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Crystal structure of (*E*)-2-[(2-hydroxy-4-methoxyphenyl)(phenyl)methylidene]-*N*-phenylhydrazine-1-carboxamide

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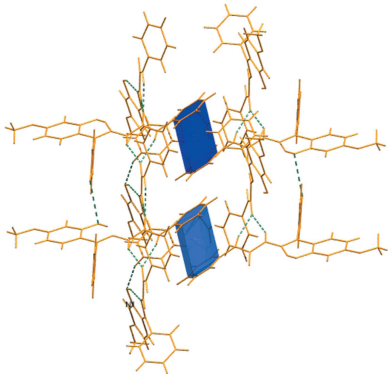
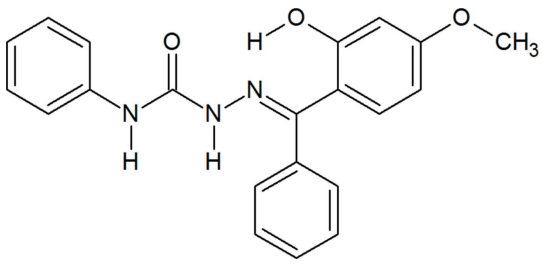
The title compound, $C_{21}H_{19}N_3O_3$, has an *E* conformation about the azomethine double bond. The central moiety of the hydrazinecarboxamide moiety [–N—N—C(═O)—N–] has an almost coplanar arrangement [maximum deviation for the C atom = 0.010 (2) Å]. This central moiety is flanked by three aromatic rings and its mean plane makes dihedral angles of 24.7 (1), 72.91 (12) and 34.26 (11) Å, respectively, with the phenolic ring, the phenyl ring attached to the same C atom as the phenolic ring, and the phenylhydrazine ring. The adjacent phenolic and phenyl rings are twisted away from each other to reduce steric hindrance and make a dihedral angle of 80.59 (12)°. The phenolic and phenylhydrazine rings are inclined to one another by 28.89 (11)°. The rigidity of the molecule is increased by an intramolecular O—H···N hydrogen bond involving the phenolic hydrogen and the azomethine N atom. In the crystal, the carbonyl O atom forms bifurcated hydrogen bonds with the two NH atoms of the hydrazinic group, leading to the formation of chains propagating along [001]. Within the chains there are also C—H···O hydrogen bonds present. The chains are linked *via* C═O···π [3.4316 (18) Å] and parallel slipped π–π interactions, involving inversion-related benzene rings [centroid–centroid distance = 3.8850 (14) Å; inter-planar distance = 3.3895 (10) Å; slippage = 1.899 Å], forming sheets lying parallel to (100).

1. Chemical context

Semicarbazones are urea derivatives exhibiting a wide spectrum of biological activities (Beraldo & Gambino, 2004). They have been found to be associated with antitumoral (Afrasiabi *et al.*, 2005), antimicrobial (Siji *et al.*, 2010), antihypertensive, hypolipidemic, antineoplastic, hypnotic and anticonvulsant properties. They can function as excellent ligands to various metal ions (Kala *et al.*, 2007; Aiswarya *et al.*, 2013; Kurup *et al.*, 2011) and can coordinate to metal ions either in the neutral (Siji *et al.*, 2011) or in the anionic forms (Reena *et al.*, 2008). Single crystals of acetophenone semicarbazones are potential organic non-linear optical (NLO) materials and they have a wide transparency window in the entire visible region, making them ideal candidates for NLO device applications (Vijayan *et al.*, 2001). Semicarbazones have been proposed as analytical reagents that can be used in selective and sensitive determination of metal ions (Garg & Jain, 1988). The crystal structure of the dimethylformamide solvate of the title compound has been reported (Annie *et al.*, 2012).





2. Structural commentary

In the molecule of the title compound (Fig. 1), the conformation about the C7═N1 bond is *E*, and the central hydrazinecarboxamide moiety [–N1—N2—C14(═O3)—N3–] is almost planar [the maximum deviation is 0.010 (2) Å for atom C14]. This central moiety is flanked by three aromatic rings (C1–C6, C8–C13 and C15–C20) which are inclined to its mean plane by 24.70 (10), 72.91 (12) and 34.26 (11) °, respectively. Rings C1–C6 and C8–C13, attached at the same C atom (C7), are twisted away from each other and make a dihedral angle of 80.59 (12)°. They are inclined to the phenylhydrazine ring (C15–C20) by 28.89 (11) and 52.42 (12)°, respectively. In the crystal structure of the dimethylformamide solvate of the title compound (Annie *et al.*, 2012), the two rings attached at the same C atom (C7) are inclined to one another by 88.47 (10)°, while they are inclined to the phenylhydrazine ring by 14.42 (10)° for the phenolic ring, and by 82.35 (11)° for the phenyl ring. There is an intramolecular O—H···N hydrogen bond (Fig. 2) involving the phenolic hydrogen and the azomethine atom N1 (Fig. 2 and Table 1). This hydrogen bond is also present in the structure of the dimethylformamide solvate of the title compound mentioned above.

