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(3*RS*)-2′-Amino-2,5′-dioxo-1,2-dihydro-5′*H*-spiro[indole-3,4′-pyrano[3,2-*c*]-chromene]-3′-carbonitrile

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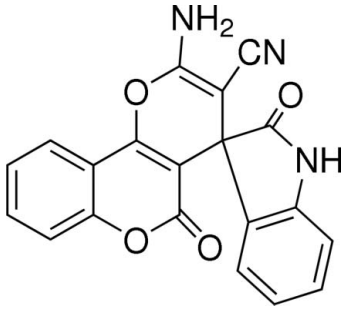
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.048; wR factor = 0.107; data-to-parameter ratio = 12.0.

The title compound, $C_{20}H_{11}N_3O_4$, was synthesized by one-pot reaction of isatin, malononitrile and 4-hydroxycoumarin in water. In the title molecule, the angle between the pyran plane and the indole ring system with a common spiro C atom is 88.23 (8)°. The molecules are linked into a three-dimensional framework by the formation of moderate N—H···O and N—H···N hydrogen bonds.

Related literature

For general background, see: Abdel-Rahman *et al.* (2004); da Silva *et al.* (2001); Joshi & Chand (1982); Wang & Ji (2006). For related literature, see: Bernstein *et al.* (1995); Spek (2003).



Experimental

Crystal data

$C_{20}H_{11}N_3O_4$
M_r = 357.32
Monoclinic, $C2/c$
a = 25.265 (4) Å
b = 11.0076 (12) Å
c = 14.864 (2) Å
β = 125.820 (3)°
V = 3351.9 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 173 (2) K
0.31 × 0.30 × 0.20 mm

Data collection

Rigaku Mercury diffractometer
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.969, T_{max} = 0.980
16029 measured reflections
3068 independent reflections
2674 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.107
S = 1.15
3068 reflections
255 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···O4^{i}	0.90 (2)	1.98 (2)	2.855 (2)	164.2 (19)
N1—H1···O2^{ii}	0.88 (2)	2.00 (2)	2.865 (2)	172.2 (19)
N3—H3A···N2^{iii}	0.91 (2)	2.13 (2)	3.022 (2)	164.7 (18)

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

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2056).

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supplementary materials

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(3*RS*)-2'-Amino-2,5'-dioxo-1,2-dihydro-5'*H*-spiro[indole-3,4'-pyrano[3,2-*c*]chromene]-3'-carbonitrile

S.-L. Zhu, S.-J. Ji and Y. Zhang

Comment

The indole nucleus is a 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 program devoted to the preparation of heterocyclic compounds involving indole derivatives (Wang *et al.*, 2006), we have synthesized a series of spirooxindoles *via* reactions of substituted isatins together with malononitrile and 4-hydroxycoumarin in water. Herein we report the crystal structure of the title compound, (I) (Fig. 1).

In (I), the atoms of the pyran ring (C1/C2/C3/C4/C5/O1) are almost coplanar with the largest deviation of O1 being 0.067 (1) Å from the mean plane (Spek, 2003).

The angle between the pyran plane and the indole ring with a common spiro atom C3 is 88.23 (8)°.

The molecules are linked into a three-dimensional framework structure by the formation of the moderate N—H···O and N—H···N hydrogen bonds. The atom N3 donates a hydrogen H3B to the atom O4^{i} [Symmetry code: (i) −*x* + 1/2, *y* + 1/2, −*z* + 1/2.] forming thus a graph set C(7) - (Fig. 2) (Bernstein *et al.*, 1995). The adjacent chains are connected by the pairs of N1—H1···O2^{ii} hydrogen bonds forming a sheet with a cyclic motif $R_2^2(14)$ (Fig. 3). [Symmetry code: (ii) −*x* + 1, −*y*, −*z* + 1.] The sheet is parallel to (001).

The sheets also interact *via* N3—H3A···N2^{iii} with a graph set $R_2^2(12)$, forming thus a three-dimensional network structure. [Symmetry code: (iii) −*x* + 1/2, −*y* + 1/2, −*z* + 1.]

