

# 1'-Methyl-4'-(4-methylphenyl)dispiro[1-benzopyran-3(4H),3'-pyrrolidine-2',3''-indoline]-2,2''-dione

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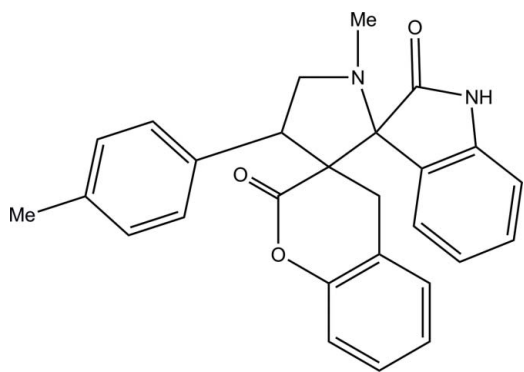
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.050;  $wR$  factor = 0.153; data-to-parameter ratio = 24.2.

In the title compound,  $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_3$ , the pyrrolidine ring adopts a twist conformation, while the six-membered pyranone ring of the coumarin ring system is in a sofa conformation. In the crystal, pairs of  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds link the molecules into inversion  $R_2^2(8)$  dimers. These dimers are further connected *via*  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For applications of pyrrolidine derivatives, see: Huryn *et al.* (1991); Suzuki *et al.* (1994); Waldmann (1995). For ring puckering parameters, see: Cremer & Pople (1975) and for asymmetry parameters, see: Duax *et al.* (1976). For closely related pyrrolidine structures, see: Selvanayagam *et al.* (2011); Ali *et al.* (2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



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## Experimental

### Crystal data

$\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_3$   
 $M_r = 424.48$   
 Monoclinic,  $P2_1/c$   
 $a = 10.4543$  (3) Å  
 $b = 14.6018$  (4) Å  
 $c = 14.7266$  (4) Å  
 $\beta = 104.043$  (2)°  
 $V = 2180.85$  (10) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.26 \times 0.23 \times 0.18$  mm

### Data collection

Bruker APEXII CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.978$ ,  $T_{\max} = 0.985$   
 30221 measured reflections  
 7055 independent reflections  
 4544 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.153$   
 $S = 1.02$   
 7055 reflections  
 291 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.23$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}^i$	0.86	2.02	2.874 (1)	174
$\text{C5}-\text{H5B}\cdots\text{O3}^{ii}$	0.96	2.59	3.407 (2)	143

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

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5735).

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**supplementary materials**

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## 1'-Methyl-4'-(4-methylphenyl)dispiro[1-benzopyran-3(4H),3'-pyrrolidine-2',3''-indoline]-2,2''-dione

D. Lakshmanan, S. Murugavel, D. Kannan and M. Bakthadoss

### Comment

Highly functionalized pyrrolidines have gained much interest in the past few years as they constitute the main structural element of many natural and synthetic pharmacologically active compounds (Waldmann, 1995). Optically active pyrrolidines have been used as intermediates, chiral ligands or auxiliaries in controlled asymmetric synthesis (Suzuki *et al.*, 1994; Huryñ *et al.*, 1991). In view of this importance, the crystal structure of the title compound has been carried out and the results are presented here.

The title compound consists of a pyrrolidine ring connected to a oxindole ring system at C1, a coumarine moiety at C2 and a benzene ring at C3. The X-ray analysis confirms the molecular structure and atom connectivity as illustrated in Fig. 1.