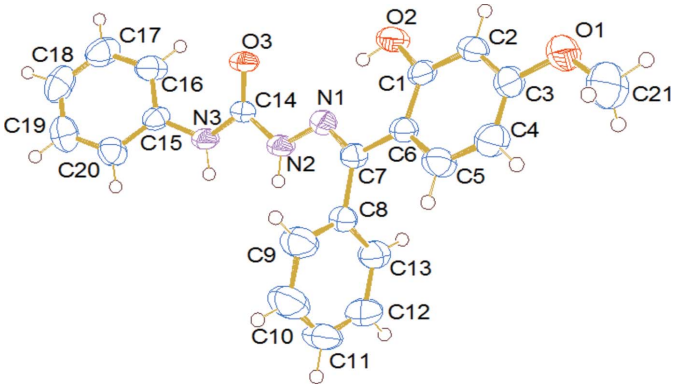


Figure 1
A view of the molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

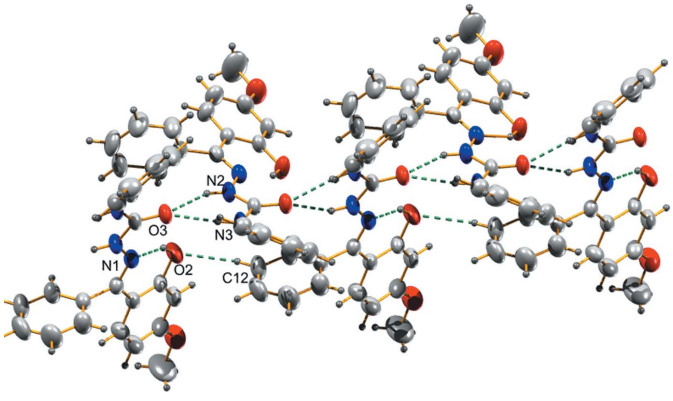


Figure 2
A view of the hydrogen-bonding interactions (dashed lines) in the title compound, forming chains propagating along [001] (see Table 1 for details).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···N1	0.89 (1)	1.76 (2)	2.563 (2)	149 (3)
N2—H2*N*···O3^{i}	0.87 (1)	2.13 (1)	2.9301 (19)	152 (2)
N3—H3*N*···O3^{i}	0.88 (1)	2.09 (1)	2.935 (2)	161 (2)
C12—H12···O2^{ii}	0.93	2.44	3.252 (3)	146

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

3. Supramolecular features

In the crystal, the carbonyl O atom (O3) acts as the acceptor in bifurcated hydrogen bonds with the NH atoms of atoms N2 and N3 of the hydrazinic group, leading to the formation of chains propagating along [001]; Table 1 and Fig. 2. Within the chains there are also C—H···O hydrogen bonds present (Table 1 and Fig. 2). The chains are linked *via* C14═O3···π interactions [distance O3···*Cg*^{i} = 3.4316 (18) Å; angle C14═O3···*Cg* = 95.3 (1)°; *Cg* is the centroid of the C8–C13 ring; symmetry code: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$], as shown in Fig. 3.

