Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

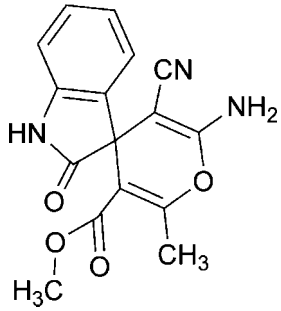
Received 17 November 2010; accepted 18 December 2010

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–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, $C_{16}H_{13}N_3O_4$, 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 N—H···N and N—H···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

$C_{16}H_{13}N_3O_4$ M_r = 311.29
Monoclinic, $P2_1/c$
a = 15.0260 (15) Å
b = 10.0614 (11) Å
c = 10.4862 (12) Å
β = 105.956 (1)°
V = 1524.3 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 K
0.48 × 0.46 × 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_{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
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N3^{i}	0.86	2.09	2.928 (3)	165
N2—H2A···O1^{ii}	0.86	2.17	2.925 (2)	147
N2—H2B···O1^{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).

References

Abdel-Rahman, A. H., Keshk, E. M., Hanna, M. A. & El-Bady, Sh. M. (2004). *Bioorg. Med. Chem.* **12**, 2483–2488.
Bruker (2004). *SAINT* and *SMART*. Bruker AXS Inc., Madinson, Wisconsin, USA.
Da-Silva, J. F. M., Garden, S. J. & Pinto, A. C. (2001). *J. Braz. Chem. Soc.* **12**, 273–324.
Joshi, K. C. & Chand, P. (1982). *Pharmazie*, **37**, 1–12.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhu, S. L., Ji, S. J. & Zhang, Y. (2007). *Tetrahedron*, **63**, 9365–9372.

supplementary materials

Acta Cryst. (2011). E**67**, o238 [**doi:10.1107/S1600536810053274**]

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

S.-L. Zhu and T. Liu

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).

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, ν , cm^{-1}): 3458, 3362, 3217, 2212, 1729, 1628, 1464, 1376, 1284, 1210, 1057, 751, 676, 622. ^{1}H NMR (400 MHz, DMSO-d_6): 10.32 (s, 1H, NH), 7.21-7.25 (m, 3H, NH_2 + ArH), 6.97-7.03 (m, 2H, ArH), 6.78 (d, J = 10.4 Hz, 1H, ArH), 3.76 (s, 3H, CH_3), 2.25 (s, 3H, CH_3).

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, respectivly and constrained to ride on their parent atoms with U_{iso}(H) = xU_{eq}(C,N), where x = 1.5 for methyl H and x = 1.2 for all other H atoms.

Figures

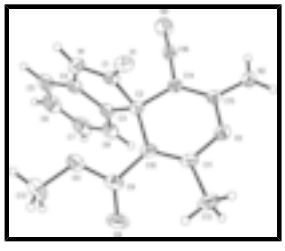


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 45% probability level.

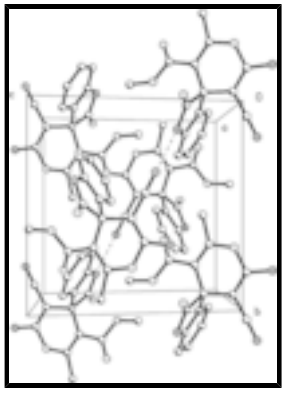


Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

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

Crystal data

$C_{16}H_{13}N_3O_4$	$F(000) = 648$
$M_r = 311.29$	$D_x = 1.357$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point = 535–536 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.0260$ (15) Å	Cell parameters from 2324 reflections
$b = 10.0614$ (11) Å	$\theta = 2.5$–$25.2°$
$c = 10.4862$ (12) Å	$\mu = 0.10$ mm^{-1}
$\beta = 105.956$ (1)°	$T = 298$ K
$V = 1524.3$ (3) Å^3	Block, colorless
$Z = 4$	0.48 × 0.46 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2686 independent reflections
Radiation source: fine-focus sealed tube	1868 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.032$
phi and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 1.4°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -17 \rightarrow 17$
$T_{min} = 0.954$, $T_{max} = 0.971$	$k = -11 \rightarrow 11$
7311 measured reflections	$l = -10 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.127$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.418P]$

	where $P = (F_o^2 + 2F_c^2)/3$
2686 reflections	$(\Delta/\sigma)_{max} < 0.001$
210 parameters	$\Delta\rho_{max} = 0.21$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.26$ e Å^{-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 $F^2 > 2\text{sigma}(F^2)$ 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}
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^2)

	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 (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N3^{i}	0.86	2.09	2.928 (3)	165
N2—H2A···O1^{ii}	0.86	2.17	2.925 (2)	147
N2—H2B···O1^{iii}	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.

Fig. 1

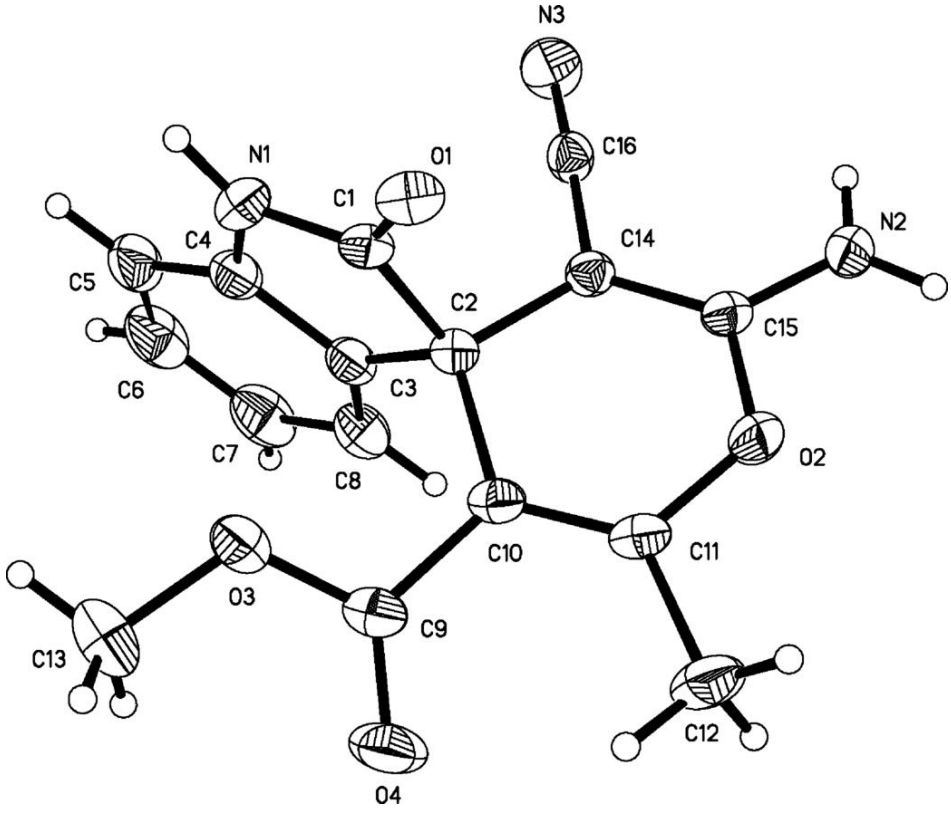

N3
C16
N1
O1
C1
C14
N2
C4
C5
C2
C15
C6
C3
C7
C8
O2
C10
C11
O3
C9
C13
C12
O4

Fig. 2