

5'-Nitro-1,4-dihydrospiro[3,1-benzoxazine-2,3'-indolin]-2'-one

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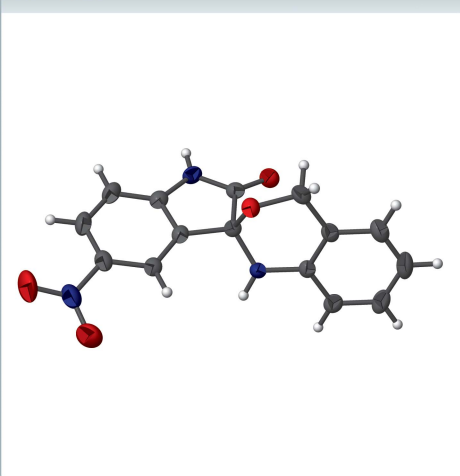
Keywords: crystal structure; spirocompounds; spiro-oxazines; indoline; N—H···O and C—H···O hydrogen bonding.

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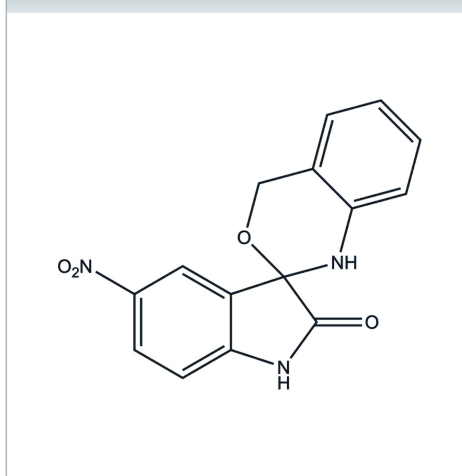
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, C₁₅H₁₁N₃O₄, the six-membered oxazine ring adopts a half-chair conformation and is oriented at an angle of 78.63 (9)° with respect to the pyrrolidine ring of the indoline ring system, which adopts an envelope conformation. The spiro centre C atom is tetrahedral and lies 0.147 (1) Å out of the plane of other four pyrrolidone ring atoms. The nitrobenzene and benzene rings exhibit near planar conformations with C—C—C—N and C—C—C—C torsion angles of 178.1 (2) and 178.8 (2)°, respectively. In the crystal, N—H···O and C—H···O hydrogen bonds connect the molecules, generating a sheet-like structure parallel to the *bc* plane. Within the sheets, pairs of intermolecular N—H···O hydrogen bonds form inversion dimers enclosing R₂²(8) ring motifs. In addition, the N—H···O and C—H···O hydrogen bonds generate R₃²(11) and R₂²(10) graph-set ring motifs extending the two-dimensional structure. A supramolecular R₆⁶(28) loop for each set of six molecules is formed by N—H···O hydrogen bonds within the extended sheet structure and stabilizes the packing. π – π stacking interactions between the nitrobenzene and benzene rings [intercentroid distance = 3.711 (1) Å] and N—O··· π interactions further consolidate the crystal packing.

3D view



Chemical scheme



Structure description

The biological properties of spiro compounds containing cyclic structures are evident from their presence in many natural products (Molvi *et al.*, 2014). A number of spiro compounds show diverse biological activities such as anticancer (Chin *et al.*, 2008), antibacterial (van der Sar *et al.*, 2006), anticonvulsant (Obniska & Kamiński, 2006), antimicrobial (Pawar *et al.*, 2009), antituberculosis (Chande *et al.*, 2005), anti-oxidant

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H3A···O4 ⁱ	0.86	2.51	3.0614 (18)	123
N2—H2···O3 ⁱⁱ	0.86	2.11	2.9057 (19)	153
C3—H3···O1 ⁱⁱⁱ	0.93	2.53	3.439 (3)	165
C6—H6···O3 ^{iv}	0.93	2.33	3.256 (2)	176
C9—H9B···O3	0.97	2.54	3.014 (2)	110