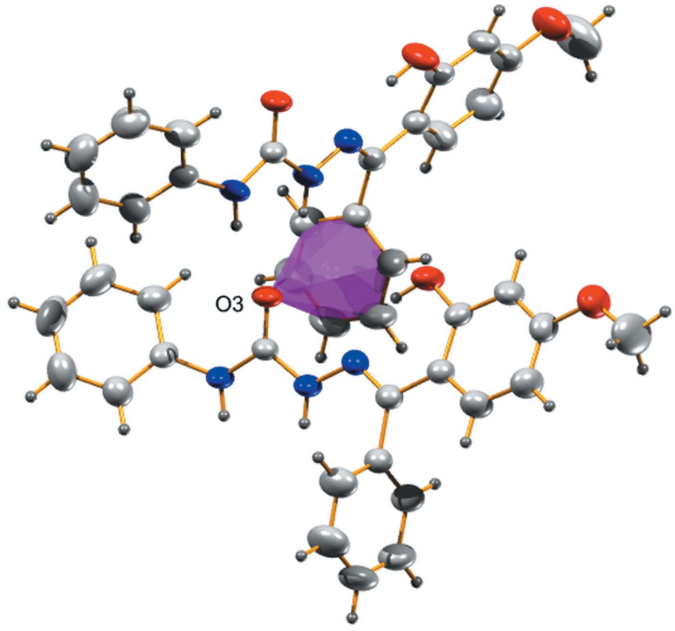


Figure 3
C═O···π interaction in the crystal structure of the title compound.

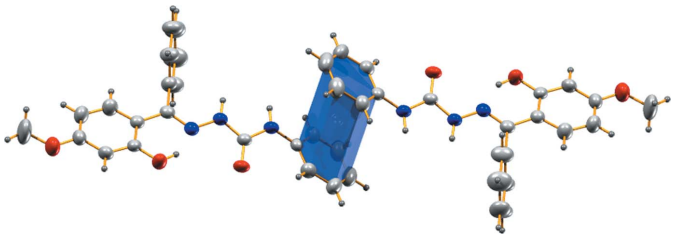


Figure 4
π–π interaction in the crystal structure of the title compound.

There are also parallel slipped π–π interactions present (Fig. 4), involving inversion-related benzene rings (C15–C20) with a centroid–centroid distance of 3.8850 (14) Å [interplanar distance = 3.3895 (10) Å; slippage = 1.899 Å]. The result of these interactions leads to the formation of sheets lying parallel to (100), as shown in Fig. 5.

4. Synthesis and crystallization

To a warm methanolic solution (25 ml) of N^4-phenylsemicarbazide (0.302 g, 2 mmol), a methanolic solution (25 ml) of 2-hydroxy-4-methoxybenzophenone (0.4566 g, 2 mmol) was added and the resulting solution was boiled under reflux for 2 h, after adding three drops of conc. HCl. On slow evaporation at room temperature, colourless crystals separated out. They were filtered off and washed with methanol and ether. Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of a solution in methanol (yield: 0.1735 g, 76%; m.p.: 498 K). FT–IR (KBr, cm^{-1}) ν_{max}: 3316 (s, OH), 3249 (m, NH), 3145 (m, NH), 1662 (s, C═O), 1631 (m, C═N), 1059 (m, N–N). ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 12.94 (s, 1H, OH), 9.10 (s, 1H, NH), 9.03 (s, 1H, NH), 3.90 (s, 3H, OMe), 6.33–7.672 (m, 13H, Ar-H). ESI mass spectrum, m/z: 362.3 (M+1). Analysis calculated for $C_{21}H_{19}N_3O_3$: C, 69.79, H, 5.30, N, 11.63%. Found: C, 69.68, H, 5.72, N, 11.93%.