Experimental

The title compound was prepared by the reaction of isatin (1 mmol), malononitrile (1 mmol) and 4-hydroxycoumarin (1 mmol) in water (5 ml). The reaction was catalyzed by TEBA (triethylbenzylammonium chloride, 1 mmol). After stirring at 333 K for 2 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 95% aqueous ethanol solution by slow evaporation at room temperature (yield 80%; m.p. 563–564 K). Spectroscopic analysis: IR (KBr, n, cm^{-1}): 3357, 3303, 3195, 2955, 2199, 1721, 1667, 1613, 1523, 1474, 1366, 1227, 1132, 1072, 972, 864, 748, 563 ^{1}H NMR (400 MHz, DMSO-d$_6$): 7.95 (d, 1H, J = 8.0 Hz, ArH), 7.77 (t, 1H, J = 7.6 Hz, ArH), 7.67 (br s, 2H, NH2), 7.57 (t, 1H, J = 7.6 Hz, ArH), 7.50 (d, 1H, J = 8.4 Hz, ArH), 7.22 (t, 2H, J = 7.6 Hz, ArH), 6.93 (t, 1H, J = 7.6 Hz, ArH), 6.85 (d, 1H, J = 8.0 Hz, ArH).

Refinement

Despite the fact that all the H atoms were discernible in the difference Fourier maps all the *C*-aryl H atoms were situated into the idealized positions and allowed to ride on their parent atoms, with C–H = 0.95 and U_{iso}(H) = 1.2U_{eq}(C). As to the H atoms attached to the N atoms their coordinates were freely refined since these atoms are involved in the hydrogen bonds

while U_{iso}(H) = 1.2U_{eq}(C) or 1.2 U_{eq}(N).

Figures

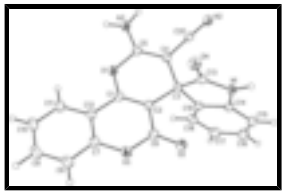

Fig. 1. The molecular structure of the title structure, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

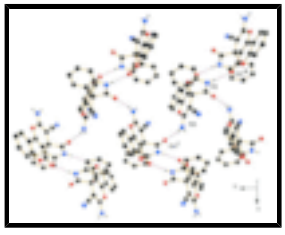

Fig. 2. Part of the title crystal structure, showing the a (001) sheet with the N—H···O hydrogen bonds. For the sake of clarity, the H atoms bonded to C atoms have been omitted. O, N, C atoms are depicted in red, blue and black, respectively. [Symmetry codes: (i) −*x* + 1/2, *y* + 1/2, −*z* + 1/2; (ii) −*x* + 1, −*y*, −*z* + 1.]

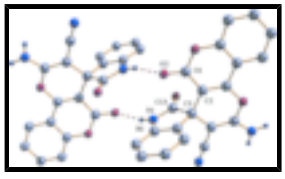

Fig. 3. Part of the title crystal structure, showing a cyclic motif $R_2^2(14)$ of the N1—H1···O2^{ii} hydrogen bond pattern. O, N, C atoms are depicted in red, blue and black, respectively. [Symmetry code: (ii) −*x* + 1, −*y*, −*z* + 1.]

(3*RS*)-2'-Amino-2,5'-dioxo-1,2-dihydro-5'*H*-spiro[indole-3,4'- pyrano[3,2-*c*]chromene]-3'-carbonitrile

Crystal data

$C_{20}H_{11}N_3O_4$	F_{000} = 1472
M_r = 357.32	D_x = 1.416 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 5284 reflections
a = 25.265 (4) Å	θ = 3.0–25.3º
b = 11.0076 (12) Å	μ = 0.10 mm^{-1}
c = 14.864 (2) Å	*T* = 173 (2) K
β = 125.820 (3)º	Block, colourless
V = 3351.9 (8) Å^3	0.31 × 0.30 × 0.20 mm
Z = 8	

Data collection

Rigaku Mercury diffractometer	3068 independent reflections
Radiation source: fine-focus sealed tube	2674 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.035$
$T = 173(2)$ K	$\theta_{max} = 25.4^{o}$
ω scans	$\theta_{min} = 3.0^{o}$
Absorption correction: multi-scan (Jacobson, 1998)	$h = -30 \rightarrow 30$
$T_{min} = 0.969$, $T_{max} = 0.980$	$k = -13 \rightarrow 12$
16029 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.048$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 2.3453P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} < 0.001$
3068 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
255 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
35 constraints	Extinction correction: SHELXL97, $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0011 (2)

