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Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate at 100 K

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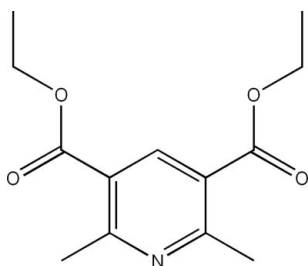
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.048; wR factor = 0.128; data-to-parameter ratio = 17.5.

In the structure of the title compound, $\text{C}_{13}\text{H}_{17}\text{NO}_4$, the packing is stabilized by weak $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ interactions, resulting in the formation of a three-dimensional network.

Related literature

For our studies on nitrogen heterocycles, see: Debache *et al.* (2008*a,b*); Boulcina *et al.* (2007).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{17}\text{NO}_4$
 $M_r = 251.28$
 Monoclinic, $P2_1/c$
 $a = 4.5380$ (6) Å
 $b = 15.440$ (2) Å
 $c = 18.722$ (2) Å
 $\beta = 90.502$ (6)°

$V = 1311.7$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 100$ K
 $0.58 \times 0.34 \times 0.25$ mm

Data collection

Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.942$, $T_{\max} = 0.977$

9968 measured reflections
 2977 independent reflections
 2442 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.128$
 $S = 1.04$
 2977 reflections
 170 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C9}-\text{H9A}\cdots\text{O3}^i$	0.97	2.51	3.2478 (18)	133
$\text{C6}-\text{H6B}\cdots\text{Cg}^{\text{ii}}$	0.96	2.67	3.4279 (16)	136

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - 1, y, z$. Cg is the centroid of the N1, C1–C5 ring.

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SIR2002 (Burla *et al.*, 2003); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and DIAMOND (Brandenburg & Berndt, 2001); software used to prepare material for publication: WinGX (Farrugia, 1999).

The authors are grateful to Dr Thierry Roisnel, Centre de Diffractométrie X (CDIFX) de Rennes, Université de Rennes 1, France, for data-collection facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5104).

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supporting information

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Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate at 100 K

Wassima Ghalem, Ratiba Belhouas, Raouf Boulcina, Sofiane Bouacida and Abdelmadjid Debache

S1. Comment

In continuation of our interest in the synthesis and structure determination of nitrogen heterocyclic compounds (*e.g.* Boulcina *et al.*, 2007; Debache *et al.*, 2008a; Debache *et al.*, 2008b), herein, we report synthesis and crystallographic study of the title compound, (I), (Fig. 1), obtained from the oxidation of the corresponding 1,4-DHP.

The asymmetric unit of title compound contains a pyridine four times substituted by two dimethyl and two diethoxy-carbonyl groups. As expected, The molecule is approximately planar, the r.m.s. deviation for non-H atoms = 0.130 Å with a maximum deviation from the mean plane = -0.3409 (19) Å for C13 atom.

The crystal structure can be described by two crossed layers which dihydropyridine ring is parallel to (-110) and (110) planes respectively (Fig.2).