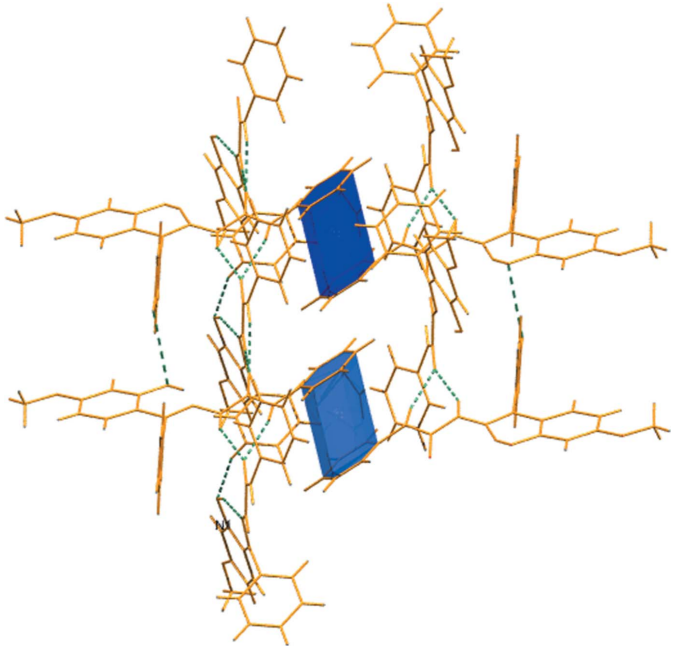


Figure 5
A view along the *a* axis of the formation of the sheets lying parallel to (100) in the crystal structure of the title compound.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{19}N_3O_3$
M_r	361.39
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	19.965 (2), 9.9788 (9), 9.3366 (7)
β (°)	90.340 (5)
V (Å^3)	1860.1 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.28 × 0.24 × 0.21
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.955, 0.961
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18641, 4268, 2092
R_{int}	0.057
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.143, 1.00
No. of reflections	4240
No. of parameters	257
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.19

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2010), and *publCIF* (Westrip, 2010).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The OH and NH H atoms were located in a difference Fourier map and refined with distances restraints of 0.88 (1) Å. The C-bound H atoms were placed in calculated positions and refined as riding atoms: C—H = 0.93–0.96 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms.

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supporting information

Acta Cryst. (2015). E**71**, 427-430 [doi:10.1107/S2056989015005757]

Crystal structure of (*E*)-2-[(2-hydroxy-4-methoxyphenyl)(phenyl)methylidene]-*N*-phenylhydrazine-1-carboxamide

C. F. Annie, M. Sithambaresan and M. R. Prathapachandra Kurup

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *publCIF* (Westrip, 2010).

(*E*)-2-[(2-Hydroxy-4-methoxyphenyl)(phenyl)methylidene]-*N*-phenylhydrazine-1-carboxamide

Crystal data

$C_{21}H_{19}N_3O_3$
M_r = 361.39
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 19.965 (2) Å
b = 9.9788 (9) Å
c = 9.3366 (7) Å
β = 90.340 (5)°
V = 1860.1 (3) Å^3
Z = 4
$F(000)$ = 760.0
D_x = 1.291 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2338 reflections
θ = 2.9–22.7°
μ = 0.09 mm^{-1}
T = 296 K
Block, colourless
0.28 × 0.24 × 0.21 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.955, T_{max} = 0.961
18641 measured reflections
4268 independent reflections
2092 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 27.5°, θ_{min} = 2.9°
h = −25→25
k = −12→12
l = −10→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.143
S = 1.00
4240 reflections
257 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.0804P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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}
N1	0.24470 (9)	0.62277 (18)	0.17814 (16)	0.0444 (4)
N2	0.19511 (9)	0.68714 (18)	0.10330 (17)	0.0469 (5)
O3	0.14953 (7)	0.76718 (14)	0.30843 (12)	0.0480 (4)
O2	0.32524 (9)	0.62214 (17)	0.39293 (14)	0.0621 (5)
C14	0.14865 (10)	0.7582 (2)	0.17789 (19)	0.0394 (5)
N3	0.10153 (9)	0.81374 (18)	0.09207 (17)	0.0491 (5)
O1	0.49774 (9)	0.31233 (18)	0.41036 (17)	0.0779 (6)
C7	0.27941 (10)	0.5321 (2)	0.11323 (19)	0.0415 (5)
C2	0.40967 (11)	0.4616 (2)	0.3955 (2)	0.0522 (6)
H2	0.4235	0.4949	0.4838	0.063*
C6	0.33388 (10)	0.4695 (2)	0.19314 (19)	0.0411 (5)
C1	0.35550 (11)	0.5171 (2)	0.32703 (19)	0.0436 (5)
C5	0.36938 (12)	0.3632 (2)	0.1362 (2)	0.0574 (6)
H5	0.3562	0.3293	0.0476	0.069*
C4	0.42306 (13)	0.3056 (2)	0.2043 (2)	0.0632 (7)
H4	0.4452	0.2332	0.1635	0.076*
C15	0.03853 (11)	0.8599 (2)	0.1368 (2)	0.0435 (5)
C3	0.44366 (12)	0.3566 (2)	0.3338 (2)	0.0540 (6)
C8	0.26680 (11)	0.4937 (2)	−0.03890 (19)	0.0434 (5)
C20	−0.01559 (12)	0.8337 (2)	0.0487 (2)	0.0545 (6)
H20	−0.0097	0.7861	−0.0359	0.065*
C13	0.30627 (12)	0.5462 (2)	−0.1443 (2)	0.0596 (6)
H13	0.3413	0.6035	−0.1204	0.072*
C16	0.02980 (13)	0.9330 (2)	0.2607 (2)	0.0580 (6)
H16	0.0663	0.9534	0.3192	0.070*
C9	0.21564 (14)	0.4095 (3)	−0.0764 (2)	0.0700 (8)
H9	0.1883	0.3734	−0.0059	0.084*
C17	−0.03359 (15)	0.9754 (3)	0.2968 (3)	0.0700 (8)
H17	−0.0398	1.0237	0.3809	0.084*
C19	−0.07808 (14)	0.8781 (2)	0.0864 (3)	0.0682 (7)
H19	−0.1144	0.8608	0.0265	0.082*
C11	0.24422 (16)	0.4294 (3)	−0.3212 (3)	0.0796 (9)

