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## Structure Reports

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# Methyl 6'-amino-5'-cyano-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-3'-carboxylate

Song-Lei Zhu\* and Ting Liu

Department of Chemistry, Xuzhou Medical College, Xuzhou 221004, People's Republic of China

Correspondence e-mail: songleizhu@126.com

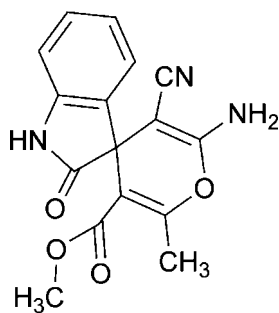
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.045;  $wR$  factor = 0.127; data-to-parameter ratio = 12.8.

In the molecule of the title compound,  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4$ , the atoms of the spiro pyran ring are nearly planar with a maximum deviation of 0.095 (2) Å. The indole and pyran rings are oriented at a dihedral angle of 87.3 (9)°. In the crystal, molecules are linked by intermolecular  $\text{N}-\text{H}\cdots\text{N}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the indole nucleus, see: Da-Silva *et al.* (2001). Compounds carrying the indole moiety exhibit antibacterial and fungicidal activity, see: Joshi & Chand (1982). Spirooxindole ring systems are found in a number of alkaloids like horsifiline, spirotryprostatin and elacomine, see: Abdel-Rahman *et al.* (2004). For our work on the preparation of heterocyclic compounds involving indole derivatives, see: Zhu *et al.* (2007).



## Experimental

### Crystal data

 $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4$  $M_r = 311.29$ 

Monoclinic,  $P2_1/c$   
 $a = 15.0260$  (15) Å  
 $b = 10.0614$  (11) Å  
 $c = 10.4862$  (12) Å  
 $\beta = 105.956$  (1)°  
 $V = 1524.3$  (3) Å<sup>3</sup>

$Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.48 \times 0.46 \times 0.30$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.954$ ,  $T_{\max} = 0.971$

7311 measured reflections  
 2686 independent reflections  
 1868 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.127$   
 $S = 1.04$   
 2686 reflections

210 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.26$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{N3}^{\text{i}}$	0.86	2.09	2.928 (3)	165
$\text{N2}-\text{H2A}\cdots\text{O1}^{\text{ii}}$	0.86	2.17	2.925 (2)	147
$\text{N2}-\text{H2B}\cdots\text{O1}^{\text{iii}}$	0.86	2.34	3.022 (2)	136

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

Data collection: SMART (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

This work was partially supported by the Natural Science Foundation of Higher Education Institutions of Jiangsu Province (grant No. 09KJB150012) and the Special Presidential Foundation of Xuzhou Medical College (grant Nos. 09KJZ19 and 2010KJZ20) and the Open Foundation of the Key Laboratory of Cancer Biotherapy of Xuzhou Medical College (grant No. C0901).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2334).

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## supporting information

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## Methyl 6'-amino-5'-cyano-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-3'-carboxylate