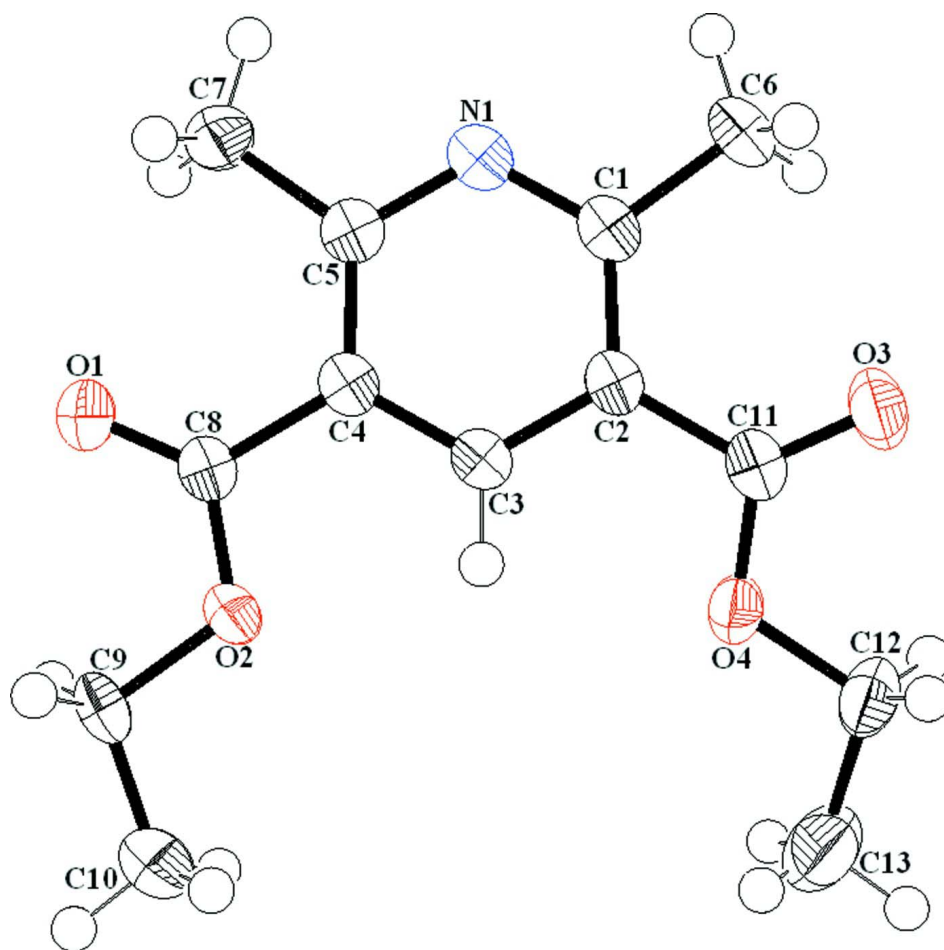
The packing is stabilized by weak intermolecular interactions of C—H \cdots O type (Figure 3) and the layers of dihydropyridine are linked together by C—H \cdots π interactions (figure 4) involving the nitrogen heterocyclic ring (*Cg*), resulting in the formation of three dimensional network and reinforcing a cohesion of structure. Hydrogen-bonding parameters are listed in (table 1).

S2. Experimental

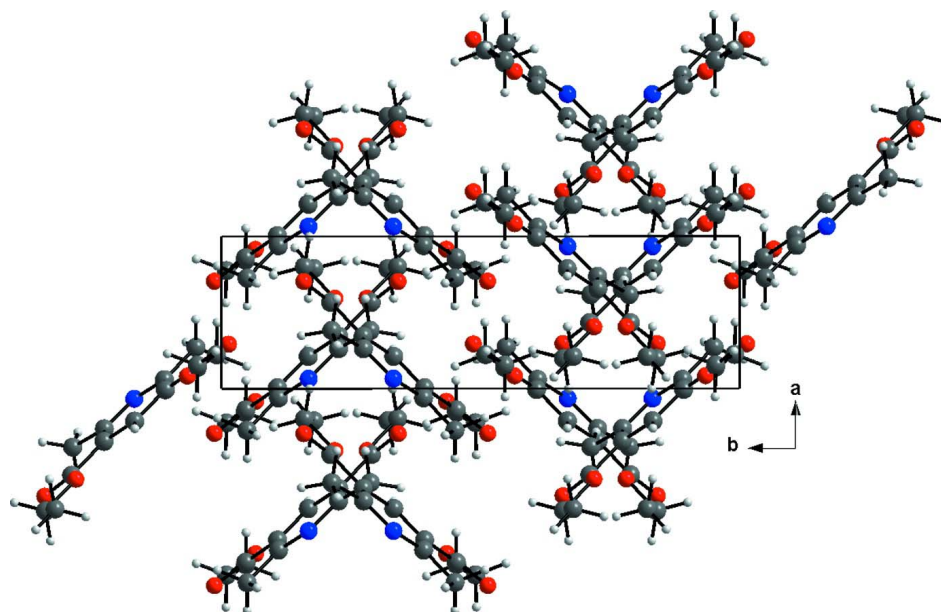
A 25-ml round-bottomed flask was charged with ethyl acetoacetate (2.0 mmol), 2-chloroquinoline-3-carboxaldehyde (1.0 mmol) and ammonium acetate (1.0 mmol), followed by 5 ml of water. The mixture was then refluxed until the reaction was completed (monitored by TLC). The reaction mixture was treated with brine solution, then extracted with ethyl acetate. After evaporation of the solvent, the crude yellow product was recrystallized from ethanol to give DHP in 85% yields. A solution of FeCl₃.6H₂O (0.1 mmol) in H₂O (5 ml) was added to the obtained 1,4-dihydropyridines (1 mmol). The reaction mixture was stirred under refluxing until no starting material is detected. After the reaction was completed, the mixture was cooled to room temperature, quenched with 20 ml of H₂O, neutralized with saturated aqueous solution of NaHCO₃, and then extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate, and concentrated under a reduced pressure. Colourless blocks of (I) were obtained by a slow recrystallization from toluene.

