organic compounds

(E,E)-1-(2-Hydroxyimino-1-phenylethyl-idene)semicarbazide monohydrate

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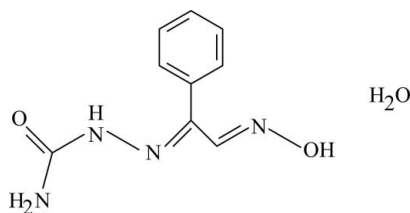Correspondence e-mail: merzifon@hacettepe.edu.tr

In the title compound, $C_9H_{10}N_4O_2 \cdot H_2O$, the oxime unit has an E configuration, and an intramolecular N—H⋯N hydrogen bond results in the formation of a planar five-membered ring, which is oriented with respect to the aromatic ring at a dihedral angle of 74.82 (17)°. In the crystal structure, intermolecular O—H⋯O and N—H⋯O hydrogen bonds link the molecules and $R_2^2(8)$ ring motifs are apparent.

Related literature

For general background, see: Balsamo et al. (1990); Marsman et al. (1999); Karle et al. (1996); Etter et al. (1990). For related structures, see: Sarıkavaklı et al. (2007, 2008); Özel Güven et al. (2007); Hökelek, Batı et al. (2001); Hökelek, Zülfikaroğlu et al. (2001); Büyükgüngör et al. (2003); Hökelek et al. (2004); Hökelek et al. (2004a,b). For reference structural data, see: Allen et al. (1987). For ring motifs, see: Bernstein et al. (1995).

Experimental

Crystal data

$C_9H_{10}N_4O_2 \cdot H_2O$	$\gamma = 78.538$ (5)°
$M_r = 224.23$	$V = 539.29$ (4) Å³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 5.5593$ (2) Å	Mo $K\alpha$ radiation
$b = 8.2701$ (3) Å	$\mu = 0.11$ mm⁻¹
$c = 12.6193$ (5) Å	$T = 294$ K
$\alpha = 71.900$ (3)°	$0.40 \times 0.25 \times 0.20$ mm
$\beta = 89.998$ (5)°	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	1752 independent reflections
Absorption correction: ψ scan (North et al., 1968)	867 reflections with $I > 2\sigma(I)$
$T_{min} = 0.968$, $T_{max} = 0.978$	$R_{int} = 0.048$
1953 measured reflections	3 standard reflections frequency: 120 min intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.185$	
$S = 1.05$	
1752 reflections	$\Delta\rho_{max} = 0.19$ e Å⁻³
171 parameters	$\Delta\rho_{min} = -0.34$ e Å⁻³
5 restraints	

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3A⋯N1	0.88 (3)	2.32 (6)	2.647 (8)	102 (5)
O3—H31⋯O1	0.88 (7)	1.92 (8)	2.776 (9)	164 (8)
O3—H32⋯O3^i	0.90 (3)	2.17 (7)	2.909 (11)	140 (7)
N2—H22⋯O3^{ii}	0.82 (3)	2.10 (4)	2.901 (10)	162 (5)
N3—H3B⋯O1^{iii}	0.96 (7)	1.96 (6)	2.909 (8)	169 (6)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae et al., 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

(*E*,*E*)-1-(2-Hydroxyimino-1-phenylethylidene)semicarbazide monohydrate

Aslı Öztürk, İlknur Babahan, Nursabah Sarıkavaklı and Tuncer Hökelek

S1. Comment

Oxime and dioxime derivatives have a broad pharmacological activity spectrum, encompassing antibacterial, antidepressant and antifungal activities (e.g. Balsamo *et al.*, 1990). The oxime (–C=N—OH) moiety is potentially ambidentate, with possibilities of coordination to metal ions through nitrogen and/or oxygen atoms. Oxime groups possess stronger hydrogen-bonding capabilities than alcohols, phenols, and carboxylic acids (Marsman *et al.*, 1999), in which intermolecular hydrogen bonding combines moderate strength and directionality (Karle *et al.*, 1996) in linking molecules to form supramolecular structures; this has received considerable attention with respect to directional noncovalent intermolecular interactions (Etter *et al.*, 1990).

