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Crystal structure of methyl 1,3-benzoxazole-2-carboxylate

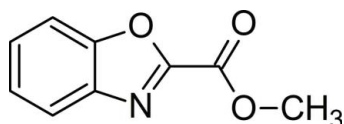
Alexandre Poirot,^a Nathalie Saffon-Merceron,^b Nadine Leygue,^a Eric Benoist^a and Suzanne Fery-Forgues^{a*}

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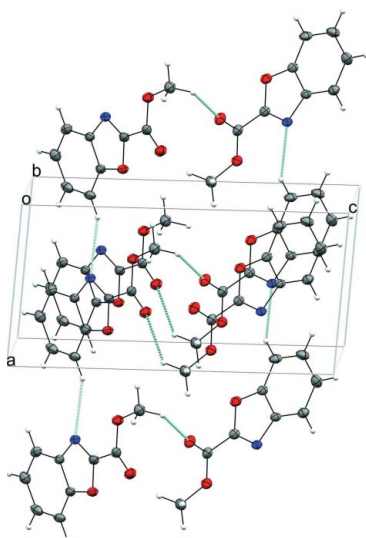
The title compound, C₉H₇NO₃, crystallizes in the monoclinic (*P*2₁) space group. In the crystal, the almost planar molecules display a flattened herringbone arrangement. Stacking molecules are slipped in the lengthwise and widthwise directions and are linked by π - π interactions [$d(Cg \cdots Cg) = 3.6640(11) \text{ \AA}$]. The structure is characterized by strong C—H...N and weak C—H...O hydrogen bonds, and further stabilized by C—O... π interactions.

1. Chemical context

Benzoxazoles are common in natural products and represent an important class of key structural motifs, often incorporated as building blocks in ligands to target a variety of receptors and enzymes in medicinal chemistry studies (Demmer & Bunch, 2015; Kamal *et al.*, 2020). They are also a scaffold of prime importance for fluorescent probes and materials (Carayon & Fery-Forgues, 2017; Fery-Forgues & Vanucci-Bacqué, 2021). Methyl-1,3-benzoxazole-2-carboxylate (**1**) belongs to this family and much attention has been paid to its preparation.



This compound was first prepared by a multi-step synthesis starting from 2,3-dioxo-1,4-benzoxazine (Dickoré *et al.*, 1970) and 2-cyanobenzoxazole (Möller, 1970), but it can be obtained much more simply from condensation of 2-aminophenol with methyl 2,2,2-trimethoxyacetate (Musser, Hudec *et al.*, 1984; Koshelev *et al.*, 2019). It has been synthesized in high yields by direct carboxylation of benzoxazole using carbon dioxide (CO₂) as a naturally abundant and renewable C1 source, with (Zhang *et al.*, 2010; Inomata *et al.*, 2012) or without any metal catalyst (Vechorkin *et al.*, 2010; Fenner & Ackermann, 2016). Recently, it has been produced by oxidative cyclization of glycine catalysed by copper (Liu *et al.*, 2021) or induced by irradiation with visible light (Zhu *et al.*, 2021). The molecule is commercially available. It has been used to complex europium, resulting in a very efficient electroluminescent layer for applications in the field of organic light-emitting diodes (OLEDs) (Koshelev *et al.*, 2019). Used as a synthetic inter-



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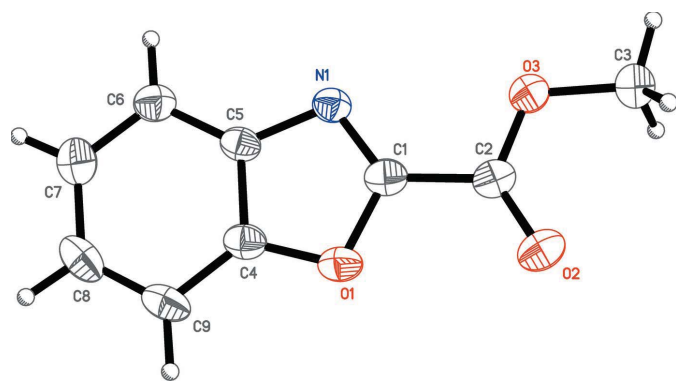


Figure 1
The molecular structure of the title compound with the atom numbering. The displacement ellipsoids are drawn at the 50% probability level.

mediate, methyl-1,3-benzoxazole-2-carboxylate has led to various pharmacologically active agents with anti-allergic (Musser, Brown *et al.*, 1984), anti-microbial (Vodela *et al.*, 2013) and neuro-anti-inflammatory (Shang *et al.*, 2020) activity, to name just a few.