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 $F^2 > 2\text{sigma}(F^2)$ 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}
O1	0.27661 (6)	0.34373 (11)	0.22134 (10)	0.0312 (3)
O2	0.48118 (6)	0.16044 (12)	0.36788 (11)	0.0377 (4)
O3	0.42608 (6)	0.24176 (13)	0.20112 (11)	0.0383 (3)

O4	0.37375 (6)	−0.00143 (12)	0.37643 (11)	0.0392 (4)
N1	0.46001 (7)	0.07244 (14)	0.54446 (12)	0.0292 (4)
H1	0.4763 (9)	0.0014 (19)	0.5746 (17)	0.035*
N2	0.31587 (8)	0.17282 (17)	0.55027 (14)	0.0411 (4)
N3	0.21451 (7)	0.32125 (16)	0.28103 (14)	0.0337 (4)
H3A	0.2087 (10)	0.3088 (19)	0.3354 (19)	0.040*
H3B	0.1874 (10)	0.369 (2)	0.2224 (18)	0.040*
C1	0.32893 (8)	0.31103 (16)	0.22205 (15)	0.0274 (4)
C2	0.38132 (8)	0.25213 (16)	0.30683 (14)	0.0267 (4)
C3	0.38915 (8)	0.21902 (15)	0.41237 (14)	0.0254 (4)
C4	0.32491 (8)	0.24481 (16)	0.39560 (14)	0.0267 (4)
C5	0.27354 (8)	0.30078 (16)	0.30509 (14)	0.0275 (4)
C6	0.43259 (9)	0.21535 (16)	0.29663 (15)	0.0302 (4)
C7	0.37258 (9)	0.30335 (17)	0.11484 (15)	0.0331 (4)
C8	0.37033 (10)	0.32238 (19)	0.02064 (17)	0.0407 (5)
H8	0.4044	0.2945	0.0165	0.049*
C9	0.31716 (11)	0.38302 (19)	−0.06707 (17)	0.0433 (5)
H9	0.3148	0.3971	−0.1324	0.052*
C10	0.26699 (10)	0.42402 (19)	−0.06187 (17)	0.0423 (5)
H10	0.2308	0.4657	−0.1233	0.051*
C11	0.26960 (9)	0.40437 (18)	0.03233 (15)	0.0365 (5)
H11	0.2354	0.4326	0.0360	0.044*
C12	0.32293 (9)	0.34260 (16)	0.12260 (14)	0.0301 (4)
C13	0.40581 (8)	0.08170 (16)	0.43953 (15)	0.0281 (4)
C14	0.48718 (8)	0.18667 (16)	0.59080 (15)	0.0287 (4)
C15	0.54420 (9)	0.21274 (19)	0.69336 (16)	0.0370 (5)
H15	0.5713	0.1499	0.7432	0.044*
C16	0.56031 (10)	0.3339 (2)	0.72057 (17)	0.0435 (5)
H16	0.5991	0.3547	0.7905	0.052*
C17	0.52090 (10)	0.42502 (19)	0.64776 (17)	0.0428 (5)
H17	0.5328	0.5075	0.6687	0.051*
C18	0.46399 (9)	0.39779 (17)	0.54424 (16)	0.0342 (4)
H18	0.4371	0.4605	0.4940	0.041*
C19	0.44769 (8)	0.27733 (16)	0.51654 (14)	0.0258 (4)
C20	0.31907 (8)	0.20584 (17)	0.47984 (15)	0.0299 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0286 (7)	0.0382 (8)	0.0272 (6)	0.0093 (5)	0.0166 (6)	0.0074 (6)
O2	0.0327 (7)	0.0409 (8)	0.0439 (8)	0.0105 (6)	0.0248 (7)	0.0131 (6)
O3	0.0372 (8)	0.0490 (8)	0.0364 (8)	0.0095 (6)	0.0259 (7)	0.0107 (6)
O4	0.0398 (8)	0.0314 (7)	0.0386 (8)	−0.0057 (6)	0.0185 (7)	−0.0072 (6)
N1	0.0286 (8)	0.0256 (8)	0.0289 (8)	0.0044 (6)	0.0142 (7)	0.0056 (7)
N2	0.0298 (9)	0.0597 (12)	0.0331 (9)	0.0053 (8)	0.0181 (8)	0.0090 (8)
N3	0.0268 (8)	0.0467 (10)	0.0262 (8)	0.0111 (7)	0.0147 (7)	0.0074 (8)
C1	0.0262 (9)	0.0274 (9)	0.0278 (9)	0.0010 (7)	0.0154 (8)	0.0003 (8)
C2	0.0267 (9)	0.0258 (9)	0.0268 (9)	−0.0001 (7)	0.0152 (8)	0.0011 (7)