The structures of some oxime and dioxime derivatives have been determined in our laboratory, including those of 2,3-dimethylquinoxaline-dimethyl-glyoxime (1/1), [(II) Hökelek, Batı *et al.*, 2001], 1-(2,6-dimethylphenylamino) propane-1,2-dione dioxime, [(III) (Hökelek, Zülfikaroğlu *et al.*, 2001), *N*-hydroxy-2-oxo-2,*N*′-diphenylacetamidine, [(IV) (Büyükgüngör *et al.*, 2003], *N*-(3,4-dichlorophenyl)-*N*′-hydroxy-2-oxo-2-phenylacetamidine, [(V) Hökelek *et al.*, 2004], *N*-hydroxy-*N*′-(1-naphthyl)-2-phenylacetamidin-2-one [(VI) Hökelek *et al.*, 2004*a*], *N*-(3-chloro-4-methylphenyl)-*N*′-hydroxy-2 -oxo-2-phenylacetamidine [(VII) Hökelek *et al.*, 2004*b*], 2-(1*H*-benzimidazol -1-yl)-1-phenylethanone oxime [(VIII) Özel Güven *et al.*, 2007], (1*Z*,2E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethane-1,2-dione dioxime [(IX) Sarıkavaklı *et al.*, 2007] and 2-hydroxyimino-1-phenylethanone thiosemicar bazone monohydrate [(*X*) Sarıkavaklı *et al.*, 2008].

As part of our ongoing studies in this area, the structure determination of the title compound, (I), an oxime derivative with one semicarbazide, one phenylacetaldehyde oxime moieties and one uncoordinated water molecule, was carried out in order to investigate the strength of the hydrogen bonding capability of the oxime and semicarbazide groups and to compare the geometry of the oxime moiety with the previously reported ones.

In the molecule of the title compound, (I), (Fig. 1) the bond lengths (Allen *et al.*, 1987) and angles are generally within normal ranges. Ring A (C1—C6) is, of course, planar. The intramolecular N—H⋯N hydrogen bond (Table 1) results in the formation of a planar five-membered ring B (N1—N3/C8/H3A). The dihedral angle between the planar rings is A/B = 74.82 (17)°.

In the crystal structure, intramolecular O—H⋯O and N—H⋯N and intermolecular O—H⋯O and N—H⋯O hydrogen bonds (Table 1) link the molecules through $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995) (Fig. 2).

S2. Experimental

Semicarbazide hydrochloride (1.12 g, 10 mmol) and sodium acetate (0.82 g, 10 mmol) were dissolved in double distilled water in the molar ratio 1:1. Then, the solution was mixed with a solution of 2-isonitrosoacetophenone (1.49 g, 10 mmol) in ethanol (10 ml) yielding a turbid mixture. The excess ethanol was added to get a clear solution and was stirred in a magnetic stirrer at room temparature for 4 h. The precipitate formed was filtered, washed with water and dried at room temperature in vacuum desiccator. It was recrystallized from ethanol/water (2:1) solution to yield colourless prisms of (I)

(yield; 1.80 g, 85%, m.p. 409 K).

S3. Refinement

Atoms H9 (for CH), H21 (for OH), H22 (for NH), H3A, H3B (for NH$_2$) and H31, H32 (for H$_2$O) were located in difference Fourier maps and refined isotropically, with restrains of O3—H31 = 0.88 (7), O3—H32 = 0.90 (3), N2—H22 = 0.82 (3), N3—H3A = 0.88 (3) Å and H31—O3—H32 = 105 (4)° [U_{iso}(H) = 0.064 (19) Å^2 (for CH), 0.09 (3) Å^2 (for OH), 0.040 (17) Å^2 (for NH), 0.08 (2) Å^2 (for NH$_2$) and 0.125 Å^2 (for H$_2$O)]. The remaining H atoms were positioned geometrically with C—H = 0.93 Å and refined as riding with U_{iso}(H) = 1.2U_{eq}(C).
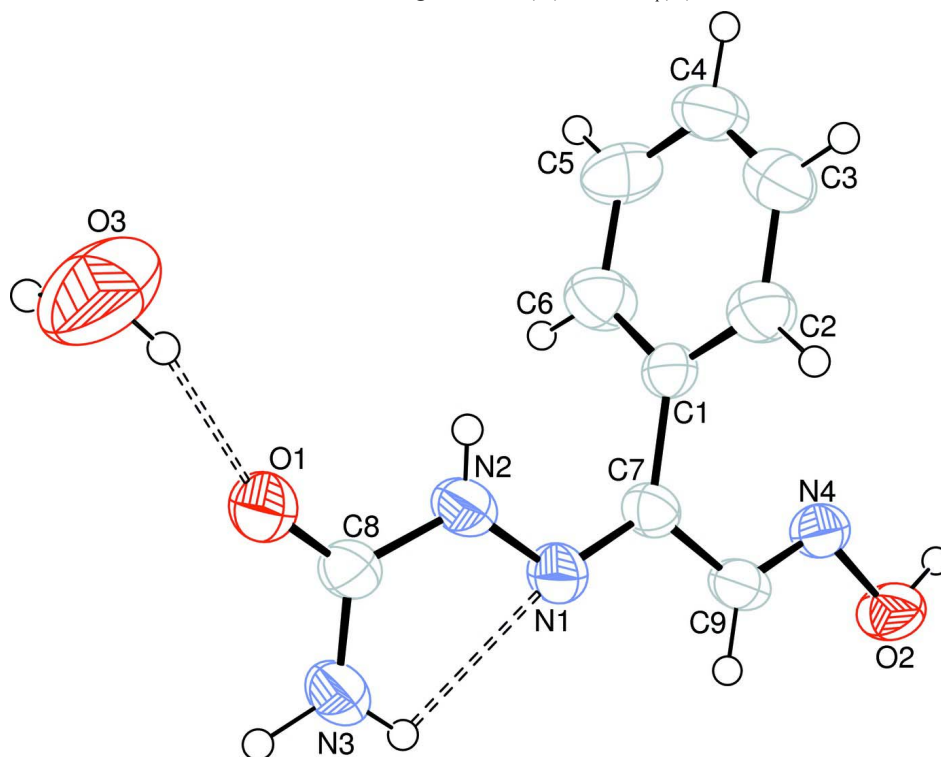