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### S1. Comment

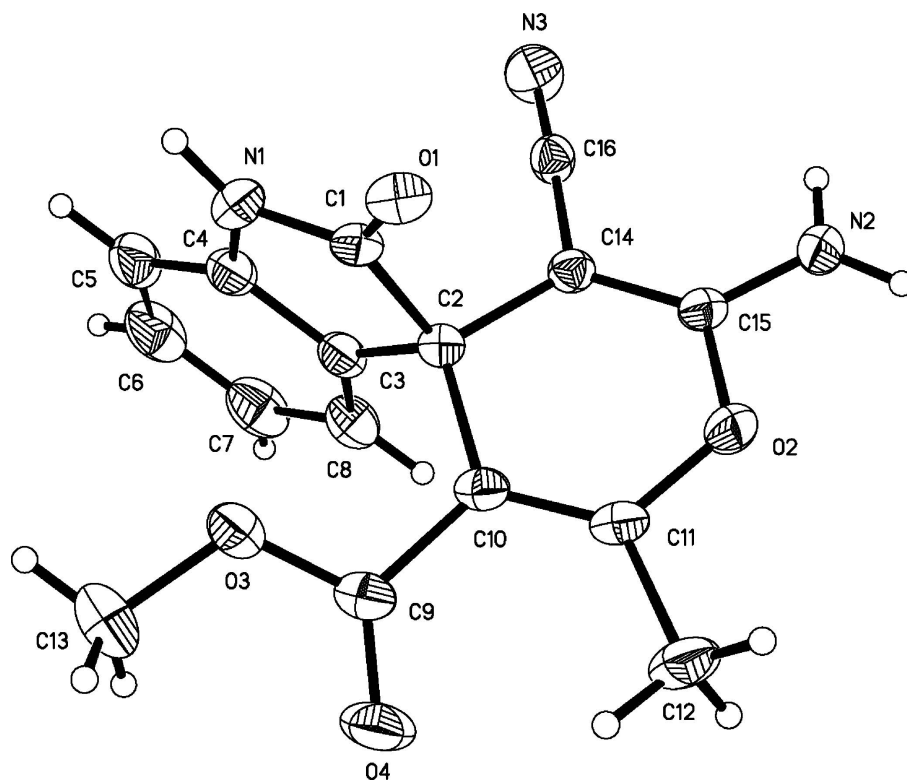
The indole nucleus is the well known heterocycle (Da-Silva *et al.*, 2001). Compounds carrying the indole moiety exhibit antibacterial and fungicidal activities (Joshi & Chand, 1982). Spirooxindole ring systems are found in a number of alkaloids like horsifiline, spirotryprostatin and elacomine (Abdel-Rahman *et al.*, 2004). As a part of our programme devoted to the preparation of heterocyclic compounds involving indole derivatives (Zhu *et al.*, 2007), we have synthesized a series of spirooxindoles *via* reactions of isatins together with malononitrile and methyl 3-oxobutanoate in water. We report herein the crystal structure of the title compound, (I), (Fig. 1). The new formed spiro pyran ring A (O2/C2/C10/C11/C14/C15) adopts nearly planar conformation. The indole system and pyran ring are oriented at a dihedral angle of 87.3 (9)°. In the crystal structure, the molecules are linked by intermolecular N—H···N and N—H···O hydrogen bonds, Table 1, (Fig. 2).

### S2. Experimental

Compound (I) was prepared by the reaction of isatin (1 mmol), malononitrile (1 mmol) and methyl 3-oxobutanoate (1 mmol) in water (5 ml). The reaction was catalyzed by TEBAC (triethylbenzylammonium chloride, 1 mmol). After stirring at 333 K for 5 h, the reaction mixture was cooled and washed with small amount of ethanol. The crude product was filtered and single crystals of the title compound were obtained from ethanol solution by slow evaporation at room temperature (yield; 82%, m.p. 535-536 K). Spectroscopic analysis: IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3458, 3362, 3217, 2212, 1729, 1628, 1464, 1376, 1284, 1210, 1057, 751, 676, 622.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): 10.32 (s, 1H, NH), 7.21-7.25 (m, 3H,  $\text{NH}_2$  + ArH), 6.97-7.03 (m, 2H, ArH), 6.78 (d,  $J = 10.4$  Hz, 1H, ArH), 3.76 (s, 3H,  $\text{CH}_3$ ), 2.25 (s, 3H,  $\text{CH}_3$ ).