S3. Refinement

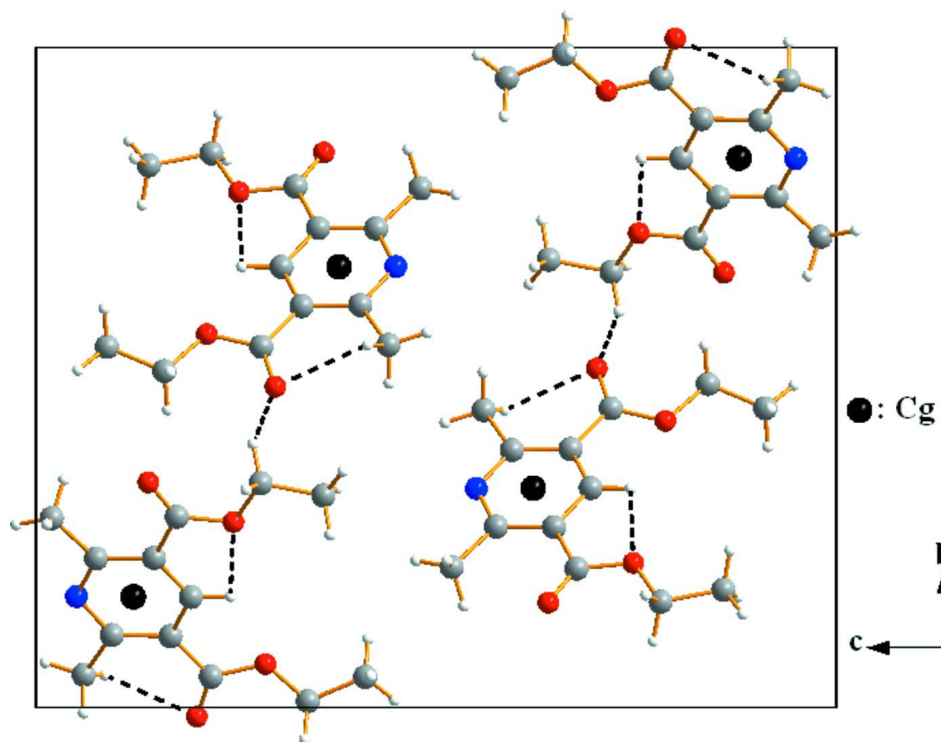
In the final stages of refinement, all H atoms were localized in Fourier maps but introduced in calculated positions, with C—H distances of 0.96 and 0.97 for methylene and methyl H atoms, respectively, and refined using a riding model with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for methylene H atoms. Except for H3 atom were located in a difference Fourier map and refined isotropically. All non-H atoms were refined with anisotropic atomic displacement parameters.