C3	0.0225 (9)	0.0266 (9)	0.0252 (9)	0.0020 (7)	0.0129 (7)	0.0018 (7)
C4	0.0242 (9)	0.0303 (10)	0.0241 (9)	0.0023 (7)	0.0133 (8)	0.0011 (7)
C5	0.0271 (9)	0.0310 (10)	0.0239 (9)	0.0011 (7)	0.0146 (8)	−0.0023 (7)
C6	0.0310 (10)	0.0296 (10)	0.0330 (10)	0.0011 (8)	0.0203 (9)	0.0032 (8)
C7	0.0343 (10)	0.0341 (10)	0.0302 (10)	−0.0011 (8)	0.0184 (8)	0.0021 (8)
C8	0.0469 (12)	0.0455 (12)	0.0393 (11)	−0.0030 (10)	0.0306 (10)	0.0017 (10)
C9	0.0580 (13)	0.0429 (12)	0.0324 (11)	−0.0093 (10)	0.0283 (10)	0.0014 (9)
C10	0.0499 (12)	0.0372 (12)	0.0320 (11)	−0.0015 (9)	0.0196 (10)	0.0082 (9)
C11	0.0382 (11)	0.0341 (11)	0.0329 (10)	0.0003 (8)	0.0184 (9)	0.0039 (9)
C12	0.0334 (10)	0.0292 (10)	0.0265 (9)	−0.0015 (8)	0.0169 (8)	0.0022 (8)
C13	0.0280 (9)	0.0299 (10)	0.0294 (9)	−0.0008 (8)	0.0186 (8)	−0.0004 (8)
C14	0.0244 (9)	0.0333 (10)	0.0287 (9)	0.0023 (7)	0.0156 (8)	0.0012 (8)
C15	0.0258 (10)	0.0473 (12)	0.0291 (10)	0.0026 (8)	0.0112 (8)	0.0022 (9)
C16	0.0314 (11)	0.0545 (14)	0.0329 (11)	−0.0094 (9)	0.0122 (9)	−0.0074 (10)
C17	0.0438 (12)	0.0385 (12)	0.0433 (12)	−0.0128 (9)	0.0238 (10)	−0.0089 (10)
C18	0.0352 (10)	0.0308 (10)	0.0367 (10)	−0.0016 (8)	0.0210 (9)	0.0005 (9)
C19	0.0244 (9)	0.0288 (9)	0.0252 (9)	0.0002 (7)	0.0151 (8)	0.0008 (7)
C20	0.0197 (9)	0.0376 (11)	0.0281 (10)	0.0023 (7)	0.0116 (8)	0.0016 (8)

Geometric parameters (Å, °)

O1—C1	1.364 (2)	C4—C20	1.411 (3)
O1—C5	1.375 (2)	C7—C8	1.384 (3)
O2—C6	1.213 (2)	C7—C12	1.394 (3)
O3—C6	1.361 (2)	C8—C9	1.378 (3)
O3—C7	1.379 (2)	C8—H8	0.9500
O4—C13	1.218 (2)	C9—C10	1.390 (3)
N1—C13	1.348 (2)	C9—H9	0.9500
N1—C14	1.405 (2)	C10—C11	1.380 (3)
N1—H1	0.88 (2)	C10—H10	0.9500
N2—C20	1.155 (2)	C11—C12	1.401 (3)
N3—C5	1.334 (2)	C11—H11	0.9500
N3—H3A	0.91 (2)	C14—C15	1.382 (3)
N3—H3B	0.90 (2)	C14—C19	1.386 (2)
C1—C2	1.345 (2)	C15—C16	1.384 (3)
C1—C12	1.438 (2)	C15—H15	0.9500
C2—C6	1.447 (2)	C16—C17	1.381 (3)
C2—C3	1.507 (2)	C16—H16	0.9500
C3—C4	1.518 (2)	C17—C18	1.391 (3)
C3—C19	1.522 (2)	C17—H17	0.9500
C3—C13	1.558 (2)	C18—C19	1.378 (3)
C4—C5	1.353 (2)	C18—H18	0.9500
C1—O1—C5	118.03 (13)	C8—C9—C10	121.36 (19)
C6—O3—C7	121.95 (14)	C8—C9—H9	119.3
C13—N1—C14	111.93 (15)	C10—C9—H9	119.3
C13—N1—H1	120.9 (13)	C11—C10—C9	120.14 (19)
C14—N1—H1	126.9 (13)	C11—C10—H10	119.9
C5—N3—H3A	118.2 (13)	C9—C10—H10	119.9
C5—N3—H3B	117.1 (13)	C10—C11—C12	119.74 (19)