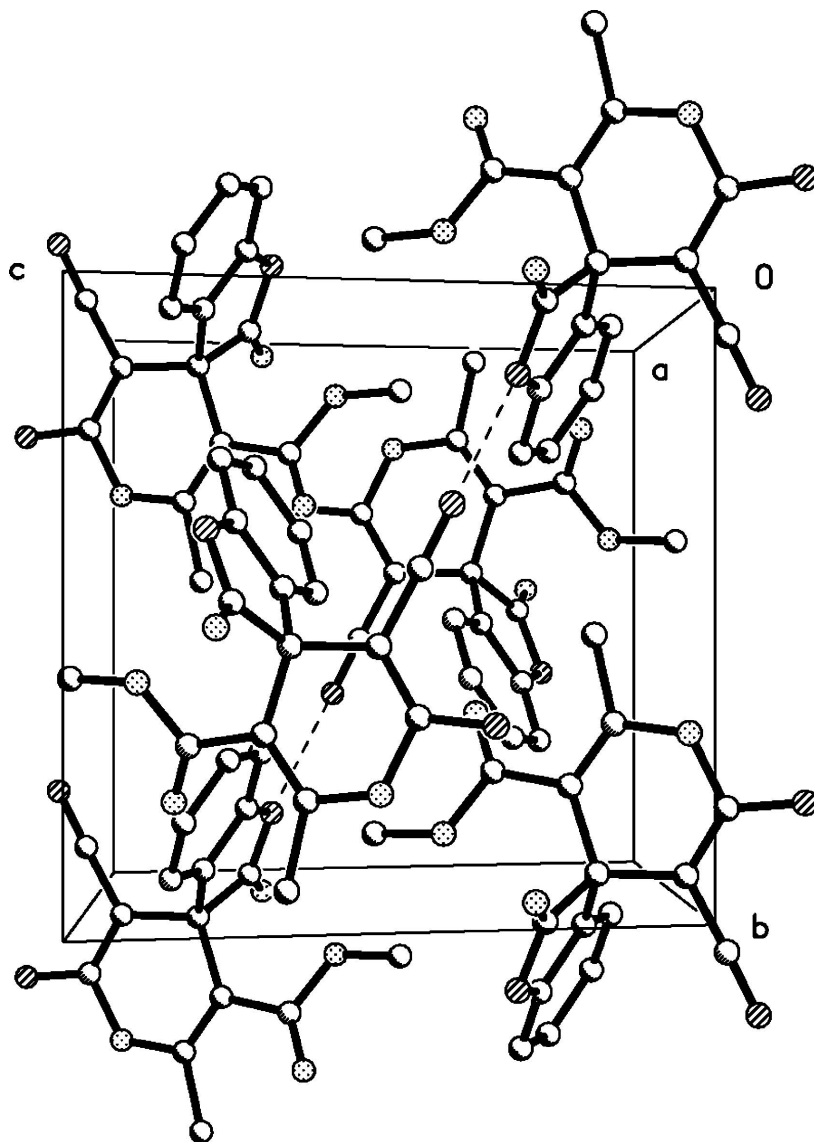
### S3. Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å (for NH) and C—H = 0.93 and 0.96 Å for aromatic and methyl H, respectively and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{N})$ , where  $x = 1.5$  for methyl H and  $x = 1.2$  for all other H atoms.



**Figure 1**

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 45% probability level.



**Figure 2**

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

**Methyl 6'-amino-5'-cyano-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-3'-carboxylate**

*Crystal data*

$C_{16}H_{13}N_3O_4$

$M_r = 311.29$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 15.0260$  (15) Å

$b = 10.0614$  (11) Å

$c = 10.4862$  (12) Å

$\beta = 105.956$  (1)°

$V = 1524.3$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 648$

$D_x = 1.357$  Mg m<sup>-3</sup>

Melting point = 535–536 K

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

Cell parameters from 2324 reflections

$\theta = 2.5$ – $25.2$ °

$\mu = 0.10$  mm<sup>-1</sup>

$T = 298$  K

Block, colorless

$0.48 \times 0.46 \times 0.30$  mm

*Data collection*

Bruker SMART CCD area-detector  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
phi and  $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.954$ ,  $T_{\max} = 0.971$

7311 measured reflections  
2686 independent reflections  
1868 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$   
 $\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 1.4^\circ$   
 $h = -17 \rightarrow 17$   
 $k = -11 \rightarrow 11$   
 $l = -10 \rightarrow 12$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.127$   
 $S = 1.04$   
2686 reflections  
210 parameters  
0 restraints  
Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map  
Hydrogen site location: inferred from  
neighbouring sites  
H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.418P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.19598 (12)	0.37685 (18)	0.79711 (19)	0.0494 (5)
H1	0.1769	0.3191	0.8441	0.059*
N2	0.04118 (12)	0.68602 (18)	0.34455 (18)	0.0465 (5)
H2A	0.0244	0.6167	0.2958	0.056*
H2B	0.0196	0.7628	0.3159	0.056*
N3	0.10939 (15)	0.3376 (2)	0.4093 (2)	0.0615 (6)
O1	0.08135 (10)	0.53203 (14)	0.77799 (14)	0.0455 (4)
O2	0.11839 (10)	0.79566 (13)	0.52291 (15)	0.0471 (4)
O3	0.31267 (10)	0.62292 (17)	0.91261 (15)	0.0547 (4)
O4	0.35592 (12)	0.82091 (18)	0.85572 (19)	0.0712 (6)
C1	0.15256 (14)	0.4927 (2)	0.7562 (2)	0.0384 (5)
C2	0.20453 (13)	0.56267 (19)	0.66513 (19)	0.0349 (5)
C3	0.28596 (13)	0.4696 (2)	0.6779 (2)	0.0407 (5)
C4	0.27590 (15)	0.3614 (2)	0.7541 (2)	0.0464 (6)
C5	0.33919 (17)	0.2580 (2)	0.7802 (3)	0.0633 (7)
H5	0.3323	0.1857	0.8319	0.076*