H11	0.2372	0.4064	−0.4166	0.096*
C10	0.20429 (16)	0.3776 (3)	−0.2181 (3)	0.0865 (9)
H10	0.1693	0.3205	−0.2429	0.104*
C12	0.29420 (15)	0.5144 (3)	−0.2855 (2)	0.0732 (8)
H12	0.3207	0.5516	−0.3568	0.088*
C21	0.53543 (18)	0.2044 (3)	0.3538 (4)	0.1201 (14)
H21A	0.5074	0.1265	0.3459	0.180*
H21B	0.5726	0.1854	0.4164	0.180*
H21C	0.5518	0.2283	0.2608	0.180*
C18	−0.08757 (14)	0.9475 (3)	0.2108 (3)	0.0732 (8)
H18	−0.1303	0.9754	0.2368	0.088*
H2N	0.1922 (10)	0.6792 (19)	0.0104 (10)	0.050 (6)*
H3N	0.1063 (11)	0.795 (2)	0.0004 (11)	0.058 (7)*
H2O	0.2911 (10)	0.647 (3)	0.337 (3)	0.107 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0438 (11)	0.0557 (11)	0.0336 (9)	0.0068 (9)	−0.0022 (8)	0.0030 (8)
N2	0.0493 (12)	0.0655 (12)	0.0257 (9)	0.0148 (10)	−0.0033 (8)	0.0010 (8)
O3	0.0552 (10)	0.0646 (9)	0.0241 (7)	0.0057 (8)	−0.0020 (6)	−0.0009 (6)
O2	0.0721 (12)	0.0777 (11)	0.0363 (8)	0.0328 (10)	−0.0091 (8)	−0.0112 (8)
C14	0.0411 (13)	0.0493 (12)	0.0277 (10)	0.0010 (10)	−0.0007 (9)	0.0003 (9)
N3	0.0490 (12)	0.0733 (13)	0.0249 (9)	0.0157 (10)	−0.0021 (8)	0.0011 (8)
O1	0.0732 (13)	0.0986 (14)	0.0617 (10)	0.0413 (11)	−0.0122 (9)	−0.0005 (9)
C7	0.0430 (13)	0.0478 (12)	0.0337 (10)	−0.0016 (10)	0.0007 (9)	0.0023 (9)
C2	0.0576 (15)	0.0664 (15)	0.0326 (11)	0.0137 (13)	−0.0040 (10)	0.0012 (10)
C6	0.0449 (13)	0.0450 (12)	0.0335 (10)	0.0024 (10)	0.0007 (9)	0.0005 (9)
C1	0.0487 (14)	0.0509 (12)	0.0314 (10)	0.0094 (11)	0.0062 (9)	0.0031 (9)
C5	0.0663 (17)	0.0582 (14)	0.0476 (12)	0.0123 (13)	−0.0096 (12)	−0.0118 (11)
C4	0.0706 (18)	0.0619 (16)	0.0571 (14)	0.0247 (14)	−0.0020 (13)	−0.0077 (12)
C15	0.0489 (14)	0.0469 (12)	0.0347 (10)	0.0093 (11)	0.0040 (10)	0.0075 (9)
C3	0.0530 (15)	0.0617 (14)	0.0473 (13)	0.0181 (12)	−0.0004 (11)	0.0072 (11)
C8	0.0457 (13)	0.0489 (12)	0.0355 (11)	0.0019 (11)	−0.0007 (10)	−0.0007 (9)
C20	0.0558 (16)	0.0542 (14)	0.0534 (13)	0.0072 (12)	−0.0064 (12)	−0.0015 (10)
C13	0.0611 (17)	0.0745 (16)	0.0432 (12)	−0.0076 (14)	0.0038 (11)	−0.0028 (11)
C16	0.0703 (18)	0.0616 (15)	0.0421 (12)	0.0153 (13)	−0.0028 (11)	−0.0033 (11)
C9	0.078 (2)	0.0788 (18)	0.0527 (14)	−0.0260 (16)	−0.0001 (13)	−0.0057 (13)
C17	0.079 (2)	0.0709 (17)	0.0598 (15)	0.0280 (16)	0.0135 (15)	−0.0021 (13)
C19	0.0517 (17)	0.0654 (16)	0.0873 (19)	0.0040 (14)	−0.0091 (14)	0.0015 (15)
C11	0.094 (2)	0.103 (2)	0.0423 (14)	0.0101 (19)	−0.0110 (15)	−0.0219 (14)
C10	0.095 (2)	0.099 (2)	0.0659 (18)	−0.0282 (19)	−0.0122 (17)	−0.0209 (16)
C12	0.083 (2)	0.098 (2)	0.0383 (13)	0.0036 (18)	0.0053 (13)	0.0006 (13)
C21	0.116 (3)	0.138 (3)	0.106 (3)	0.086 (3)	−0.024 (2)	−0.019 (2)
C18	0.0589 (18)	0.0712 (18)	0.090 (2)	0.0184 (15)	0.0185 (16)	0.0137 (16)