The pyrrolidine (N1/C1–C4) ring adopts a twist conformation, with twist about the C4–N1 bond; the puckering parameters (Cremer & Pople, 1975),  $q_2 = 0.4216(14) \text{ \AA}$  and  $\varphi_2 = 156.9(2)^\circ$ , and asymmetry parameters (Duax *et al.*, 1976)  $\Delta C_2[C4–N1] = 5.0 \text{ \AA}$ . The six membered pyranone ring (O2/C2/C13/C14/C19/C20) of the coumarine moiety adopts screw-boat conformation as indicated from the puckering parameters:  $Q = 0.5296(15) \text{ \AA}$ ,  $\theta = 65.9(2)^\circ$  and  $\varphi = 215.9(2)^\circ$ . The oxindole unit (N2/C1/C6–C12) is essentially planar [maximum deviation =  $0.048(1) \text{ \AA}$  for the C1 atom] and is oriented at a dihedral angles of  $87.1(1)^\circ$  and  $28.6(1)^\circ$ , respectively, with the pyrrolidine and coumarine rings. The sum of angles at N1 of the pyrrolidine ring ( $337^\circ$ ) is in accordance with  $sp^3$  hybridization, and the sum of angles at N2 of the indole moiety ( $360^\circ$ ) is in accordance with  $sp^2$  hybridization. The geometric parameters of the title molecule agrees well with those reported for similar structures (Selvanayagam *et al.*, 2011; Ali *et al.*, 2010).

The molecular structure is stabilized by C3–H3 $\cdots$ O3 and C13–H13A $\cdots$ O1 intramolecular hydrogen bonds, forming S(5) and S(6) ring motifs, respectively (Bernstein *et al.*, 1995) (Table 1). The molecular structure is further stabilized by an intramolecular  $\pi$ – $\pi$  interactions with Cg1–Cg2 separation of  $3.539(1) \text{ \AA}$ . (Fig. 2; Cg1 and Cg2 are the centroids of the (N2/C1/C6/C7/C12) indole ring, (C14–C19) benzene ring, respectively). The crystal packing is stabilized by intermolecular N–H $\cdots$ O and C–H $\cdots$ O hydrogen bonds. The molecules at  $x, y, z$  and  $2-x, 2-y, -z$  are linked by N2–H2 $\cdots$ O1 hydrogen bonds into cyclic centrosymmetric  $R_2^2(8)$  dimers. This dimers are further connected by C5–H5B $\cdots$ O3 hydrogen bonds forming supramolecular zig zag chains along the  $c$  axis (Fig. 3).

### Experimental

A mixture of *E*-3-(4-methylbenzylidene)chroman-2-one (0.125 g, 0.5 mmol), isatin (0.08 g, 0.55 mmol) and *N*-methylglycine (0.025 g, 0.55 mmol) in toluene (5 ml) as solvent was allowed to reflux for 6 hours. After work up, the crude mass was purified by column chromatography to yield the pure product (0.195 g, 92% yield). The compound was recrystallized from ethyl acetate solvent. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a ethylacetate solution at room temperature.

## Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.93–0.98 Å and constrained to ride on their parent atom, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{C})$  for other H atoms.

## Figures

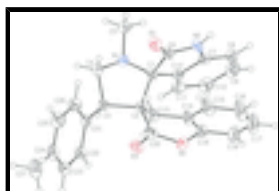


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as a small cycles of arbitrary radius.

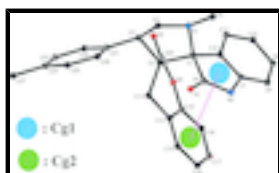


Fig. 2. A view of the  $\pi \cdots \pi$  interactions (dotted lines) in the molecular structure of the title compound. Cg1 and Cg2 are the centroids of the (N2/C1/C6/C7/C12) indole ring and (C14–C19) benzene ring, respectively.

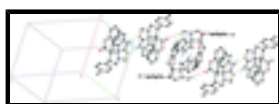


Fig. 3. View of supramolecular zig zag chain in (I) with N—H $\cdots$ O (blue dashed lines) and C—H $\cdots$ O (red dashed lines) hydrogen bonds along the *c* axis. [ Colour code: O(red), N(blue), C(black) & H(green).