Figure 1

The molecular structure of (I) with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.
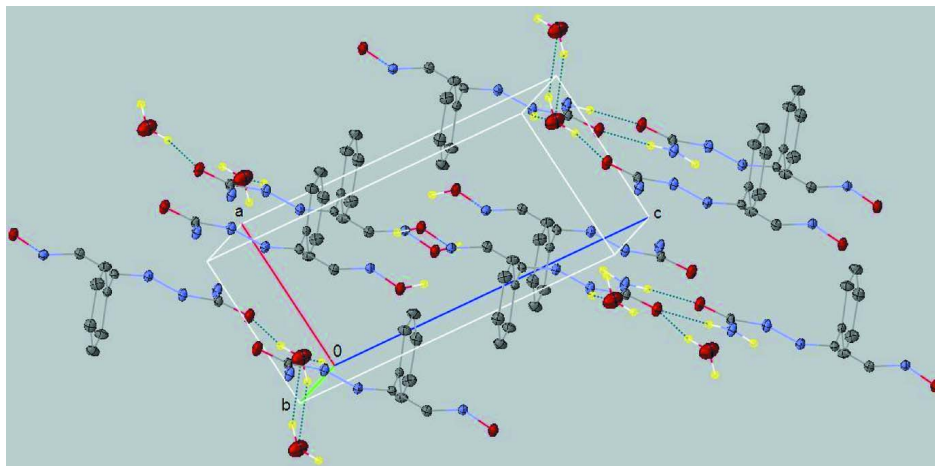
Figure 2

A partial packing diagram of (I). Hydrogen bonds are shown as dotted lines.

(*E*,*E*)-1-(2-Hydroxyimino-1-phenylethylidene)semicarbazide monohydrate

Crystal data

$C_9H_{10}N_4O_2 \cdot H_2O$	$Z = 2$
$M_r = 224.23$	$F(000) = 236$
Triclinic, $P\bar{1}$	$D_x = 1.381$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.5593$ (2) Å	Cell parameters from 25 reflections
$b = 8.2701$ (3) Å	$\theta = 8.6$–17.3°
$c = 12.6193$ (5) Å	$\mu = 0.11$ mm^{-1}
$\alpha = 71.900$ (3)°	$T = 294$ K
$\beta = 89.998$ (5)°	Prism, colorless
$\gamma = 78.538$ (5)°	$0.40 \times 0.25 \times 0.20$ mm
$V = 539.29$ (4) Å^3	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	1752 independent reflections
Radiation source: fine-focus sealed tube	867 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.048$
Non–profiled ω scans	$\theta_{max} = 24.3°$, $\theta_{min} = 3.4°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -6 \rightarrow 0$
	$k = -9 \rightarrow 9$
$T_{min} = 0.968$, $T_{max} = 0.978$	$l = -14 \rightarrow 14$
1953 measured reflections	3 standard reflections every 120 min
	intensity decay: 1%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.060$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.185$	
$S = 1.05$	Hydrogen site location: inferred from neighbouring sites
1752 reflections	
171 parameters	H atoms treated by a mixture of independent and constrained refinement
5 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0859P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

