C4—C3—C2	119.81 (14)	C18—C19—C14	120.99 (16)
C3—C4—C5	120.50 (15)	C18—C19—H19	122.2 (11)
C3—C4—H4	119.4 (10)	C14—C19—H19	116.8 (11)
C5—C4—H4	120.1 (10)	N4—C20—C14	118.63 (13)
C6—C5—C4	120.10 (16)	N4—C20—H20	122.1 (10)
C6—C5—H5	120.2 (11)	C14—C20—H20	119.3 (10)
C4—C5—H5	119.7 (11)	O6—C21—N5	122.91 (14)
C5—C6—C1	120.77 (16)	O6—C21—C22	121.54 (14)
C5—C6—H6	121.7 (10)	N5—C21—C22	115.46 (12)
C1—C6—H6	117.6 (10)	C26—C22—C23	118.00 (14)
N1—C7—C1	118.68 (13)	C26—C22—C21	118.68 (13)
N1—C7—H7	122.3 (9)	C23—C22—C21	123.15 (14)
C1—C7—H7	119.0 (9)	C24—C23—C22	118.79 (15)
O3—C8—N2	123.06 (13)	C24—C23—H23	119.8 (9)
O3—C8—C9	121.07 (13)	C22—C23—H23	121.4 (9)
N2—C8—C9	115.87 (12)	N6—C24—C23	123.50 (15)
C13—C9—C10	117.05 (14)	N6—C24—H24	116.1 (10)
C13—C9—C8	117.67 (13)	C23—C24—H24	120.4 (10)
C10—C9—C8	125.28 (13)	N6—C25—C26	123.41 (17)
C11—C10—C9	119.21 (14)	N6—C25—H25	114.1 (11)
C11—C10—H10	119.9 (10)	C26—C25—H25	122.5 (11)
C9—C10—H10	120.9 (10)	C25—C26—C22	119.33 (16)
N3—C11—C10	124.20 (15)	C25—C26—H26	121.2 (10)
N3—C11—H11	116.2 (10)	C22—C26—H26	119.4 (10)
C10—C11—H11	119.6 (10)	C7—N1—N2	119.80 (12)
N3—C12—C13	124.13 (15)	C8—N2—N1	116.67 (12)
N3—C12—H12	116.8 (11)	C8—N2—H2N	125.0 (10)
C13—C12—H12	119.1 (11)	N1—N2—H2N	118.2 (10)
C12—C13—C9	119.38 (15)	C11—N3—C12	116.00 (13)
C12—C13—H13	123.0 (10)	C20—N4—N5	120.22 (12)
C9—C13—H13	117.5 (10)	C21—N5—N4	116.50 (12)
C15—C14—C19	118.58 (14)	C21—N5—H5N	122.0 (11)
C15—C14—C20	120.91 (13)	N4—N5—H5N	121.4 (11)
C19—C14—C20	120.51 (14)	C25—N6—C24	116.96 (14)
O4—C15—C16	117.12 (12)	C2—O1—H1O	104.8 (12)