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### Crystal data

$\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_3$

$M_r = 424.48$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.4543$  (3) Å

$b = 14.6018$  (4) Å

$c = 14.7266$  (4) Å

$\beta = 104.043$  (2)°

$V = 2180.85$  (10) Å<sup>3</sup>

$Z = 4$

$F(000) = 896$

$D_x = 1.293$  Mg m<sup>-3</sup>

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

Cell parameters from 7063 reflections

$\theta = 2.0$ – $31.2$ °

$\mu = 0.09$  mm<sup>-1</sup>

$T = 293$  K

Block, colourless

$0.26 \times 0.23 \times 0.18$  mm

### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

Detector resolution: 10.0 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

7055 independent reflections

4544 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 31.2$ °,  $\theta_{\text{min}} = 2.0$ °

$h = -15 \rightarrow 14$

$k = -21 \rightarrow 21$

(SADABS; Sheldrick, 1996)

$T_{\min} = 0.978$ ,  $T_{\max} = 0.985$

$l = -20 \rightarrow 21$

30221 measured reflections

### Refinement

Refinement on  $F^2$

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.050$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.153$

H-atom parameters constrained

$S = 1.02$

$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 0.398P]$

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

7055 reflections

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

291 parameters

$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$

0 restraints

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

### 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.80511 (12)	0.84780 (8)	0.09959 (8)	0.0326 (2)
C2	0.80733 (12)	0.86879 (8)	0.20643 (8)	0.0335 (2)
C3	0.65980 (12)	0.89026 (9)	0.20385 (9)	0.0367 (3)
H3	0.6207	0.8333	0.2197	0.044*
C4	0.59877 (13)	0.90885 (11)	0.10112 (10)	0.0449 (3)
H4A	0.5042	0.8989	0.0858	0.054*
H4B	0.6166	0.9709	0.0841	0.054*
C5	0.63008 (17)	0.84632 (12)	-0.04637 (10)	0.0548 (4)
H5A	0.5385	0.8313	-0.0695	0.082*
H5B	0.6830	0.8033	-0.0705	0.082*
H5C	0.6459	0.9070	-0.0662	0.082*
C6	0.87724 (13)	0.92422 (9)	0.05686 (9)	0.0383 (3)
C7	0.97873 (13)	0.79028 (9)	0.03856 (9)	0.0382 (3)
C8	1.06331 (16)	0.72827 (11)	0.01407 (11)	0.0528 (4)
H8	1.1311	0.7470	-0.0125	0.063*

## supplementary materials

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C9	1.04343 (19)	0.63686 (12)	0.03057 (13)	0.0626 (5)
H9	1.1002	0.5932	0.0161	0.075*
C10	0.94146 (19)	0.60908 (10)	0.06787 (12)	0.0586 (4)
H10	0.9291	0.5469	0.0767	0.070*
C11	0.85666 (16)	0.67219 (9)	0.09259 (10)	0.0455 (3)
H11	0.7871	0.6532	0.1172	0.055*
C12	0.87840 (13)	0.76409 (8)	0.07963 (8)	0.0348 (3)
C13	0.90158 (13)	0.94596 (10)	0.25105 (10)	0.0450 (3)
H13A	0.8788	1.0018	0.2152	0.054*
H13B	0.8931	0.9573	0.3142	0.054*
C14	1.04058 (14)	0.91967 (12)	0.25330 (11)	0.0520 (4)
C15	1.13597 (18)	0.97997 (16)	0.23772 (14)	0.0717 (6)
H15	1.1152	1.0414	0.2254	0.086*
C16	1.2617 (2)	0.9486 (2)	0.24059 (18)	0.0957 (8)
H16	1.3259	0.9893	0.2313	0.115*
C17	1.2920 (2)	0.8584 (2)	0.2570 (2)	0.1000 (9)
H17	1.3766	0.8380	0.2578	0.120*
C18	1.19962 (18)	0.79673 (18)	0.27257 (14)	0.0791 (6)
H18	1.2205	0.7352	0.2840	0.095*
C19	1.07479 (14)	0.82966 (13)	0.27055 (10)	0.0544 (4)
C20	0.85238 (14)	0.78283 (10)	0.26401 (9)	0.0418 (3)
C21	0.63774 (12)	0.96203 (9)	0.27238 (10)	0.0395 (3)
C22	0.64635 (16)	0.93919 (11)	0.36474 (11)	0.0509 (4)
H22	0.6657	0.8791	0.3843	0.061*
C23	0.62671 (17)	1.00382 (13)	0.42869 (12)	0.0584 (4)
H23	0.6352	0.9864	0.4906	0.070*
C24	0.59504 (15)	1.09288 (12)	0.40314 (13)	0.0560 (4)
C25	0.5856 (2)	1.11562 (12)	0.31114 (15)	0.0677 (5)
H25	0.5637	1.1754	0.2915	0.081*
C26	0.60777 (18)	1.05209 (11)	0.24708 (12)	0.0576 (4)
H26	0.6024	1.0703	0.1858	0.069*
C27	0.5729 (2)	1.16348 (15)	0.47218 (17)	0.0806 (6)
H27A	0.6150	1.2198	0.4624	0.121*
H27B	0.6095	1.1420	0.5347	0.121*
H27C	0.4800	1.1737	0.4635	0.121*
N1	0.66462 (11)	0.84226 (8)	0.05524 (8)	0.0395 (2)
N2	0.97478 (11)	0.88502 (8)	0.02528 (8)	0.0430 (3)
H2	1.0282	0.9148	0.0000	0.052*
O1	0.84748 (11)	1.00547 (6)	0.05046 (8)	0.0525 (3)
O2	0.98473 (10)	0.76670 (8)	0.29036 (7)	0.0546 (3)
O3	0.78215 (12)	0.72821 (8)	0.28723 (8)	0.0607 (3)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0345 (6)	0.0302 (6)	0.0358 (6)	-0.0025 (4)	0.0135 (5)	0.0040 (4)
C2	0.0307 (6)	0.0370 (6)	0.0351 (6)	-0.0028 (5)	0.0122 (5)	0.0013 (5)
C3	0.0304 (6)	0.0405 (6)	0.0426 (7)	-0.0013 (5)	0.0154 (5)	0.0039 (5)