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

(Sarma *et al.*, 2010) and are used as pain-relief agents (Frank *et al.*, 2008). Some spiro compounds are used as pesticides (Wei *et al.*, 2009) and laser dyes (Kreuder *et al.*, 1999). They are also used as electroluminescent devices (Lupo *et al.*, 1998). 1,3-Dipolar cycloaddition reactions are widely used for construction of spiro compounds (Caramella & Grunanger, 1984). Spirooxazine is the most important member of one of the best known organic photochromic systems with fast photocoloring rates and high light-fatigue resistance (Durr & Bousas-Laurent, 1990). Over the past several decades, numerous types of spirooxazine derivatives have been characterized. Photochromic compounds continue to attract significant attention in view of their general applicability as optical information storage materials or switching devices (Durr, 1989; Ichimura, 2000). They are also used as organic photochromic materials within a plastic matrix, for example as photochromic ophthalmic lenses and vehicle roof lights (Rickwood & Hepworth, 1990). It is certain that C—O bond cleavage in spirooxazines induced by UV irradiation or heating is the main reason for their photochromism, and the C=N bond in the oxazine ring improves its durability (Clegg *et al.*, 1991; Osano *et al.*, 1991; Reboul *et al.*, 1995; Pèpe *et al.*, 1995; Malatesta *et al.*, 1995; Sun *et al.*, 1997; Liang *et al.*, 1998; Chamontin *et al.*, 1998; Guo *et al.*, 2005), but there are still some details of the structure–property relationships needing further explanation. For example, it was assumed that the more planar the oxazine ring, the less photochromatic the

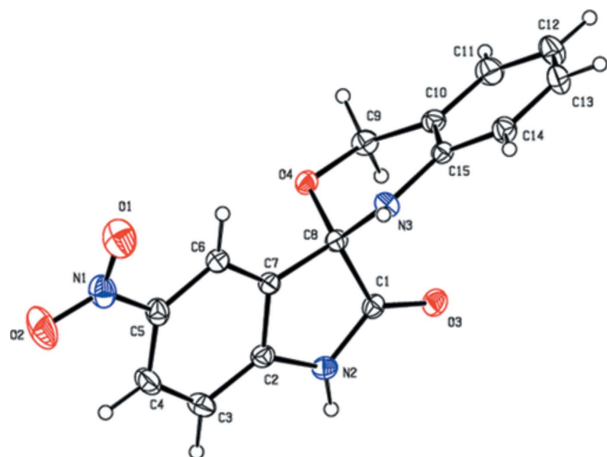


Figure 1
The molecular structure of the title molecule, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

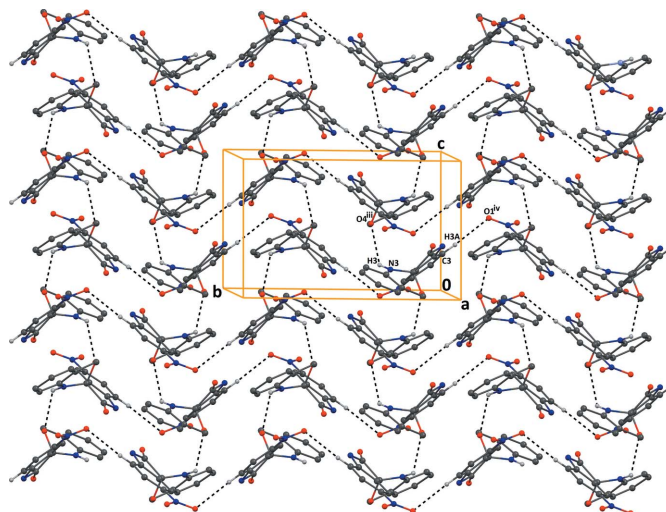


Figure 2
The crystal packing, viewed parallel to the *bc* plane, showing the N—H···O and C—H···O hydrogen bonds generating sheets. For the sake of clarity, H atoms not involved in the hydrogen bonds have been excluded.

molecule (Reboul *et al.*, 1995). In this paper we report the structure of the novel photochromic title compound.