**Figure 1**

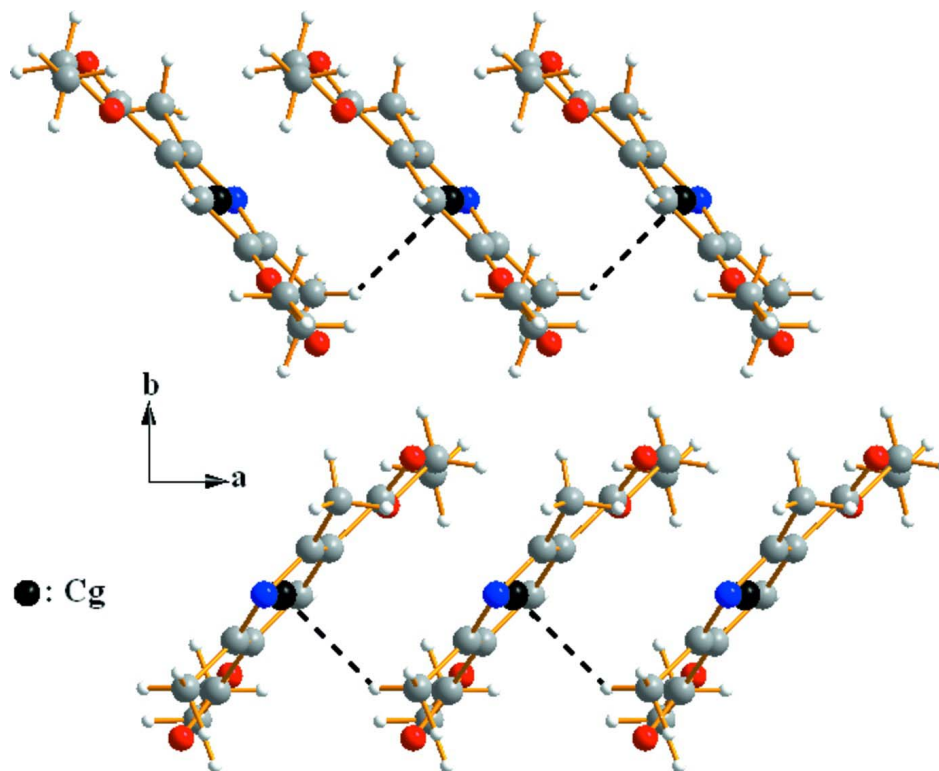
The molecular structure of (I): displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

A diagram of the layered crystal packing of (I) viewed down the c axis.

**Figure 3**

Unit cell of (I) showing hydrogen bond $[C-H\cdots O]$ as dashed line. C_g is the centroid of the nitrogen heterocyclic ring $[N1-C5]$

**Figure 4**

Part of crystal packing of (I) showing interactions between layers [C—H... π] as dashed line. Cg: is the centroid of the nitrogen heterocyclic ring [N1—C5]

Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate

Crystal data

$C_{13}H_{17}NO_4$

$M_r = 251.28$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 4.5380$ (6) Å

$b = 15.440$ (2) Å

$c = 18.722$ (2) Å

$\beta = 90.502$ (6)°

$V = 1311.7$ (3) Å³

$Z = 4$

$F(000) = 536$

$D_x = 1.272$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4103 reflections

$\theta = 2.5$ – 27.4 °

$\mu = 0.09$ mm⁻¹

$T = 100$ K

Block, white

$0.58 \times 0.34 \times 0.25$ mm

Data collection

Bruker APEXII
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.0 pixels mm⁻¹

CCD rotation images, thin slices scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 2002)

$T_{\min} = 0.942$, $T_{\max} = 0.977$

9968 measured reflections

2977 independent reflections

2442 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 27.6$ °, $\theta_{\min} = 2.5$ °

$h = -4 \rightarrow 5$

$k = -19 \rightarrow 19$

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.128$

$S = 1.04$

2977 reflections

170 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 0.4357P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$

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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4395 (3)	0.39005 (9)	0.40522 (8)	0.0176 (3)
C2	0.5062 (3)	0.39184 (8)	0.33193 (7)	0.0167 (3)
C3	0.7120 (3)	0.33252 (8)	0.30658 (8)	0.0161 (3)
H3	0.761 (5)	0.3320 (13)	0.2570 (12)	0.05*
C4	0.8450 (3)	0.27347 (8)	0.35269 (7)	0.0163 (3)
C5	0.7627 (3)	0.27417 (9)	0.42501 (7)	0.0179 (3)
C6	0.2267 (3)	0.45056 (9)	0.44050 (8)	0.0224 (3)
H6A	0.1927	0.4317	0.4886	0.034*
H6B	0.0437	0.4506	0.4144	0.034*
H6C	0.3074	0.508	0.4411	0.034*
C7	0.8829 (4)	0.21296 (10)	0.48038 (8)	0.0248 (3)
H7A	0.7855	0.2228	0.525	0.037*
H7B	1.0907	0.2226	0.4864	0.037*
H7C	0.8495	0.1544	0.4652	0.037*
C8	1.0669 (3)	0.21071 (8)	0.32422 (7)	0.0166 (3)
C9	1.3018 (3)	0.16026 (9)	0.21932 (8)	0.0206 (3)
H9A	1.2478	0.1005	0.2286	0.025*
H9B	1.4994	0.17	0.2378	0.025*
C10	1.2891 (4)	0.17865 (12)	0.14082 (9)	0.0396 (5)
H10A	1.0932	0.1679	0.1231	0.059*
H10B	1.4255	0.1417	0.1165	0.059*
H10C	1.3403	0.2381	0.1325	0.059*
C11	0.3604 (3)	0.45328 (9)	0.28148 (8)	0.0185 (3)
C12	0.2762 (4)	0.49029 (10)	0.16025 (8)	0.0268 (4)
H12A	0.3523	0.5488	0.1643	0.032*