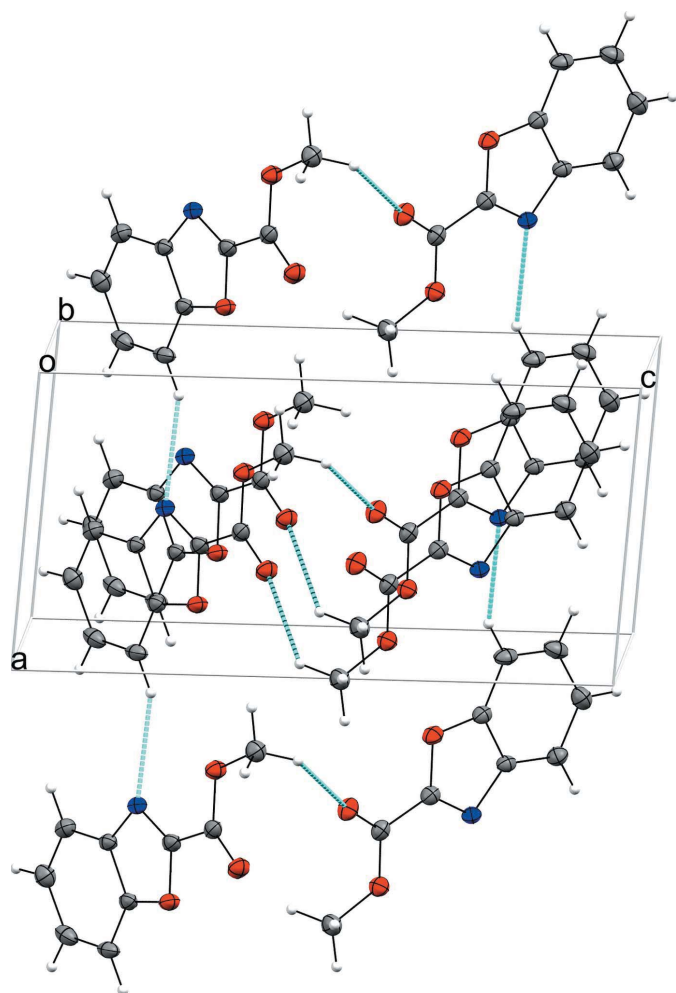


Figure 2
C—H...N and C—H...O hydrogen bonds (blue dotted lines).

2. Structural commentary

The title compound (Fig. 1) crystallizes in the monoclinic space group $P2_1$ and exhibits the expected bond lengths and angles for a benzoxazole. The N1—C1 bond, which corresponds to a double bond, is significantly shorter [1.293 (2) Å] than the other bonds (>1.36 Å) of the oxazole cycle. The molecule is almost planar [$\text{N1—C1—C2—O3} = -6.7 (2)^\circ$]. The heterocyclic and carbonyl oxygen atoms O1 and O2, respectively, are located on the same side with respect to the long axis of the molecule.

3. Supramolecular features

In the crystal structure, molecules are displayed according to the γ packing type, *i.e.* a flattened herringbone featuring stacks of parallel, translationally related molecules (Desiraju *et al.*, 1989; Campbell *et al.*, 2017) (Fig. 2). Neighboring molecules situated in almost perpendicular planes (84.4°) are linked through C—H...N interactions between the heterocyclic nitrogen atom N1 and H9 of an adjacent molecule and weak C—H...O hydrogen bonds between O2 and one hydrogen