C6	0.41318 (19)	0.2672 (3)	0.7260 (3)	0.0727 (9)
H6	0.4567	0.1991	0.7413	0.087*
C7	0.42407 (17)	0.3739 (3)	0.6501 (3)	0.0697 (8)
H7	0.4749	0.3774	0.6157	0.084*
C8	0.35978 (15)	0.4768 (3)	0.6242 (2)	0.0528 (6)
H8	0.3665	0.5487	0.5720	0.063*
C9	0.30534 (14)	0.7262 (2)	0.8305 (2)	0.0436 (5)
C10	0.23047 (13)	0.7054 (2)	0.7079 (2)	0.0369 (5)
C11	0.18724 (14)	0.8094 (2)	0.6392 (2)	0.0405 (5)
C12	0.19903 (19)	0.9537 (2)	0.6704 (3)	0.0595 (7)
H12A	0.2337	0.9650	0.7614	0.089*
H12B	0.1393	0.9945	0.6562	0.089*
H12C	0.2316	0.9947	0.6139	0.089*
C13	0.39267 (17)	0.6183 (3)	1.0257 (3)	0.0714 (8)
H13A	0.4466	0.6437	0.9993	0.107*
H13B	0.4006	0.5296	1.0608	0.107*
H13C	0.3843	0.6784	1.0925	0.107*
C14	0.14114 (13)	0.56297 (19)	0.52501 (19)	0.0344 (5)
C15	0.10030 (13)	0.67441 (19)	0.4638 (2)	0.0354 (5)
C16	0.12260 (14)	0.4396 (2)	0.4595 (2)	0.0386 (5)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0516 (11)	0.0375 (11)	0.0572 (13)	−0.0057 (9)	0.0114 (9)	0.0099 (9)
N2	0.0498 (11)	0.0354 (10)	0.0468 (12)	−0.0004 (8)	0.0007 (9)	0.0029 (8)
N3	0.0726 (14)	0.0394 (12)	0.0652 (14)	0.0061 (10)	0.0069 (11)	−0.0167 (10)
O1	0.0468 (9)	0.0417 (9)	0.0516 (10)	−0.0092 (7)	0.0195 (7)	−0.0068 (7)
O2	0.0572 (9)	0.0292 (8)	0.0498 (10)	−0.0015 (7)	0.0064 (8)	−0.0020 (7)
O3	0.0523 (9)	0.0615 (11)	0.0430 (10)	−0.0108 (8)	0.0008 (8)	−0.0016 (8)
O4	0.0635 (11)	0.0758 (13)	0.0673 (12)	−0.0367 (10)	0.0062 (9)	−0.0110 (10)
C1	0.0398 (11)	0.0331 (12)	0.0390 (12)	−0.0088 (9)	0.0053 (9)	−0.0050 (9)
C2	0.0345 (10)	0.0324 (11)	0.0363 (11)	−0.0034 (8)	0.0071 (9)	−0.0007 (9)
C3	0.0358 (11)	0.0414 (13)	0.0401 (12)	−0.0010 (9)	0.0022 (9)	−0.0051 (10)
C4	0.0409 (12)	0.0388 (12)	0.0513 (14)	−0.0006 (10)	−0.0014 (10)	−0.0034 (10)
C5	0.0586 (15)	0.0441 (15)	0.0705 (18)	0.0072 (12)	−0.0105 (14)	0.0011 (12)
C6	0.0519 (15)	0.0648 (19)	0.086 (2)	0.0207 (14)	−0.0061 (15)	−0.0161 (16)
C7	0.0434 (14)	0.085 (2)	0.076 (2)	0.0112 (14)	0.0082 (13)	−0.0167 (17)
C8	0.0405 (12)	0.0635 (16)	0.0523 (15)	0.0028 (11)	0.0091 (11)	−0.0049 (12)
C9	0.0409 (11)	0.0503 (14)	0.0415 (13)	−0.0119 (11)	0.0148 (10)	−0.0103 (11)
C10	0.0387 (11)	0.0376 (12)	0.0365 (12)	−0.0106 (9)	0.0140 (9)	−0.0054 (9)
C11	0.0456 (12)	0.0337 (12)	0.0444 (13)	−0.0115 (9)	0.0162 (10)	−0.0070 (10)
C12	0.0803 (17)	0.0336 (13)	0.0654 (17)	−0.0135 (12)	0.0217 (14)	−0.0105 (11)
C13	0.0563 (16)	0.098 (2)	0.0504 (16)	0.0052 (15)	−0.0013 (13)	−0.0040 (15)
C14	0.0353 (10)	0.0304 (11)	0.0372 (12)	−0.0012 (8)	0.0094 (9)	−0.0029 (9)
C15	0.0363 (11)	0.0303 (11)	0.0400 (13)	−0.0037 (8)	0.0110 (10)	−0.0030 (9)
C16	0.0405 (11)	0.0354 (13)	0.0378 (12)	0.0051 (9)	0.0070 (9)	−0.0005 (10)