Geometric parameters (Å, º)

N1—C7	1.293 (2)	C15—C16	1.379 (3)
N1—N2	1.369 (2)	C8—C9	1.367 (3)
N2—C14	1.362 (3)	C8—C13	1.368 (3)
N2—H2N	0.873 (9)	C20—C19	1.372 (3)
O3—C14	1.222 (2)	C20—H20	0.9300
O2—C1	1.359 (2)	C13—C12	1.376 (3)
O2—H2O	0.890 (10)	C13—H13	0.9300
C14—N3	1.351 (2)	C16—C17	1.378 (3)
N3—C15	1.405 (3)	C16—H16	0.9300
N3—H3N	0.881 (9)	C9—C10	1.377 (3)
O1—C3	1.364 (3)	C9—H9	0.9300
O1—C21	1.417 (3)	C17—C18	1.369 (3)
C7—C6	1.456 (3)	C17—H17	0.9300
C7—C8	1.491 (3)	C19—C18	1.367 (3)
C2—C1	1.370 (3)	C19—H19	0.9300
C2—C3	1.376 (3)	C11—C12	1.350 (4)
C2—H2	0.9300	C11—C10	1.357 (4)
C6—C5	1.384 (3)	C11—H11	0.9300
C6—C1	1.403 (3)	C10—H10	0.9300
C5—C4	1.369 (3)	C12—H12	0.9300
C5—H5	0.9300	C21—H21A	0.9600
C4—C3	1.373 (3)	C21—H21B	0.9600
C4—H4	0.9300	C21—H21C	0.9600
C15—C20	1.379 (3)	C18—H18	0.9300
C7—N1—N2	118.52 (16)	C13—C8—C7	119.48 (19)
C14—N2—N1	118.42 (15)	C19—C20—C15	119.8 (2)
C14—N2—H2N	120.9 (13)	C19—C20—H20	120.1
N1—N2—H2N	120.6 (13)	C15—C20—H20	120.1
C1—O2—H2O	106.6 (19)	C8—C13—C12	120.1 (2)
O3—C14—N3	124.56 (19)	C8—C13—H13	119.9
O3—C14—N2	122.83 (18)	C12—C13—H13	119.9
N3—C14—N2	112.59 (16)	C17—C16—C15	119.2 (2)
C14—N3—C15	125.39 (17)	C17—C16—H16	120.4
C14—N3—H3N	114.4 (14)	C15—C16—H16	120.4
C15—N3—H3N	117.3 (14)	C8—C9—C10	120.4 (2)
C3—O1—C21	118.1 (2)	C8—C9—H9	119.8
N1—C7—C6	117.45 (17)	C10—C9—H9	119.8
N1—C7—C8	122.56 (18)	C18—C17—C16	121.0 (2)
C6—C7—C8	119.97 (18)	C18—C17—H17	119.5
C1—C2—C3	120.2 (2)	C16—C17—H17	119.5
C1—C2—H2	119.9	C18—C19—C20	120.8 (2)
C3—C2—H2	119.9	C18—C19—H19	119.6
C5—C6—C1	116.52 (19)	C20—C19—H19	119.6
C5—C6—C7	120.98 (18)	C12—C11—C10	120.0 (2)
C1—C6—C7	122.42 (18)	C12—C11—H11	120.0