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}
O1	0.5650 (8)	−0.2847 (5)	0.9749 (4)	0.0635 (13)
O2	1.6136 (8)	−0.2215 (5)	0.5421 (4)	0.0583 (13)
H21	1.658 (12)	−0.131 (10)	0.490 (6)	0.09 (3)*
O3	0.2334 (12)	−0.0741 (10)	1.0657 (7)	0.132 (3)
H31	0.344 (10)	−0.122 (11)	1.028 (6)	0.125*
H32	0.088 (7)	−0.084 (10)	1.041 (7)	0.125*
N1	1.0377 (8)	−0.2812 (6)	0.7948 (4)	0.0456 (13)
N2	0.8573 (9)	−0.2253 (6)	0.8554 (4)	0.0498 (14)
H22	0.823 (9)	−0.128 (4)	0.863 (4)	0.040 (17)*
N3	0.7601 (11)	−0.4938 (7)	0.9070 (5)	0.0594 (16)
H3A	0.884 (8)	−0.531 (8)	0.872 (5)	0.08 (2)*
H3B	0.665 (11)	−0.578 (9)	0.942 (5)	0.08 (2)*
N4	1.4358 (8)	−0.1346 (5)	0.5950 (4)	0.0435 (13)
C1	1.0910 (10)	0.0218 (7)	0.7132 (5)	0.0389 (14)
C2	1.2415 (11)	0.0996 (7)	0.7590 (5)	0.0538 (17)
H2	1.3800	0.0317	0.8044	0.065*
C3	1.1895 (12)	0.2758 (8)	0.7384 (6)	0.0646 (19)
H3	1.2905	0.3257	0.7719	0.077*
C4	0.9938 (13)	0.3786 (8)	0.6700 (6)	0.0602 (18)
H4	0.9626	0.4987	0.6543	0.072*
C5	0.8426 (12)	0.3024 (8)	0.6244 (5)	0.065 (2)
H5	0.7064	0.3716	0.5778	0.078*
C6	0.8891 (12)	0.1243 (8)	0.6466 (5)	0.0591 (18)
H6	0.7829	0.0742	0.6162	0.071*
C7	1.1479 (10)	−0.1688 (6)	0.7314 (4)	0.0387 (14)
C8	0.7189 (11)	−0.3364 (7)	0.9167 (5)	0.0455 (15)
C9	1.3383 (11)	−0.2382 (8)	0.6696 (5)	0.0444 (15)
H9	1.374 (10)	−0.359 (9)	0.687 (5)	0.064 (19)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.066 (3)	0.051 (3)	0.078 (3)	−0.018 (2)	0.036 (3)	−0.024 (2)
O2	0.062 (3)	0.044 (3)	0.064 (3)	−0.005 (2)	0.026 (2)	−0.014 (2)
O3	0.106 (5)	0.148 (6)	0.173 (7)	0.002 (5)	0.008 (5)	−0.111 (5)
N1	0.049 (3)	0.041 (3)	0.048 (3)	−0.012 (2)	0.017 (3)	−0.013 (2)
N2	0.058 (3)	0.036 (3)	0.057 (3)	−0.015 (3)	0.019 (3)	−0.014 (3)
N3	0.065 (4)	0.043 (3)	0.076 (4)	−0.022 (3)	0.030 (3)	−0.019 (3)
N4	0.046 (3)	0.037 (3)	0.046 (3)	−0.006 (2)	0.009 (2)	−0.012 (2)
C1	0.038 (3)	0.035 (3)	0.041 (3)	−0.007 (3)	0.011 (3)	−0.010 (3)
C2	0.050 (4)	0.042 (4)	0.066 (4)	−0.005 (3)	−0.008 (3)	−0.014 (3)
C3	0.062 (4)	0.046 (4)	0.089 (5)	−0.016 (4)	−0.003 (4)	−0.024 (4)
C4	0.074 (5)	0.035 (3)	0.071 (5)	−0.013 (4)	0.013 (4)	−0.016 (3)
C5	0.068 (5)	0.045 (4)	0.067 (5)	0.010 (4)	−0.011 (4)	−0.007 (4)
C6	0.060 (4)	0.045 (4)	0.065 (4)	−0.008 (3)	−0.014 (4)	−0.010 (3)
C7	0.043 (3)	0.032 (3)	0.037 (3)	−0.009 (3)	0.002 (3)	−0.005 (3)
C8	0.049 (4)	0.035 (3)	0.046 (4)	−0.009 (3)	0.012 (3)	−0.005 (3)
C9	0.051 (4)	0.031 (3)	0.051 (4)	−0.011 (3)	0.007 (3)	−0.012 (3)