The molecular structure (Fig. 1) reveals the presence of a spirojunction at atom C8. The spirocentre C8 is tetrahedral with the dihedral angle between the planes O4/C8/N3 and C1/C8/C7 being 78.63 (9)°. The spiro atom C8 displays regular sp³ hybridization. The O4—C8—N3 bond angles at the C8 spiro carbon have a mean value of 109.1 (14)°. The oxazine ring (O4/N3/C8/C9/C10/C15) adopts a half-chair conformation [*Q* = 0.452 (2) Å, *θ* = 128.8 (2)°, *φ* = 214.4 (3)°], while the five-membered pyrrolidin ring (N2/C1/C2/C7/C8) adopts an envelope conformation [*q*₂ = 0.088 (2) Å, *φ*₂ = 71.8 (12)°]. Atom C8 lies 0.147 (1) Å out of the plane of other four pyrrolidone ring atoms, with a C7—C2—N2—C1 torsion angle of 0.2 (2)°. The C2—N2 bond length is 1.397 (2) Å which is in between the value of 1.48 Å for a C—N single bond and 1.28 Å for a C=N double bond (Allen *et al.*, 1987), indicating a partial delocalization of the π electron density over the

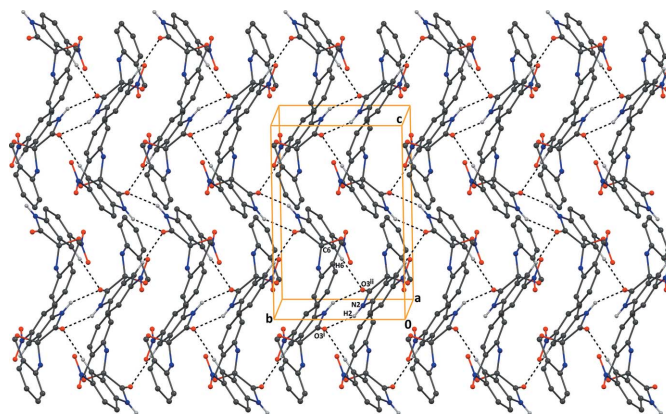


Figure 3
Part of the crystal structure showing the formation of sheets parallel to *bc* plane built from N—H···O and C—H···O hydrogen bonds and containing *R*₂²(8) inversion dimers.

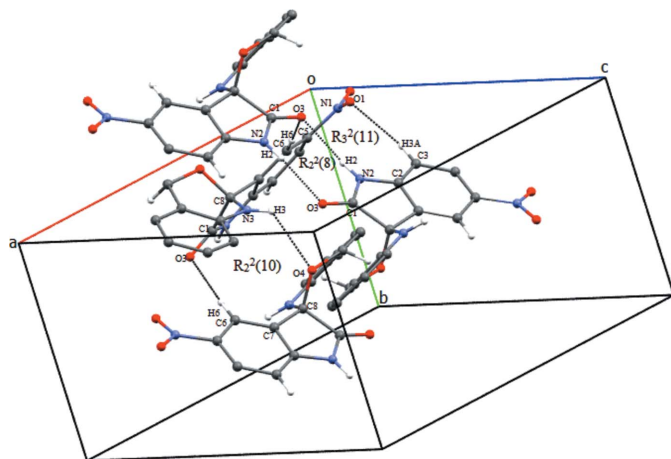


Figure 4
A view of the hydrogen-bonded ring motif. Details of the hydrogen bonds are given in Table 1.