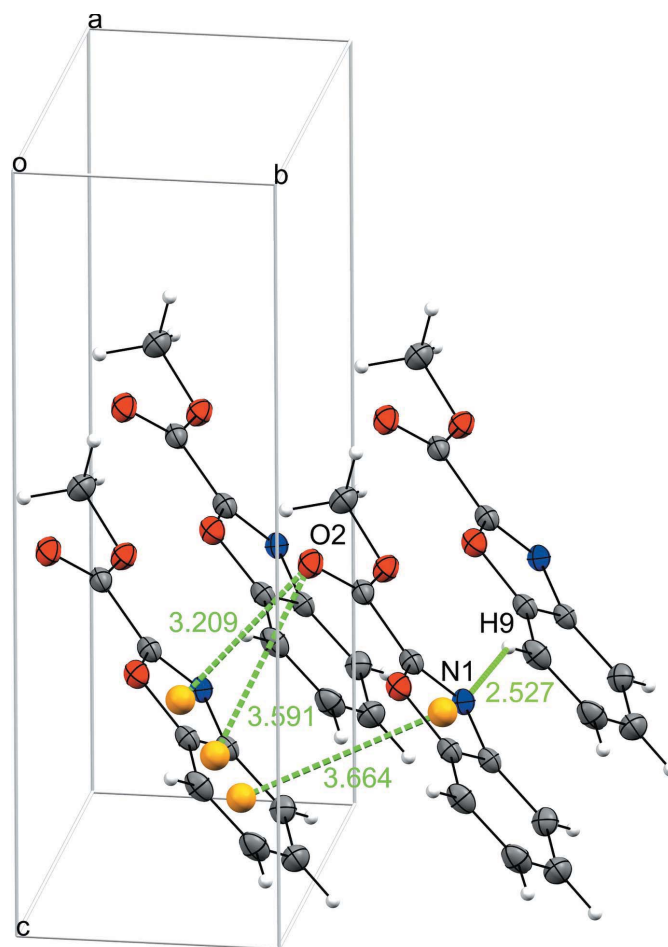


Figure 3
 π - π and C—O... π interactions (green dotted lines). Orange balls represent the ring centroids C_g .

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>
C9–H9...N1 ⁱ	0.95	2.53	3.377 (2)	149
C3–H3C...O2 ⁱⁱ	0.98	2.65	3.389 (2)	133

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

Table 2

C–O... π interactions (Å, °).

*Cg*1 is the centroid of the O1/C1/N1/C5/C4 ring and *Cg*3 is the centroid of the O1/C1/C5–C9 ring.

<i>X</i>	<i>I</i>	<i>J</i>	<i>I</i> ... <i>J</i>	<i>X</i> ... <i>J</i>	<i>X</i> – <i>I</i> ... <i>J</i>
C2	O2	<i>Cg</i> 1 ⁱⁱ	3.2088 (14)	3.5487 (18)	96.39 (10)
C2	O2	<i>Cg</i> 3 ⁱⁱ	3.5912 (14)	3.7321 (17)	87.29 (10)

Symmetry code: (ii) $x, -1 + y, z$.

atom of the methyl group (Table 1, Fig. 2). Strong C–O... π interactions are also important for the stabilization of the structure (Table 2, Fig. 3). Stacking molecules are slipped in the lengthwise and widthwise directions and linked by π – π interactions [centroid–centroid distance = 3.6640 (11) Å] (Table 3).

4. Database survey

Benzoxazole-based molecules have given an umpteen number of crystal structures. A search of the Cambridge Structural Database (CSD, version of November 2020; Groom *et al.*, 2016) found only twelve benzoxazoles substituted by a carbonyl group on the 2-position. In almost half of the cases, the benzoxazole derivative is used as a ligand to complex an Ni, Co or Cu atom (CAYSIG and CAYSOM; Iasco *et al.*, 2012; LAJNAN; Zhang *et al.*, 2010), or incorporated in a macromolecule (NESPUIY; Lim *et al.*, 2012; LUYJUL; Osowska & Miljanić, 2010), resulting in a geometry quite far from that of a small entity. Among the remaining examples, the benzoxazolylcarbonyl moiety may be linked to an aromatic group. When the latter is a phenyl group, the molecule is almost planar (ROFZUI; Boominathan *et al.*, 2014). With another benzoxazole heterocycle, the dihedral angle is only around 8° (AGESUD; Boga *et al.*, 2018). In contrast, this angle almost reaches 71° with a benzoic acid that is involved in many intermolecular interactions (DEJGEE; Ling *et al.*, 1999), and when the benzoxazole and phenyl derivative moieties are attached *via* a flexible linker (KONTEP; Deng *et al.*, 2019). Finally, the benzoxazolylcarbonyl moiety may be linked to an aliphatic moiety, which may be rather bulky like a bornane-1,2-sultam moiety (BAKRIQ; Piątek *et al.*, 2011), or smaller like a morpholine moiety (JAXMED; Xing *et al.*, 2017). In both cases, the network is structured by an interaction between the carbonyl oxygen of one molecule and the hydrogen atom borne by the C7 carbon of a neighbouring molecule. Finally, the framework closest to that of the title compound is an isopropyl 4-acetyl-5-hydroxy-1,3-benzoxazole-2-carboxylate (MIMZUG; Tangellamudi *et al.*, 2018). In

Table 3

π – π interaction (Å, °).