Geometric parameters (Å, º)

O1—C8	1.226 (6)	C2—H2	0.9300
O2—N4	1.399 (5)	C3—H3	0.9300
O2—H21	0.91 (8)	C4—C3	1.352 (9)
O3—H31	0.88 (7)	C4—C5	1.368 (9)
O3—H32	0.90 (3)	C4—H4	0.9300
N1—C7	1.281 (6)	C5—C6	1.381 (8)
N2—N1	1.357 (6)	C5—H5	0.9300
N2—C8	1.369 (7)	C6—H6	0.9300
N2—H22	0.82 (3)	C7—C1	1.489 (7)
N3—H3A	0.88 (3)	C8—N3	1.320 (7)
N3—H3B	0.96 (7)	C9—N4	1.264 (7)
C1—C2	1.376 (8)	C9—C7	1.447 (7)
C1—C6	1.365 (8)	C9—H9	0.94 (6)
C2—C3	1.368 (8)		
N4—O2—H21	101 (4)	C3—C4—C5	118.6 (6)
H31—O3—H32	105 (4)	C3—C4—H4	120.7
C7—N1—N2	118.1 (5)	C5—C4—H4	120.7
N1—N2—C8	120.5 (5)	C4—C5—C6	121.0 (6)
N1—N2—H22	126 (4)	C4—C5—H5	119.5
C8—N2—H22	113 (4)	C6—C5—H5	119.5
C8—N3—H3A	122 (4)	C1—C6—C5	120.0 (6)
C8—N3—H3B	123 (4)	C1—C6—H6	120.0
H3A—N3—H3B	115 (6)	C5—C6—H6	120.0
C9—N4—O2	112.3 (4)	N1—C7—C1	126.4 (5)
C2—C1—C7	121.7 (5)	N1—C7—C9	114.9 (5)

C6—C1—C2	118.6 (5)	C9—C7—C1	118.7 (5)
C6—C1—C7	119.7 (5)	O1—C8—N2	119.1 (5)
C1—C2—H2	119.7	O1—C8—N3	124.4 (6)
C3—C2—C1	120.7 (6)	N3—C8—N2	116.5 (5)
C3—C2—H2	119.7	N4—C9—C7	119.3 (5)
C2—C3—H3	119.5	N4—C9—H9	125 (4)
C4—C3—C2	121.1 (6)	C7—C9—H9	116 (3)
C4—C3—H3	119.5		
N2—N1—C7—C1	−2.8 (8)	C5—C4—C3—C2	2.2 (10)
N2—N1—C7—C9	179.9 (5)	C3—C4—C5—C6	−0.6 (10)
C8—N2—N1—C7	174.2 (5)	C4—C5—C6—C1	−1.2 (10)
N1—N2—C8—O1	176.6 (5)	N1—C7—C1—C2	106.3 (7)
N1—N2—C8—N3	−4.4 (8)	N1—C7—C1—C6	−75.8 (8)
C6—C1—C2—C3	0.1 (9)	C9—C7—C1—C2	−76.5 (7)
C7—C1—C2—C3	178.0 (6)	C9—C7—C1—C6	101.4 (6)
C2—C1—C6—C5	1.4 (9)	N4—C9—C7—N1	171.4 (5)
C7—C1—C6—C5	−176.5 (6)	N4—C9—C7—C1	−6.1 (8)
C1—C2—C3—C4	−2.0 (10)	C7—C9—N4—O2	−179.2 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N1	0.88 (3)	2.32 (6)	2.647 (8)	102 (5)
O3—H31···O1	0.88 (7)	1.92 (8)	2.776 (9)	164 (8)
O3—H32···O3ⁱ	0.90 (3)	2.17 (7)	2.909 (11)	140 (7)
N2—H22···O3ⁱⁱ	0.82 (3)	2.10 (4)	2.901 (10)	162 (5)
N3—H3*B*···O1ⁱⁱⁱ	0.96 (7)	1.96 (6)	2.909 (8)	169 (6)

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