indole ring. The $C_{\text{spiro}}-\text{O}$ bond length is the key point in this type of structures and cleaves upon photoexcitation to give an open form of the spiro oxazine ring. The $C_{\text{spiro}}-\text{O}$ and $C_{\text{spiro}}-\text{N}$ bond lengths are 1.431 (2) and 1.429 (2) Å, respectively. The dihedral angle between the nitrobenzene ring of the 5-nitroindolin-2-one ring system and the benzene ring (C10–C15) of the 2,4-dihydro-1*H*-benzo [*d*][1,3] oxazine ring system is 68.48 (10)°. The observed C4–C3–C2–N2, C5–C6–C7–C8 and C12–C11–C10–C9 torsion angles of 178.1 (2), 175.1 (2) and 178.8 (2)°, respectively, indicate a nearly planar configuration.

In the crystal, molecules are connected into sheets in the bc plane (011) (Table 1 and Fig. 2) by $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. Pairs of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds form inversion dimers, generating $R_2^2(8)$ ring motifs and stabilizing the sheet structure, Fig. 3. The occurrence of two different sets of $R_3^2(11)$ and $R_2^2(10)$ graph-set ring motifs, Fig. 4, via $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds extends the two-dimensional structure. The $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds

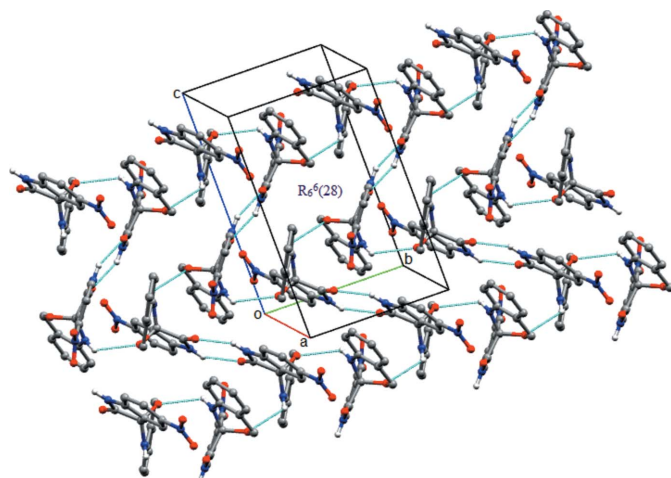


Figure 5
A part of crystal structure showing the formation of a sheet along [010], generating an $R_6^6(28)$ loop for each set of six molecules.

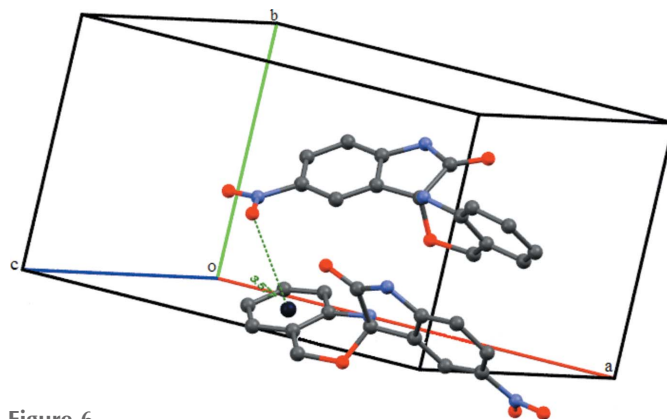


Figure 6
A partial view of the crystal packing of the title compound, showing the $\text{N}-\text{O}\cdots\pi$ interactions.

stabilize the crystal structure by forming a supramolecular $R_6^6(28)$ loop for each set of six molecules, Fig. 5, within the extended sheet structure. $\pi-\pi$ stacking interactions between the nitrobenzene and benzene rings [intercentroid distance = 3.7105 (12) Å] and $\text{N}-\text{O}\cdots\pi$ interactions [$\text{N}\cdots\text{p}$ = 3.6438 (19) Å, $\text{N}-\text{O}\cdots\pi$ = 83.34 (12)°] further consolidate the crystal structure (Fig. 6).