*Cg*1 is the centroid of the O1/C1/N1/C5/C4 ring and *Cg*2 is the centroid of the C4–C9 ring. *Cg**I*...*Cg**J* is the distance between ring centroids. α is the dihedral angle between the planes of the rings *I* and *J*. *Cg**I*_{perp} and *Cg**J*_{perp} are the perpendicular distances of *Cg**I* from ring *J* and of *Cg**J* from ring *I*, respectively. *Cg**I*_{Offset} and *Cg**J*_{Offset} are the distances between *Cg**I* and the perpendicular projection of *Cg**J* on ring *I*, and between *Cg**J* and the perpendicular projection of *Cg**I* on ring *J*, respectively.

<i>I</i>	<i>J</i>	<i>Cg</i> <i>I</i> ... <i>Cg</i> <i>J</i>	α	<i>Cg</i> <i>I</i> _{perp}	<i>Cg</i> <i>J</i> _{perp}	<i>Cg</i> <i>I</i> _{Offset}	<i>Cg</i> <i>J</i> _{Offset}
1	2 ⁱⁱ	3.6640 (11)	0.19 (9)	3.3115 (7)	3.3065 (8)	1.579	1.568

Symmetry code: (ii) $x, -1 + y, z$.

this molecule, the hydroxyl and the acetyl substituents form intramolecular hydrogen bonds while the carbonyl oxygen of one molecule interacts with the isopropyl group of the neighbouring one to form some kind of dimer. In general, planar molecules tend to assemble in layers (AGESUD; Boga *et al.*, 2018; MIMZUG; Tangellamudi *et al.*, 2018) and even in ribbons (JAXMED; Xing *et al.*, 2017).

5. Synthesis and crystallization

The title compound was synthesized according to a variant of the procedure described by Jacobs *et al.* (2017) (Fig. 4). To a mixture of 5-aminophenol (1.09 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in anhydrous tetrahydrofuran (40 mL) at 263 K was added slowly methyl oxalyl chloride (1.34 g, 0.011 mol). The mixture was stirred at room temperature for 3 h and then cooled onto an ice–water bath. Triphenylphosphine (5.64 g, 0.0215 mol), diisopropyl azodicarboxylate (2.25 g, 0.011 mol) and tetrahydrofuran (50 mL) were then added. The solution was allowed to stir at room temperature for 16 h and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO₂, petroleum ether/dichloromethane 70/30 *v/v* until 60/40 *v/v*) to give a white solid (1.2 g) in 83% yield. ¹H NMR (300 MHz, CDCl₃): δ = 7.90 (*ddd*, *J* = 7.9, 1.5, 0.8 Hz, 1H), 7.67 (*ddd*, *J* = 8.1, 1.2, 0.8 Hz, 1H), 7.57–7.44 (*m*, 2H), 4.10 (*s*, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 156.9, 152.5, 150.9, 140.5, 128.2, 125.8, 122.2, 111.7, 53.7.

Single crystals of the title compound, suitable for X-ray analysis, were grown by slow evaporation of a dichloromethane solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were fixed geome-

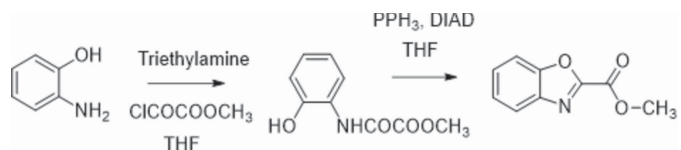


Figure 4
Synthesis route to methyl-1,3-benzoxazole-2-carboxylate.

Table 4

Experimental details.

Crystal data	
Chemical formula	C ₉ H ₇ NO ₃
<i>M_r</i>	177.16
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	193
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.8165 (3), 4.4676 (2), 13.2879 (6)
β (°)	95.1319 (16)
<i>V</i> (Å ³)	403.04 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.40 × 0.30 × 0.10
Data collection	
Diffractionmeter	Bruker D8-Venture Photon III detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.698, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	9084, 1954, 1860
<i>R_{int}</i>	0.022
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.667
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.077, 1.10
No. of reflections	1954
No. of parameters	119
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.20, -0.16

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020), *PLATON* (Spek 2020) and *pubCIF* (Westrip 2010).

trically and treated as riding atoms with C–H = 0.95 Å (aromatic) or 0.98 Å (CH₃), with *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(CH₃).