H12B	0.0648	0.4918	0.1674	0.032*
C13	0.3448 (6)	0.45354 (13)	0.08850 (10)	0.0491 (6)
H13A	0.5544	0.4527	0.082	0.074*
H13B	0.2549	0.4887	0.0521	0.074*
H13C	0.2692	0.3956	0.0853	0.074*
N1	0.5655 (3)	0.33183 (7)	0.44964 (6)	0.0189 (3)
O1	1.2043 (2)	0.15896 (6)	0.35969 (6)	0.0236 (3)
O2	1.0940 (2)	0.21896 (6)	0.25334 (5)	0.0201 (2)
O3	0.2067 (2)	0.51374 (7)	0.29916 (6)	0.0286 (3)
O4	0.4163 (2)	0.43422 (6)	0.21325 (5)	0.0238 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0130 (6)	0.0164 (7)	0.0233 (7)	-0.0039 (5)	0.0008 (5)	-0.0038 (5)
C2	0.0142 (6)	0.0138 (6)	0.0219 (7)	-0.0025 (5)	0.0003 (5)	-0.0023 (5)
C3	0.0144 (6)	0.0148 (6)	0.0190 (7)	-0.0036 (5)	0.0008 (5)	-0.0025 (5)
C4	0.0136 (6)	0.0144 (6)	0.0208 (7)	-0.0039 (5)	0.0004 (5)	-0.0019 (5)
C5	0.0162 (7)	0.0161 (6)	0.0213 (7)	-0.0045 (5)	-0.0002 (5)	-0.0007 (5)
C6	0.0198 (7)	0.0206 (7)	0.0269 (8)	0.0005 (6)	0.0046 (6)	-0.0056 (6)
C7	0.0285 (8)	0.0245 (7)	0.0215 (8)	0.0017 (6)	0.0030 (6)	0.0034 (6)
C8	0.0152 (7)	0.0129 (6)	0.0218 (7)	-0.0030 (5)	-0.0001 (5)	-0.0018 (5)
C9	0.0178 (7)	0.0164 (6)	0.0276 (8)	0.0033 (5)	0.0031 (6)	-0.0047 (5)
C10	0.0495 (11)	0.0414 (10)	0.0280 (9)	0.0200 (9)	0.0102 (8)	-0.0003 (7)
C11	0.0143 (6)	0.0149 (6)	0.0264 (8)	-0.0032 (5)	0.0008 (5)	-0.0020 (5)
C12	0.0327 (9)	0.0193 (7)	0.0281 (8)	0.0036 (6)	-0.0081 (6)	0.0023 (6)
C13	0.0827 (16)	0.0362 (10)	0.0283 (10)	0.0183 (10)	-0.0110 (10)	0.0008 (8)
N1	0.0156 (6)	0.0184 (6)	0.0227 (6)	-0.0039 (5)	0.0021 (5)	-0.0022 (5)
O1	0.0253 (6)	0.0200 (5)	0.0255 (6)	0.0054 (4)	-0.0004 (4)	0.0016 (4)
O2	0.0209 (5)	0.0190 (5)	0.0205 (5)	0.0047 (4)	0.0036 (4)	-0.0014 (4)
O3	0.0287 (6)	0.0220 (5)	0.0351 (6)	0.0089 (5)	0.0045 (5)	-0.0002 (5)
O4	0.0301 (6)	0.0188 (5)	0.0225 (6)	0.0076 (4)	-0.0033 (4)	0.0004 (4)

Geometric parameters (Å, °)