H3A—N3—H3B	121.4 (19)	C10—C11—H11	120.1
C2—C1—O1	123.54 (16)	C12—C11—H11	120.1
C2—C1—C12	122.25 (16)	C7—C12—C11	118.61 (17)
O1—C1—C12	114.19 (15)	C7—C12—C1	116.86 (16)
C1—C2—C6	119.16 (16)	C11—C12—C1	124.45 (17)
C1—C2—C3	123.35 (16)	O4—C13—N1	126.97 (17)
C6—C2—C3	117.47 (15)	O4—C13—C3	124.92 (16)
C2—C3—C4	107.92 (14)	N1—C13—C3	108.10 (15)
C2—C3—C19	114.49 (14)	C15—C14—C19	121.91 (18)
C4—C3—C19	113.41 (14)	C15—C14—N1	128.42 (17)
C2—C3—C13	110.83 (14)	C19—C14—N1	109.67 (15)
C4—C3—C13	108.96 (14)	C14—C15—C16	117.44 (18)
C19—C3—C13	101.03 (13)	C14—C15—H15	121.3
C5—C4—C20	118.91 (16)	C16—C15—H15	121.3
C5—C4—C3	124.04 (16)	C17—C16—C15	121.13 (18)
C20—C4—C3	117.04 (15)	C17—C16—H16	119.4
N3—C5—C4	127.95 (17)	C15—C16—H16	119.4
N3—C5—O1	110.22 (15)	C16—C17—C18	120.98 (19)
C4—C5—O1	121.82 (15)	C16—C17—H17	119.5
O2—C6—O3	117.36 (16)	C18—C17—H17	119.5
O2—C6—C2	123.94 (17)	C19—C18—C17	118.20 (18)
O3—C6—C2	118.69 (15)	C19—C18—H18	120.9
O3—C7—C8	116.93 (17)	C17—C18—H18	120.9
O3—C7—C12	121.00 (16)	C18—C19—C14	120.33 (17)
C8—C7—C12	122.07 (18)	C18—C19—C3	130.72 (16)
C9—C8—C7	118.07 (19)	C14—C19—C3	108.94 (15)
C9—C8—H8	121.0	N2—C20—C4	178.28 (19)
C7—C8—H8	121.0		
C5—O1—C1—C2	−8.6 (2)	O3—C7—C12—C11	−179.78 (17)
C5—O1—C1—C12	170.11 (15)	C8—C7—C12—C11	−0.7 (3)
O1—C1—C2—C6	176.44 (16)	O3—C7—C12—C1	−2.7 (3)
C12—C1—C2—C6	−2.1 (3)	C8—C7—C12—C1	176.34 (18)
O1—C1—C2—C3	−2.0 (3)	C10—C11—C12—C7	0.6 (3)
C12—C1—C2—C3	179.40 (16)	C10—C11—C12—C1	−176.26 (18)
C1—C2—C3—C4	9.1 (2)	C2—C1—C12—C7	3.5 (3)
C6—C2—C3—C4	−169.42 (15)	O1—C1—C12—C7	−175.24 (15)
C1—C2—C3—C19	−118.24 (19)	C2—C1—C12—C11	−179.66 (18)
C6—C2—C3—C19	63.3 (2)	O1—C1—C12—C11	1.6 (3)
C1—C2—C3—C13	128.30 (18)	C14—N1—C13—O4	175.88 (18)
C6—C2—C3—C13	−50.2 (2)	C14—N1—C13—C3	−5.80 (19)
C2—C3—C4—C5	−6.8 (2)	C2—C3—C13—O4	−54.4 (2)
C19—C3—C4—C5	121.10 (19)	C4—C3—C13—O4	64.2 (2)
C13—C3—C4—C5	−127.24 (18)	C19—C3—C13—O4	−176.12 (17)
C2—C3—C4—C20	172.28 (16)	C2—C3—C13—N1	127.26 (15)
C19—C3—C4—C20	−59.8 (2)	C4—C3—C13—N1	−114.14 (15)
C13—C3—C4—C20	51.9 (2)	C19—C3—C13—N1	5.52 (18)
C20—C4—C5—N3	−2.9 (3)	C13—N1—C14—C15	−176.13 (18)
C3—C4—C5—N3	176.17 (17)	C13—N1—C14—C19	3.6 (2)
C20—C4—C5—O1	178.32 (16)	C19—C14—C15—C16	1.0 (3)