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supporting information

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Crystal structure of methyl 1,3-benzoxazole-2-carboxylate

Alexandre Poirot, Nathalie Saffon-Merceron, Nadine Leygue, Eric Benoist and Suzanne Fery-Forgues

Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINTE* (Bruker, 2018); data reduction: *SAINTE* (Bruker, 2018); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *PLATON* (Spek 2020) and *pubCIF* (Westrip 2010).

Methyl 1,3-benzoxazole-2-carboxylate

Crystal data

$C_9H_7NO_3$	$F(000) = 184$
$M_r = 177.16$	$D_x = 1.460 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 6.8165 (3) \text{ \AA}$	Cell parameters from 6695 reflections
$b = 4.4676 (2) \text{ \AA}$	$\theta = 3.3\text{--}28.2^\circ$
$c = 13.2879 (6) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$\beta = 95.1319 (16)^\circ$	$T = 193 \text{ K}$
$V = 403.04 (3) \text{ \AA}^3$	Plate, colourless
$Z = 2$	$0.40 \times 0.30 \times 0.10 \text{ mm}$

Data collection

Bruker D8-Venture Photon III detector diffractometer	1954 independent reflections
Radiation source: Fine-focus sealed tube	1860 reflections with $I > 2\sigma(I)$
Phi and ω scans	$R_{\text{int}} = 0.022$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\text{max}} = 28.3^\circ$, $\theta_{\text{min}} = 3.3^\circ$
$T_{\text{min}} = 0.698$, $T_{\text{max}} = 0.746$	$h = -8 \rightarrow 9$
9084 measured reflections	$k = -5 \rightarrow 5$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.0403P]$
$wR(F^2) = 0.077$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1954 reflections	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
119 parameters	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
1 restraint	
Primary atom site location: dual	

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.25255 (16)	0.3885 (3)	0.69933 (9)	0.0329 (3)
O2	0.43981 (19)	−0.0004 (3)	0.57993 (9)	0.0382 (3)
O3	0.73220 (17)	0.2017 (3)	0.63833 (9)	0.0341 (3)
N1	0.54541 (19)	0.5493 (3)	0.77177 (10)	0.0277 (3)
C1	0.4528 (2)	0.3789 (4)	0.70473 (12)	0.0296 (3)
C2	0.5378 (2)	0.1703 (4)	0.63294 (12)	0.0297 (3)
C3	0.8319 (3)	0.0125 (4)	0.57015 (13)	0.0381 (4)
H3A	0.794777	−0.196824	0.579791	0.057*
H3B	0.974729	0.034297	0.584461	0.057*
H3C	0.793506	0.072127	0.500188	0.057*
C4	0.2149 (2)	0.5919 (4)	0.77264 (12)	0.0291 (3)
C5	0.3947 (2)	0.6919 (4)	0.81779 (11)	0.0273 (3)
C6	0.4014 (2)	0.9009 (4)	0.89607 (13)	0.0347 (4)
H6	0.522730	0.971603	0.928121	0.042*
C7	0.2220 (3)	0.9998 (4)	0.92465 (14)	0.0401 (4)
H7	0.220300	1.141802	0.977785	0.048*
C8	0.0429 (3)	0.8959 (5)	0.87719 (15)	0.0406 (4)
H8	−0.076652	0.971435	0.898830	0.049*
C9	0.0342 (2)	0.6878 (5)	0.80018 (14)	0.0370 (4)
H9	−0.087048	0.615698	0.768384	0.044*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0259 (5)	0.0362 (6)	0.0359 (6)	−0.0064 (5)	−0.0013 (4)	0.0001 (5)
O2	0.0406 (6)	0.0349 (6)	0.0380 (6)	−0.0087 (5)	−0.0024 (5)	−0.0035 (5)
O3	0.0315 (6)	0.0342 (6)	0.0364 (6)	−0.0025 (5)	0.0009 (4)	−0.0061 (5)
N1	0.0241 (6)	0.0274 (6)	0.0312 (6)	−0.0017 (5)	0.0008 (4)	0.0002 (5)
C1	0.0288 (7)	0.0286 (7)	0.0311 (7)	−0.0048 (6)	0.0007 (6)	0.0048 (6)
C2	0.0329 (8)	0.0264 (7)	0.0292 (7)	−0.0042 (6)	−0.0006 (6)	0.0039 (6)
C3	0.0384 (9)	0.0380 (10)	0.0381 (8)	0.0030 (8)	0.0047 (7)	−0.0042 (8)
C4	0.0259 (7)	0.0305 (8)	0.0308 (7)	−0.0049 (6)	0.0010 (5)	0.0063 (6)
C5	0.0233 (7)	0.0278 (7)	0.0306 (7)	−0.0019 (6)	0.0013 (5)	0.0057 (6)
C6	0.0311 (8)	0.0357 (8)	0.0366 (8)	−0.0030 (7)	−0.0006 (6)	−0.0014 (7)
C7	0.0438 (10)	0.0370 (9)	0.0407 (9)	0.0020 (8)	0.0096 (7)	−0.0015 (8)
C8	0.0302 (8)	0.0431 (10)	0.0505 (10)	0.0040 (8)	0.0146 (7)	0.0107 (9)
C9	0.0220 (7)	0.0429 (9)	0.0461 (9)	−0.0035 (7)	0.0032 (6)	0.0104 (8)