*Geometric parameters (Å, °)*

N1—C1	1.347 (3)	C4—C5	1.385 (3)
N1—C4	1.403 (3)	C5—C6	1.384 (4)
N1—H1	0.8600	C5—H5	0.9300
N2—C15	1.325 (3)	C6—C7	1.372 (4)
N2—H2A	0.8600	C6—H6	0.9300
N2—H2B	0.8600	C7—C8	1.391 (3)
N3—C16	1.146 (3)	C7—H7	0.9300
O1—C1	1.220 (2)	C8—H8	0.9300
O2—C15	1.361 (2)	C9—C10	1.472 (3)
O2—C11	1.372 (3)	C10—C11	1.333 (3)
O3—C9	1.334 (3)	C11—C12	1.489 (3)
O3—C13	1.439 (3)	C12—H12A	0.9600
O4—C9	1.202 (2)	C12—H12B	0.9600
C1—C2	1.558 (3)	C12—H12C	0.9600
C2—C14	1.515 (3)	C13—H13A	0.9600
C2—C3	1.517 (3)	C13—H13B	0.9600
C2—C10	1.523 (3)	C13—H13C	0.9600
C3—C8	1.377 (3)	C14—C15	1.352 (3)
C3—C4	1.382 (3)	C14—C16	1.409 (3)
C1—N1—C4	112.07 (18)	C3—C8—C7	118.4 (2)
C1—N1—H1	124.0	C3—C8—H8	120.8
C4—N1—H1	124.0	C7—C8—H8	120.8
C15—N2—H2A	120.0	O4—C9—O3	122.7 (2)
C15—N2—H2B	120.0	O4—C9—C10	126.1 (2)
H2A—N2—H2B	120.0	O3—C9—C10	111.16 (18)
C15—O2—C11	120.13 (15)	C11—C10—C9	120.16 (19)
C9—O3—C13	117.34 (19)	C11—C10—C2	122.26 (18)
O1—C1—N1	126.4 (2)	C9—C10—C2	117.58 (18)
O1—C1—C2	125.59 (19)	C10—C11—O2	122.51 (17)
N1—C1—C2	107.80 (18)	C10—C11—C12	129.5 (2)
C14—C2—C3	111.31 (16)	O2—C11—C12	107.98 (18)
C14—C2—C10	108.97 (16)	C11—C12—H12A	109.5
C3—C2—C10	114.92 (16)	C11—C12—H12B	109.5
C14—C2—C1	107.93 (15)	H12A—C12—H12B	109.5
C3—C2—C1	101.24 (16)	C11—C12—H12C	109.5
C10—C2—C1	112.12 (16)	H12A—C12—H12C	109.5
C8—C3—C4	120.4 (2)	H12B—C12—H12C	109.5
C8—C3—C2	130.7 (2)	O3—C13—H13A	109.5
C4—C3—C2	108.86 (18)	O3—C13—H13B	109.5
C3—C4—C5	121.8 (2)	H13A—C13—H13B	109.5
C3—C4—N1	109.75 (18)	O3—C13—H13C	109.5
C5—C4—N1	128.4 (2)	H13A—C13—H13C	109.5
C6—C5—C4	117.0 (3)	H13B—C13—H13C	109.5
C6—C5—H5	121.5	C15—C14—C16	119.74 (18)
C4—C5—H5	121.5	C15—C14—C2	122.94 (17)