Synthesis and crystallization

A mixture of 5-nitroisatin 1 (1.0 mmol) and 2-aminobenzyl alcohol 2 (1.0 mmol) was refluxed in ethanol in the presence of

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_4$
M_r	297.27
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	12.8698 (6), 8.1365 (3), 13.0309 (6)
β (°)	107.275 (5)
V (Å ³)	1302.98 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.20 × 0.15 × 0.10
Data collection	
Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2008)
$T_{\text{min}}, T_{\text{max}}$	0.980, 0.989
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6269, 2294, 1945
R_{int}	0.023
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.042, 0.118, 1.04
No. of reflections	2294
No. of parameters	200
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.43, -0.52

Computer programs: APEX2 and SAINT (Bruker, 2008), SHELXS97 and SHELXL97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2009).

10 mol % of InCl_3 . The reaction mixture was refluxed for 2.5 h. After the reaction was complete, as indicated by TLC, the mixture was cooled to room temperature. The solid formed in the reaction mixture was filtered, dried and recrystallized from ethanol to obtain the title compound in good yield (88%).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2018). 3, x180664 [https://doi.org/10.1107/S2414314618006648]

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Crystal data

$C_{15}H_{11}N_3O_4$	$F(000) = 616$
$M_r = 297.27$	$D_x = 1.515 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 12.8698 (6) \text{ \AA}$	Cell parameters from 1945 reflections
$b = 8.1365 (3) \text{ \AA}$	$\theta = 3.0\text{--}25.0^\circ$
$c = 13.0309 (6) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$\beta = 107.275 (5)^\circ$	$T = 293 \text{ K}$
$V = 1302.98 (10) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.20 \times 0.15 \times 0.10 \text{ mm}$