C3—C4—C5—O1	−2.6 (3)	N1—C14—C15—C16	−179.36 (18)
C1—O1—C5—N3	−168.19 (15)	C14—C15—C16—C17	−0.1 (3)
C1—O1—C5—C4	10.8 (2)	C15—C16—C17—C18	−0.6 (3)
C7—O3—C6—O2	179.72 (16)	C16—C17—C18—C19	0.5 (3)
C7—O3—C6—C2	0.7 (3)	C17—C18—C19—C14	0.3 (3)
C1—C2—C6—O2	−178.94 (18)	C17—C18—C19—C3	178.86 (18)
C3—C2—C6—O2	−0.4 (3)	C15—C14—C19—C18	−1.1 (3)
C1—C2—C6—O3	0.0 (3)	N1—C14—C19—C18	179.20 (16)
C3—C2—C6—O3	178.58 (15)	C15—C14—C19—C3	−179.91 (16)
C6—O3—C7—C8	−178.35 (17)	N1—C14—C19—C3	0.4 (2)
C6—O3—C7—C12	0.8 (3)	C2—C3—C19—C18	58.7 (2)
O3—C7—C8—C9	179.59 (17)	C4—C3—C19—C18	−65.7 (2)
C12—C7—C8—C9	0.5 (3)	C13—C3—C19—C18	177.87 (18)
C7—C8—C9—C10	−0.1 (3)	C2—C3—C19—C14	−122.58 (16)
C8—C9—C10—C11	0.0 (3)	C4—C3—C19—C14	112.97 (17)
C9—C10—C11—C12	−0.2 (3)	C13—C3—C19—C14	−3.45 (18)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3B···O4^{i}	0.90 (2)	1.98 (2)	2.855 (2)	164.2 (19)
N1—H1···O2^{ii}	0.88 (2)	2.00 (2)	2.865 (2)	172.2 (19)
N3—H3A···N2^{iii}	0.91 (2)	2.13 (2)	3.022 (2)	164.7 (18)

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+1/2; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+1/2, −*y*+1/2, −*z*+1.