O4—C15—C14	122.88 (13)	C3—O2—H2O	109.8 (13)
C16—C15—C14	119.99 (13)	C15—O4—H4O	103.7 (12)
O5—C16—C17	119.26 (14)	C16—O5—H5O	110.2 (15)
C6—C1—C2—O1	179.80 (14)	O4—C15—C16—C17	179.97 (14)
C7—C1—C2—O1	−0.3 (2)	C14—C15—C16—C17	−0.7 (2)
C6—C1—C2—C3	0.2 (2)	O5—C16—C17—C18	179.45 (16)
C7—C1—C2—C3	−179.86 (13)	C15—C16—C17—C18	−0.5 (2)
O1—C2—C3—O2	0.5 (2)	C16—C17—C18—C19	1.0 (3)
C1—C2—C3—O2	−179.93 (14)	C17—C18—C19—C14	−0.3 (3)
O1—C2—C3—C4	−178.75 (14)	C15—C14—C19—C18	−0.8 (2)
C1—C2—C3—C4	0.9 (2)	C20—C14—C19—C18	178.64 (16)
O2—C3—C4—C5	179.84 (16)	C15—C14—C20—N4	2.2 (2)
C2—C3—C4—C5	−0.9 (3)	C19—C14—C20—N4	−177.30 (15)
C3—C4—C5—C6	−0.1 (3)	O6—C21—C22—C26	20.5 (2)
C4—C5—C6—C1	1.1 (3)	N5—C21—C22—C26	−162.84 (14)
C2—C1—C6—C5	−1.2 (2)	O6—C21—C22—C23	−154.54 (15)
C7—C1—C6—C5	178.86 (16)	N5—C21—C22—C23	22.1 (2)
C6—C1—C7—N1	−177.40 (15)	C26—C22—C23—C24	1.0 (2)
C2—C1—C7—N1	2.7 (2)	C21—C22—C23—C24	176.10 (14)
O3—C8—C9—C13	−2.3 (2)	C22—C23—C24—N6	−0.3 (2)
N2—C8—C9—C13	177.47 (14)	N6—C25—C26—C22	0.3 (3)
O3—C8—C9—C10	176.64 (16)	C23—C22—C26—C25	−1.0 (2)
N2—C8—C9—C10	−3.5 (2)	C21—C22—C26—C25	−176.33 (15)
C13—C9—C10—C11	1.4 (2)	C1—C7—N1—N2	−179.80 (13)
C8—C9—C10—C11	−177.64 (16)	O3—C8—N2—N1	0.7 (2)
C9—C10—C11—N3	0.1 (3)	C9—C8—N2—N1	−179.09 (12)
N3—C12—C13—C9	0.4 (3)	C7—N1—N2—C8	177.63 (14)
C10—C9—C13—C12	−1.6 (2)	C10—C11—N3—C12	−1.3 (3)
C8—C9—C13—C12	177.49 (16)	C13—C12—N3—C11	1.0 (3)
C19—C14—C15—O4	−179.38 (14)	C14—C20—N4—N5	−177.10 (13)
C20—C14—C15—O4	1.2 (2)	O6—C21—N5—N4	9.1 (2)
C19—C14—C15—C16	1.3 (2)	C22—C21—N5—N4	−167.49 (12)
C20—C14—C15—C16	−178.15 (14)	C20—N4—N5—C21	174.77 (14)
O4—C15—C16—O5	0.0 (2)	C26—C25—N6—C24	0.5 (3)
C14—C15—C16—O5	179.39 (14)	C23—C24—N6—C25	−0.5 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···N1	0.96 (2)	1.65 (2)	2.5281 (15)	149.7 (18)
N2—H2N···N6^{i}	0.913 (18)	2.051 (17)	2.9407 (17)	164.7 (15)
O2—H2O···O1	0.96 (2)	2.20 (2)	2.7022 (14)	111.3 (15)
O2—H2O···O4	0.96 (2)	1.97 (2)	2.8605 (15)	153.3 (18)
O4—H4O···N4	0.97 (2)	1.65 (2)	2.5441 (15)	151.2 (19)
N5—H5N···N3^{ii}	0.900 (18)	2.129 (17)	2.9914 (18)	160.2 (14)
O5—H5O···O1	0.91 (2)	1.96 (2)	2.8138 (16)	154 (2)
O5—H5O···O4	0.91 (2)	2.25 (2)	2.7171 (16)	111.6 (18)
C10—H10···N6^{i}	0.964 (17)	2.429 (17)	3.369 (2)	164.8 (15)

C11—H11···O6^{iii}	0.953 (18)	2.317 (18)	3.2485 (18)	165.4 (13)
C20—H20···O2^{iv}	0.967 (18)	2.533 (17)	3.4652 (18)	162.0 (13)
C24—H24···O3^{v}	0.949 (18)	2.395 (18)	3.3373 (18)	172.1 (14)

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) −*x*, *y*+1/2, −*z*+3/2; (iii) −*x*, −*y*+1, −*z*+1; (iv) *x*, −*y*+3/2, *z*+1/2; (v) *x*, −*y*+3/2, *z*−1/2.