C7—C6—C5	121.8 (3)	C16—C14—C2	117.29 (17)
C7—C6—H6	119.1	N2—C15—C14	128.29 (19)
C5—C6—H6	119.1	N2—C15—O2	110.40 (17)
C6—C7—C8	120.6 (3)	C14—C15—O2	121.30 (18)
C6—C7—H7	119.7	N3—C16—C14	178.0 (2)
C8—C7—H7	119.7		
C4—N1—C1—O1	179.4 (2)	O3—C9—C10—C11	153.2 (2)
C4—N1—C1—C2	4.4 (2)	O4—C9—C10—C2	152.4 (2)
O1—C1—C2—C14	-63.3 (2)	O3—C9—C10—C2	-26.1 (3)
N1—C1—C2—C14	111.82 (18)	C14—C2—C10—C11	12.2 (3)
O1—C1—C2—C3	179.74 (19)	C3—C2—C10—C11	137.8 (2)
N1—C1—C2—C3	-5.2 (2)	C1—C2—C10—C11	-107.3 (2)
O1—C1—C2—C10	56.7 (3)	C14—C2—C10—C9	-168.64 (16)
N1—C1—C2—C10	-128.16 (18)	C3—C2—C10—C9	-42.9 (2)
C14—C2—C3—C8	67.4 (3)	C1—C2—C10—C9	71.9 (2)
C10—C2—C3—C8	-57.0 (3)	C9—C10—C11—O2	178.62 (18)
C1—C2—C3—C8	-178.1 (2)	C2—C10—C11—O2	-2.2 (3)
C14—C2—C3—C4	-110.22 (19)	C9—C10—C11—C12	-3.6 (3)
C10—C2—C3—C4	125.30 (19)	C2—C10—C11—C12	175.6 (2)
C1—C2—C3—C4	4.3 (2)	C15—O2—C11—C10	-9.0 (3)
C8—C3—C4—C5	0.6 (3)	C15—O2—C11—C12	172.84 (18)
C2—C3—C4—C5	178.6 (2)	C3—C2—C14—C15	-140.8 (2)
C8—C3—C4—N1	-179.97 (19)	C10—C2—C14—C15	-13.0 (3)
C2—C3—C4—N1	-2.0 (2)	C1—C2—C14—C15	108.9 (2)
C1—N1—C4—C3	-1.6 (2)	C3—C2—C14—C16	41.4 (2)
C1—N1—C4—C5	177.7 (2)	C10—C2—C14—C16	169.18 (17)
C3—C4—C5—C6	-0.4 (3)	C1—C2—C14—C16	-68.8 (2)
N1—C4—C5—C6	-179.6 (2)	C16—C14—C15—N2	0.6 (3)
C4—C5—C6—C7	0.3 (4)	C2—C14—C15—N2	-177.10 (18)
C5—C6—C7—C8	-0.6 (4)	C16—C14—C15—O2	-178.37 (18)
C4—C3—C8—C7	-0.8 (3)	C2—C14—C15—O2	3.9 (3)
C2—C3—C8—C7	-178.3 (2)	C11—O2—C15—N2	-171.11 (16)
C6—C7—C8—C3	0.8 (4)	C11—O2—C15—C14	8.0 (3)
C13—O3—C9—O4	-9.1 (3)	C15—C14—C16—N3	176 (100)
C13—O3—C9—C10	169.40 (19)	C2—C14—C16—N3	-6 (7)
O4—C9—C10—C11	-28.4 (3)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

<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>
N1—H1 $\cdots$ N3 <sup>i</sup>	0.86	2.09	2.928 (3)	165
N2—H2 <i>A</i> $\cdots$ O1 <sup>ii</sup>	0.86	2.17	2.925 (2)	147
N2—H2 <i>B</i> $\cdots$ O1 <sup>iii</sup>	0.86	2.34	3.022 (2)	136

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