O2—C1—C2	116.90 (18)	C10—C11—H11	120.0
O2—C1—C6	121.97 (18)	C11—C10—C9	120.0 (3)
C2—C1—C6	121.10 (19)	C11—C10—H10	120.0
C4—C5—C6	123.0 (2)	C9—C10—H10	120.0
C4—C5—H5	118.5	C11—C12—C13	120.5 (3)
C6—C5—H5	118.5	C11—C12—H12	119.8
C5—C4—C3	118.9 (2)	C13—C12—H12	119.8
C5—C4—H4	120.5	O1—C21—H21A	109.5
C3—C4—H4	120.5	O1—C21—H21B	109.5
C20—C15—C16	119.9 (2)	H21A—C21—H21B	109.5
C20—C15—N3	117.38 (19)	O1—C21—H21C	109.5
C16—C15—N3	122.7 (2)	H21A—C21—H21C	109.5
O1—C3—C4	125.0 (2)	H21B—C21—H21C	109.5
O1—C3—C2	114.7 (2)	C19—C18—C17	119.3 (3)
C4—C3—C2	120.3 (2)	C19—C18—H18	120.4
C9—C8—C13	118.92 (19)	C17—C18—H18	120.4
C9—C8—C7	121.58 (19)		

C7—N1—N2—C14	164.67 (18)	C5—C4—C3—O1	−177.4 (2)
N1—N2—C14—O3	0.2 (3)	C5—C4—C3—C2	1.7 (4)
N1—N2—C14—N3	−178.30 (17)	C1—C2—C3—O1	178.3 (2)
O3—C14—N3—C15	−17.1 (3)	C1—C2—C3—C4	−0.8 (4)
N2—C14—N3—C15	161.40 (19)	N1—C7—C8—C9	−79.3 (3)
N2—N1—C7—C6	177.23 (17)	C6—C7—C8—C9	102.6 (3)
N2—N1—C7—C8	−0.9 (3)	N1—C7—C8—C13	99.2 (3)
N1—C7—C6—C5	174.0 (2)	C6—C7—C8—C13	−78.9 (3)
C8—C7—C6—C5	−7.8 (3)	C16—C15—C20—C19	−1.4 (3)
N1—C7—C6—C1	−9.4 (3)	N3—C15—C20—C19	−179.1 (2)
C8—C7—C6—C1	168.75 (19)	C9—C8—C13—C12	0.2 (4)
C3—C2—C1—O2	−178.7 (2)	C7—C8—C13—C12	−178.4 (2)
C3—C2—C1—C6	−0.5 (3)	C20—C15—C16—C17	2.0 (3)
C5—C6—C1—O2	179.1 (2)	N3—C15—C16—C17	179.6 (2)
C7—C6—C1—O2	2.4 (3)	C13—C8—C9—C10	0.3 (4)
C5—C6—C1—C2	1.0 (3)	C7—C8—C9—C10	178.8 (2)
C7—C6—C1—C2	−175.72 (19)	C15—C16—C17—C18	−0.8 (4)
C1—C6—C5—C4	−0.1 (4)	C15—C20—C19—C18	−0.4 (4)
C7—C6—C5—C4	176.6 (2)	C12—C11—C10—C9	−1.4 (5)
C6—C5—C4—C3	−1.2 (4)	C8—C9—C10—C11	0.3 (4)
C14—N3—C15—C20	−139.5 (2)	C10—C11—C12—C13	1.8 (4)
C14—N3—C15—C16	42.9 (3)	C8—C13—C12—C11	−1.2 (4)
C21—O1—C3—C4	−0.9 (4)	C20—C19—C18—C17	1.6 (4)
C21—O1—C3—C2	−179.9 (2)	C16—C17—C18—C19	−0.9 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···N1	0.89 (1)	1.76 (2)	2.563 (2)	149 (3)
N2—H2*N*···O3^{i}	0.87 (1)	2.13 (1)	2.9301 (19)	152 (2)

N3—H3*N*···O3^{i}	0.88 (1)	2.09 (1)	2.935 (2)	161 (2)
C12—H12···O2^{ii}	0.93	2.44	3.252 (3)	146

Symmetry codes: (i) x, $-y+3/2$, $z-1/2$; (ii) x, y, $z-1$.