Geometric parameters (Å, °)

O1—C1	1.3610 (19)	C4—C9	1.384 (2)
O1—C4	1.373 (2)	C4—C5	1.390 (2)
O2—C2	1.200 (2)	C5—C6	1.395 (2)
O3—C2	1.3281 (19)	C6—C7	1.385 (3)
O3—C3	1.452 (2)	C6—H6	0.9500
N1—C1	1.293 (2)	C7—C8	1.402 (3)
N1—C5	1.395 (2)	C7—H7	0.9500
C1—C2	1.488 (2)	C8—C9	1.380 (3)
C3—H3A	0.9800	C8—H8	0.9500
C3—H3B	0.9800	C9—H9	0.9500
C3—H3C	0.9800		
C1—O1—C4	103.51 (12)	C9—C4—C5	123.92 (17)
C2—O3—C3	115.17 (14)	C4—C5—N1	108.64 (15)
C1—N1—C5	103.74 (13)	C4—C5—C6	120.36 (15)
N1—C1—O1	116.33 (15)	N1—C5—C6	131.00 (14)
N1—C1—C2	128.06 (14)	C7—C6—C5	116.58 (16)
O1—C1—C2	115.61 (13)	C7—C6—H6	121.7
O2—C2—O3	126.82 (17)	C5—C6—H6	121.7
O2—C2—C1	123.11 (16)	C6—C7—C8	121.71 (18)
O3—C2—C1	110.07 (14)	C6—C7—H7	119.1
O3—C3—H3A	109.5	C8—C7—H7	119.1
O3—C3—H3B	109.5	C9—C8—C7	122.32 (17)
H3A—C3—H3B	109.5	C9—C8—H8	118.8
O3—C3—H3C	109.5	C7—C8—H8	118.8
H3A—C3—H3C	109.5	C8—C9—C4	115.10 (16)
H3B—C3—H3C	109.5	C8—C9—H9	122.4
O1—C4—C9	128.30 (15)	C4—C9—H9	122.4
O1—C4—C5	107.78 (14)		
C5—N1—C1—O1	0.05 (19)	C9—C4—C5—N1	179.93 (15)
C5—N1—C1—C2	-179.34 (15)	O1—C4—C5—C6	-179.61 (14)
C4—O1—C1—N1	0.03 (18)	C9—C4—C5—C6	0.2 (2)
C4—O1—C1—C2	179.50 (13)	C1—N1—C5—C4	-0.11 (17)
C3—O3—C2—O2	1.7 (2)	C1—N1—C5—C6	179.60 (17)
C3—O3—C2—C1	-178.99 (13)	C4—C5—C6—C7	-0.2 (2)
N1—C1—C2—O2	172.61 (18)	N1—C5—C6—C7	-179.92 (16)
O1—C1—C2—O2	-6.8 (2)	C5—C6—C7—C8	-0.1 (3)
N1—C1—C2—O3	-6.7 (2)	C6—C7—C8—C9	0.6 (3)
O1—C1—C2—O3	173.92 (14)	C7—C8—C9—C4	-0.6 (3)
C1—O1—C4—C9	-179.89 (17)	O1—C4—C9—C8	180.00 (16)
C1—O1—C4—C5	-0.10 (16)	C5—C4—C9—C8	0.2 (3)
O1—C4—C5—N1	0.14 (17)		

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>
C9—H9···N1 ⁱ	0.95	2.53	3.377 (2)	149
C3—H3C···O2 ⁱⁱ	0.98	2.65	3.389 (2)	133

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