Data collection

Bruker SMART APEXII CCD diffractometer	2294 independent reflections
Radiation source: fine-focus sealed tube	1945 reflections with $I > 2\sigma(I)$
ω and ϕ scans	$R_{\text{int}} = 0.023$
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2008)	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 3.0^\circ$
$T_{\text{min}} = 0.980$, $T_{\text{max}} = 0.989$	$h = -15 \rightarrow 13$
6269 measured reflections	$k = -9 \rightarrow 9$
	$l = -15 \rightarrow 13$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.5946P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.118$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$
2294 reflections	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
200 parameters	Extinction correction: SHELXL2014 (Sheldrick, 2015),
0 restraints	$F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
Hydrogen site location: inferred from neighbouring sites	Extinction coefficient: 0.025 (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. The N- and C-bound H atoms were positioned geometrically (N—H = 0.86 Å, C—H = 0.93–0.97 Å) and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,C})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.50260 (15)	0.1988 (2)	0.59411 (14)	0.0266 (4)
C2	0.31973 (15)	0.2340 (2)	0.56038 (14)	0.0285 (4)
C3	0.20908 (16)	0.2224 (2)	0.51299 (16)	0.0381 (5)
H3	0.1802	0.1587	0.4519	0.046*
C4	0.14245 (16)	0.3091 (3)	0.55982 (17)	0.0393 (5)
H4	0.0673	0.3055	0.5295	0.047*
C5	0.18727 (15)	0.4006 (2)	0.65135 (15)	0.0325 (5)
C6	0.29914 (15)	0.4182 (2)	0.69722 (14)	0.0280 (4)
H6	0.3280	0.4826	0.7580	0.034*
C7	0.36486 (14)	0.3360 (2)	0.64857 (14)	0.0256 (4)
C8	0.48666 (14)	0.3376 (2)	0.67193 (14)	0.0250 (4)
C9	0.63047 (15)	0.5016 (2)	0.64088 (15)	0.0313 (4)
H9A	0.6488	0.6156	0.6332	0.038*
H9B	0.6427	0.4405	0.5816	0.038*
C10	0.70370 (15)	0.4361 (2)	0.74414 (14)	0.0284 (4)
C11	0.81548 (16)	0.4608 (2)	0.77324 (17)	0.0395 (5)
H11	0.8455	0.5176	0.7270	0.047*
C12	0.88258 (17)	0.4028 (3)	0.86935 (19)	0.0474 (6)
H12	0.9574	0.4191	0.8875	0.057*
C13	0.83782 (16)	0.3201 (3)	0.93859 (18)	0.0426 (5)
H13	0.8825	0.2836	1.0046	0.051*
C14	0.72727 (16)	0.2913 (2)	0.91047 (15)	0.0333 (5)
H14	0.6978	0.2351	0.9574	0.040*
C15	0.65979 (14)	0.3459 (2)	0.81216 (14)	0.0251 (4)
O1	0.15323 (14)	0.5344 (2)	0.79367 (14)	0.0608 (5)
O2	0.01794 (13)	0.4940 (3)	0.65155 (16)	0.0720 (6)
O3	0.58905 (11)	0.14139 (15)	0.59145 (10)	0.0350 (4)
O4	0.51663 (10)	0.49075 (14)	0.63476 (10)	0.0279 (3)
N1	0.11430 (14)	0.4820 (2)	0.70211 (16)	0.0436 (5)
N2	0.40246 (13)	0.15524 (18)	0.52997 (12)	0.0310 (4)
H2	0.3914	0.0875	0.4772	0.037*
N3	0.54687 (11)	0.31629 (18)	0.78242 (11)	0.0268 (4)
H3A	0.5154	0.2865	0.8291	0.032*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0313 (10)	0.0237 (8)	0.0250 (9)	0.0028 (8)	0.0087 (7)	0.0030 (7)
C2	0.0319 (10)	0.0242 (8)	0.0278 (9)	-0.0013 (7)	0.0064 (8)	0.0012 (7)
C3	0.0339 (11)	0.0392 (11)	0.0350 (11)	-0.0069 (9)	0.0009 (9)	-0.0060 (8)
C4	0.0247 (10)	0.0445 (11)	0.0436 (12)	-0.0060 (9)	0.0022 (9)	0.0022 (9)
C5	0.0271 (10)	0.0336 (10)	0.0378 (11)	0.0017 (8)	0.0112 (8)	0.0060 (8)
C6	0.0276 (10)	0.0266 (9)	0.0291 (9)	-0.0003 (7)	0.0074 (8)	0.0008 (7)
C7	0.0256 (9)	0.0229 (8)	0.0264 (9)	-0.0007 (7)	0.0049 (7)	0.0017 (7)
C8	0.0265 (9)	0.0231 (8)	0.0254 (9)	-0.0003 (7)	0.0075 (7)	-0.0004 (7)

C9	0.0324 (11)	0.0308 (9)	0.0348 (10)	-0.0033 (8)	0.0166 (8)	0.0005 (8)
C10	0.0279 (10)	0.0263 (8)	0.0330 (10)	-0.0009 (7)	0.0124 (8)	-0.0044 (8)
C11	0.0317 (11)	0.0408 (11)	0.0504 (13)	-0.0035 (9)	0.0187 (10)	-0.0037 (9)
C12	0.0241 (10)	0.0533 (13)	0.0612 (15)	0.0002 (10)	0.0070 (10)	-0.0066 (11)
C13	0.0294 (11)	0.0470 (12)	0.0434 (12)	0.0077 (9)	-0.0013 (9)	-0.0008 (10)
C14	0.0336 (11)	0.0341 (9)	0.0303 (10)	0.0027 (8)	0.0067 (8)	0.0007 (8)
C15	0.0245 (9)	0.0234 (8)	0.0278 (9)	0.0011 (7)	0.0084 (7)	-0.0046 (7)
O1	0.0531 (11)	0.0818 (12)	0.0535 (11)	0.0109 (9)	0.0250 (9)	-0.0081 (9)
O2	0.0277 (9)	0.1054 (16)	0.0836 (14)	0.0114 (9)	0.0178 (9)	-0.0038 (11)
O3	0.0352 (8)	0.0338 (7)	0.0373 (8)	0.0061 (6)	0.0131 (6)	-0.0047 (6)
O4	0.0278 (7)	0.0237 (6)	0.0323 (7)	0.0009 (5)	0.0092 (6)	0.0025 (5)
N1	0.0324 (10)	0.0511 (11)	0.0511 (12)	0.0027 (8)	0.0184 (9)	0.0069 (9)
N2	0.0346 (9)	0.0290 (8)	0.0275 (8)	0.0003 (7)	0.0062 (7)	-0.0079 (6)
N3	0.0247 (8)	0.0342 (8)	0.0221 (8)	-0.0029 (6)	0.0082 (6)	0.0010 (6)