C4	0.0343 (6)	0.0549 (8)	0.0459 (7)	0.0033 (6)	0.0108 (6)	0.0029 (6)
C5	0.0553 (9)	0.0659 (10)	0.0397 (7)	0.0022 (7)	0.0051 (6)	0.0038 (7)
C6	0.0412 (7)	0.0345 (6)	0.0434 (7)	-0.0018 (5)	0.0184 (5)	0.0055 (5)
C7	0.0409 (7)	0.0403 (7)	0.0343 (6)	0.0031 (5)	0.0110 (5)	-0.0006 (5)
C8	0.0489 (8)	0.0610 (10)	0.0504 (8)	0.0121 (7)	0.0157 (7)	-0.0087 (7)
C9	0.0666 (11)	0.0519 (9)	0.0654 (10)	0.0217 (8)	0.0080 (9)	-0.0158 (8)
C10	0.0752 (11)	0.0342 (7)	0.0583 (9)	0.0090 (7)	0.0007 (8)	-0.0044 (6)
C11	0.0564 (8)	0.0341 (6)	0.0432 (7)	-0.0043 (6)	0.0066 (6)	0.0020 (5)
C12	0.0406 (6)	0.0319 (6)	0.0315 (6)	0.0005 (5)	0.0079 (5)	0.0013 (4)
C13	0.0368 (7)	0.0510 (8)	0.0505 (8)	-0.0090 (6)	0.0172 (6)	-0.0151 (6)
C14	0.0345 (7)	0.0732 (10)	0.0499 (8)	-0.0107 (7)	0.0131 (6)	-0.0233 (7)
C15	0.0484 (9)	0.0934 (14)	0.0787 (12)	-0.0280 (9)	0.0260 (9)	-0.0347 (10)
C16	0.0436 (10)	0.144 (2)	0.1069 (18)	-0.0334 (13)	0.0318 (11)	-0.0466 (17)
C17	0.0351 (9)	0.155 (3)	0.1101 (19)	-0.0022 (13)	0.0174 (10)	-0.0376 (18)
C18	0.0427 (9)	0.1165 (17)	0.0735 (12)	0.0177 (10)	0.0055 (8)	-0.0151 (12)
C19	0.0348 (7)	0.0841 (12)	0.0422 (8)	0.0019 (7)	0.0050 (6)	-0.0116 (7)
C20	0.0441 (7)	0.0485 (8)	0.0344 (6)	0.0056 (6)	0.0126 (5)	0.0054 (5)
C21	0.0312 (6)	0.0437 (7)	0.0471 (7)	0.0024 (5)	0.0159 (5)	0.0019 (5)
C22	0.0566 (9)	0.0508 (8)	0.0516 (8)	0.0114 (7)	0.0253 (7)	0.0060 (6)
C23	0.0592 (10)	0.0708 (11)	0.0512 (9)	0.0109 (8)	0.0248 (8)	-0.0019 (8)
C24	0.0411 (8)	0.0614 (10)	0.0685 (10)	0.0054 (7)	0.0190 (7)	-0.0145 (8)
C25	0.0757 (12)	0.0464 (9)	0.0819 (13)	0.0145 (8)	0.0208 (10)	-0.0001 (8)
C26	0.0701 (11)	0.0485 (9)	0.0561 (9)	0.0107 (7)	0.0189 (8)	0.0069 (7)
C27	0.0697 (12)	0.0794 (14)	0.0981 (16)	0.0079 (10)	0.0307 (11)	-0.0328 (11)
N1	0.0348 (5)	0.0465 (6)	0.0364 (5)	-0.0024 (4)	0.0073 (4)	0.0027 (4)
N2	0.0459 (6)	0.0404 (6)	0.0509 (7)	-0.0014 (5)	0.0274 (5)	0.0064 (5)
O1	0.0583 (6)	0.0341 (5)	0.0744 (7)	0.0032 (4)	0.0344 (5)	0.0138 (5)
O2	0.0464 (6)	0.0712 (7)	0.0436 (5)	0.0159 (5)	0.0056 (4)	0.0086 (5)
O3	0.0682 (7)	0.0571 (7)	0.0645 (7)	0.0054 (5)	0.0314 (6)	0.0256 (5)