C1—N1	1.3483 (19)	C8—O2	1.3397 (17)
C1—C2	1.408 (2)	C9—O2	1.4584 (16)
C1—C6	1.5011 (19)	C9—C10	1.497 (2)
C2—C3	1.3945 (19)	C9—H9A	0.97
C2—C11	1.489 (2)	C9—H9B	0.97
C3—C4	1.3899 (19)	C10—H10A	0.96
C3—H3	0.96 (2)	C10—H10B	0.96
C4—C5	1.4079 (19)	C10—H10C	0.96
C4—C8	1.4986 (19)	C11—O3	1.2132 (17)
C5—N1	1.3466 (18)	C11—O4	1.3374 (18)
C5—C7	1.502 (2)	C12—O4	1.4586 (18)
C6—H6A	0.96	C12—C13	1.493 (2)
C6—H6B	0.96	C12—H12A	0.97

C6—H6C	0.96	C12—H12B	0.97
C7—H7A	0.96	C13—H13A	0.96
C7—H7B	0.96	C13—H13B	0.96
C7—H7C	0.96	C13—H13C	0.96
C8—O1	1.2089 (17)		
N1—C1—C2	121.38 (12)	O2—C9—C10	106.94 (12)
N1—C1—C6	114.49 (12)	O2—C9—H9A	110.3
C2—C1—C6	124.13 (13)	C10—C9—H9A	110.3
C3—C2—C1	117.97 (13)	O2—C9—H9B	110.3
C3—C2—C11	119.84 (12)	C10—C9—H9B	110.3
C1—C2—C11	122.18 (12)	H9A—C9—H9B	108.6
C4—C3—C2	120.54 (13)	C9—C10—H10A	109.5
C4—C3—H3	119.5 (13)	C9—C10—H10B	109.5
C2—C3—H3	119.9 (13)	H10A—C10—H10B	109.5
C3—C4—C5	118.34 (12)	C9—C10—H10C	109.5
C3—C4—C8	119.52 (12)	H10A—C10—H10C	109.5
C5—C4—C8	122.13 (12)	H10B—C10—H10C	109.5
N1—C5—C4	121.15 (13)	O3—C11—O4	122.98 (13)
N1—C5—C7	114.72 (12)	O3—C11—C2	124.78 (13)
C4—C5—C7	124.13 (13)	O4—C11—C2	112.24 (11)
C1—C6—H6A	109.5	O4—C12—C13	107.06 (13)
C1—C6—H6B	109.5	O4—C12—H12A	110.3
H6A—C6—H6B	109.5	C13—C12—H12A	110.3
C1—C6—H6C	109.5	O4—C12—H12B	110.3
H6A—C6—H6C	109.5	C13—C12—H12B	110.3
H6B—C6—H6C	109.5	H12A—C12—H12B	108.6
C5—C7—H7A	109.5	C12—C13—H13A	109.5
C5—C7—H7B	109.5	C12—C13—H13B	109.5
H7A—C7—H7B	109.5	H13A—C13—H13B	109.5
C5—C7—H7C	109.5	C12—C13—H13C	109.5
H7A—C7—H7C	109.5	H13A—C13—H13C	109.5
H7B—C7—H7C	109.5	H13B—C13—H13C	109.5
O1—C8—O2	123.74 (12)	C5—N1—C1	120.60 (12)
O1—C8—C4	125.24 (13)	C8—O2—C9	116.03 (11)
O2—C8—C4	111.02 (11)	C11—O4—C12	115.71 (11)
C1—C2—C3—C4	0.29 (19)	C9—C10—C11—C12	-176.91 (12)
C2—C3—C4—C5	1.11 (19)	C10—C11—C12—C13	13.4 (2)
C3—C4—C5—C6	-1.65 (14)	C11—C12—C13—N1	2.46 (9)
C4—C5—C6—C7	-179.72 (18)	C12—C13—N1—O1	-162.64 (16)
C5—C6—C7—C8	0.52 (11)	C13—N1—O1—O2	3.02 (4)
C6—C7—C8—C9	-172.90 (18)	N1—O1—O2—O3	3.67 (3)
C7—C8—C9—C10	167.30 (19)	O1—O2—O3—O4	-169.36 (7)
C8—C9—C10—C11	2.37 (14)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C9—H9 <i>A</i> \cdots O3 ⁱ	0.97	2.51	3.2478 (18)	133
C6—H6 <i>B</i> \cdots C <i>g</i> ⁱⁱ	0.96	2.67	3.4279 (16)	136

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