Fig. 1

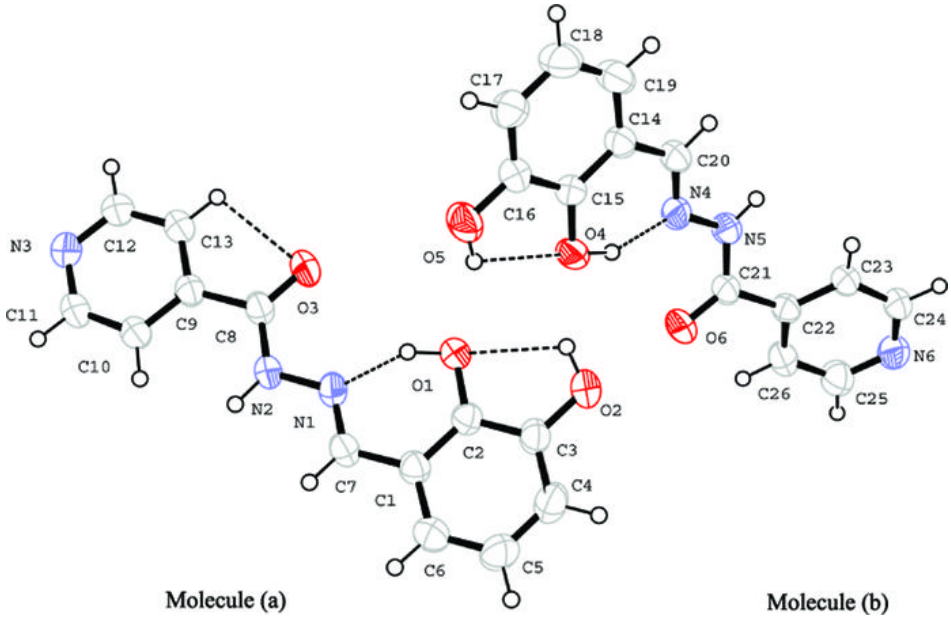

C18
C17
C19
C14
C20
C15
N4
C16
O4
N5
O5
C21
C23
O3
C12
C13
N3
C11
C9
C8
C22
C24
O6
C10
N6
O1
O2
C26
C25
N2
N1
C2
C3
C7
C1
C4
C6
C5
Molecule (a)
Molecule (b)

Fig. 2

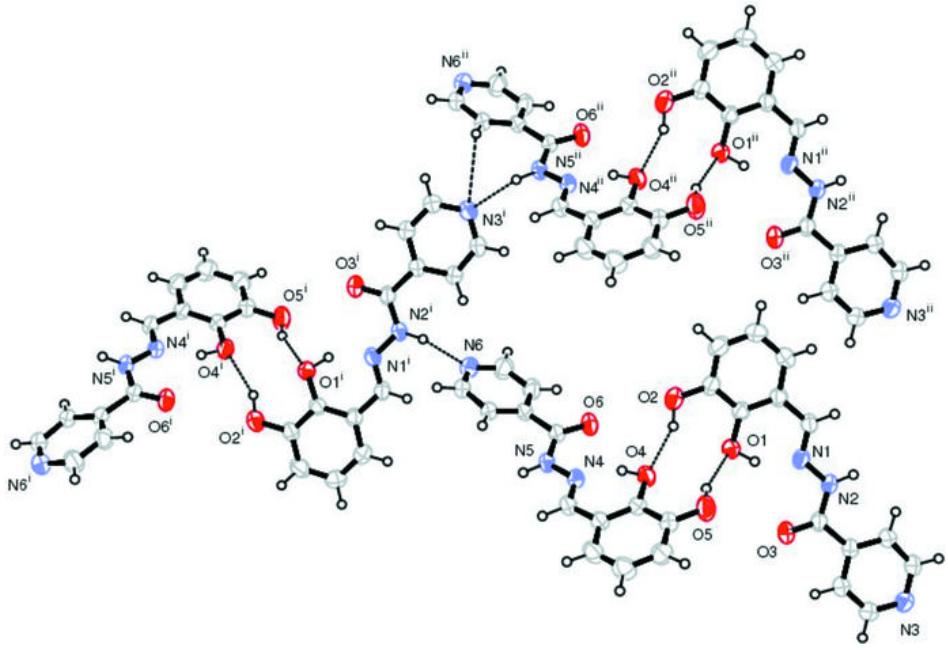

N6ii
O6ii
O2ii
O1ii
N1ii
N2ii
O3ii
N3ii
N5ii
N4ii
O4ii
O5ii
N3i
O3i
O5i
N2i
N4i
O4i
N5i
O6i
O1i
N1i
N6
O6
O2
O1
N1
N2
O3
N3
N5
N4
O4
O5
O2i
N6i

Fig. 3