Fig. 1

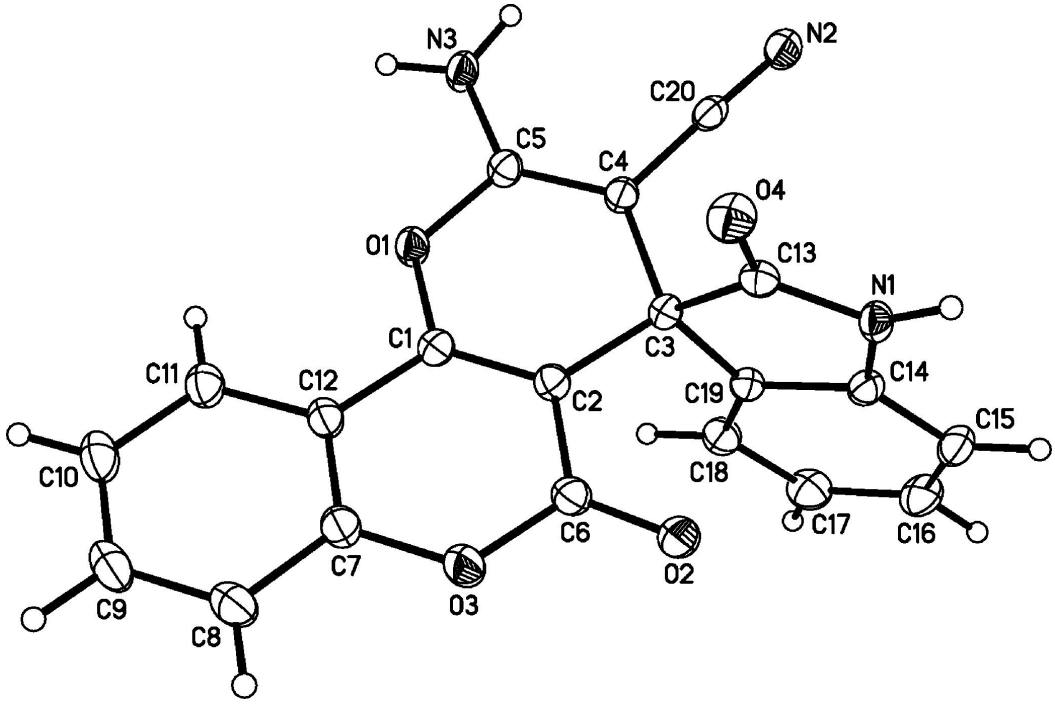
N3
N2
C20
C5
C4
O4
O1
C13
N1
C1
C3
C11
C12
C2
C19
C14
C15
C10
C18
C6
C17
C16
C7
O2
C9
O3
C8

Fig. 2

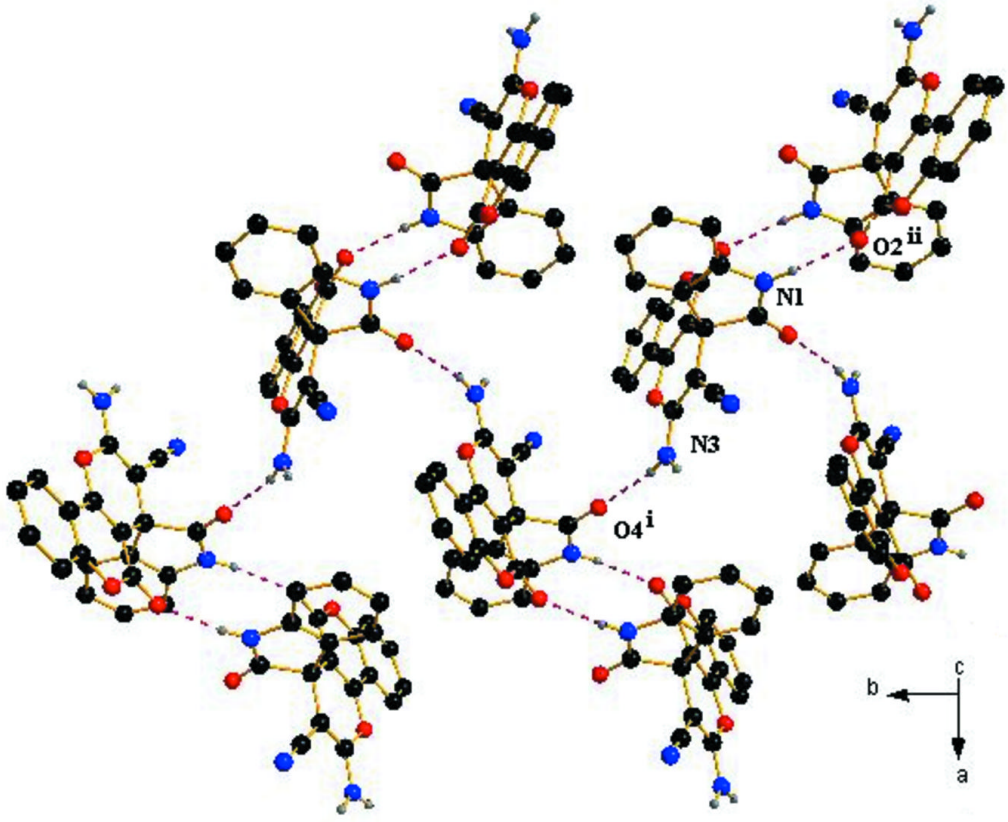

Fig. 3