Geometric parameters (Å, °)

C1—O3	1.217 (2)	C9—C10	1.493 (3)
C1—N2	1.359 (2)	C9—H9A	0.9700
C1—C8	1.571 (2)	C9—H9B	0.9700
C2—C3	1.377 (3)	C10—C11	1.389 (3)
C2—C7	1.396 (2)	C10—C15	1.393 (3)
C2—N2	1.397 (2)	C11—C12	1.376 (3)
C3—C4	1.384 (3)	C11—H11	0.9300
C3—H3	0.9300	C12—C13	1.381 (3)
C4—C5	1.379 (3)	C12—H12	0.9300
C4—H4	0.9300	C13—C14	1.380 (3)
C5—C6	1.393 (3)	C13—H13	0.9300
C5—N1	1.459 (3)	C14—C15	1.390 (3)
C6—C7	1.372 (3)	C14—H14	0.9300
C6—H6	0.9300	C15—N3	1.409 (2)
C7—C8	1.506 (2)	O1—N1	1.225 (2)
C8—N3	1.429 (2)	O2—N1	1.223 (2)
C8—O4	1.431 (2)	N2—H2	0.8600
C9—O4	1.446 (2)	N3—H3A	0.8600
O3—C1—N2	126.20 (17)	C10—C9—H9B	109.1
O3—C1—C8	126.17 (16)	H9A—C9—H9B	107.8
N2—C1—C8	107.63 (15)	C11—C10—C15	119.05 (18)
C3—C2—C7	122.13 (17)	C11—C10—C9	121.30 (17)
C3—C2—N2	127.96 (17)	C15—C10—C9	119.64 (16)
C7—C2—N2	109.89 (16)	C12—C11—C10	121.2 (2)
C2—C3—C4	117.45 (18)	C12—C11—H11	119.4
C2—C3—H3	121.3	C10—C11—H11	119.4
C4—C3—H3	121.3	C11—C12—C13	119.4 (2)
C5—C4—C3	120.11 (18)	C11—C12—H12	120.3
C5—C4—H4	119.9	C13—C12—H12	120.3
C3—C4—H4	119.9	C14—C13—C12	120.44 (19)

C4—C5—C6	122.71 (18)	C14—C13—H13	119.8
C4—C5—N1	118.51 (18)	C12—C13—H13	119.8
C6—C5—N1	118.78 (17)	C13—C14—C15	120.20 (19)
C7—C6—C5	116.87 (17)	C13—C14—H14	119.9
C7—C6—H6	121.6	C15—C14—H14	119.9
C5—C6—H6	121.6	C14—C15—C10	119.63 (17)
C6—C7—C2	120.47 (17)	C14—C15—N3	120.64 (16)
C6—C7—C8	130.52 (16)	C10—C15—N3	119.69 (16)
C2—C7—C8	108.98 (15)	C8—O4—C9	113.88 (12)
N3—C8—O4	109.07 (13)	O2—N1—O1	123.57 (19)
N3—C8—C7	115.04 (15)	O2—N1—C5	118.56 (19)
O4—C8—C7	107.96 (13)	O1—N1—C5	117.87 (18)
N3—C8—C1	115.32 (14)	C1—N2—C2	111.67 (15)
O4—C8—C1	107.89 (13)	C1—N2—H2	124.2
C7—C8—C1	101.00 (13)	C2—N2—H2	124.2
O4—C9—C10	112.71 (14)	C15—N3—C8	117.57 (14)
O4—C9—H9A	109.1	C15—N3—H3A	121.2
C10—C9—H9A	109.1	C8—N3—H3A	121.2
O4—C9—H9B	109.1		
C7—C2—C3—C4	-3.6 (3)	C9—C10—C11—C12	178.84 (18)
N2—C2—C3—C4	178.12 (18)	C10—C11—C12—C13	-0.7 (3)
C2—C3—C4—C5	-1.0 (3)	C11—C12—C13—C14	2.0 (3)
C3—C4—C5—C6	3.6 (3)	C12—C13—C14—C15	-0.3 (3)
C3—C4—C5—N1	-176.28 (18)	C13—C14—C15—C10	-2.7 (3)
C4—C5—C6—C7	-1.6 (3)	C13—C14—C15—N3	179.63 (17)
N1—C5—C6—C7	178.29 (16)	C11—C10—C15—C14	3.9 (3)
C5—C6—C7—C2	-2.9 (2)	C9—C10—C15—C14	-177.13 (16)
C5—C6—C7—C8	175.13 (16)	C11—C10—C15—N3	-178.40 (16)
C3—C2—C7—C6	5.7 (3)	C9—C10—C15—N3	0.6 (2)
N2—C2—C7—C6	-175.75 (15)	N3—C8—O4—C9	61.07 (17)
C3—C2—C7—C8	-172.75 (16)	C7—C8—O4—C9	-173.27 (13)
N2—C2—C7—C8	5.80 (19)	C1—C8—O4—C9	-64.88 (17)
C6—C7—C8—N3	48.4 (2)	C10—C9—O4—C8	-43.61 (19)
C2—C7—C8—N3	-133.37 (15)	C4—C5—N1—O2	-14.3 (3)
C6—C7—C8—O4	-73.7 (2)	C6—C5—N1—O2	165.82 (18)
C2—C7—C8—O4	104.59 (15)	C4—C5—N1—O1	165.52 (19)
C6—C7—C8—C1	173.26 (17)	C6—C5—N1—O1	-14.4 (3)
C2—C7—C8—C1	-8.50 (17)	O3—C1—N2—C2	174.52 (17)
O3—C1—C8—N3	-47.0 (2)	C8—C1—N2—C2	-5.79 (19)
N2—C1—C8—N3	133.26 (16)	C3—C2—N2—C1	178.63 (18)
O3—C1—C8—O4	75.1 (2)	C7—C2—N2—C1	0.2 (2)
N2—C1—C8—O4	-104.56 (15)	C14—C15—N3—C8	-164.55 (16)
O3—C1—C8—C7	-171.73 (17)	C10—C15—N3—C8	17.8 (2)
N2—C1—C8—C7	8.57 (17)	O4—C8—N3—C15	-47.42 (19)
O4—C9—C10—C11	-168.87 (16)	C7—C8—N3—C15	-168.86 (14)
O4—C9—C10—C15	12.2 (2)	C1—C8—N3—C15	74.13 (19)
C15—C10—C11—C12	-2.2 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H3A···O4 ⁱ	0.86	2.51	3.0614 (18)	123
N2—H2···O3 ⁱⁱ	0.86	2.11	2.9057 (19)	153
C3—H3···O1 ⁱⁱⁱ	0.93	2.53	3.439 (3)	165
C6—H6···O3 ^{iv}	0.93	2.33	3.256 (2)	176
C9—H9B···O3	0.97	2.54	3.014 (2)	110

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