*Geometric parameters (Å, °)*

C1—N1	1.4577 (16)	C13—H13A	0.9700
C1—C12	1.5089 (17)	C13—H13B	0.9700
C1—C6	1.5621 (16)	C14—C19	1.370 (3)
C1—C2	1.5975 (17)	C14—C15	1.391 (2)
C2—C20	1.5240 (18)	C15—C16	1.383 (3)
C2—C13	1.5356 (18)	C15—H15	0.9300
C2—C3	1.5652 (17)	C16—C17	1.363 (4)
C3—C21	1.5110 (18)	C16—H16	0.9300
C3—C4	1.5169 (19)	C17—C18	1.380 (4)
C3—H3	0.9800	C17—H17	0.9300
C4—N1	1.4497 (18)	C18—C19	1.384 (2)
C4—H4A	0.9700	C18—H18	0.9300
C4—H4B	0.9700	C19—O2	1.396 (2)
C5—N1	1.4529 (18)	C20—O3	1.1892 (17)
C5—H5A	0.9600	C20—O2	1.3637 (17)
C5—H5B	0.9600	C21—C26	1.382 (2)
C5—H5C	0.9600	C21—C22	1.382 (2)

## supplementary materials

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C6—O1	1.2243 (16)	C22—C23	1.383 (2)
C6—N2	1.3467 (17)	C22—H22	0.9300
C7—C8	1.3736 (19)	C23—C24	1.372 (2)
C7—C12	1.3857 (18)	C23—H23	0.9300
C7—N2	1.3964 (18)	C24—C25	1.375 (3)
C8—C9	1.381 (2)	C24—C27	1.505 (2)
C8—H8	0.9300	C25—C26	1.382 (2)
C9—C10	1.374 (3)	C25—H25	0.9300
C9—H9	0.9300	C26—H26	0.9300
C10—C11	1.387 (2)	C27—H27A	0.9600
C10—H10	0.9300	C27—H27B	0.9600
C11—C12	1.3820 (18)	C27—H27C	0.9600
C11—H11	0.9300	N2—H2	0.8600
C13—C14	1.496 (2)		
N1—C1—C12	111.83 (10)	C2—C13—H13B	109.7
N1—C1—C6	113.05 (10)	H13A—C13—H13B	108.2
C12—C1—C6	100.52 (9)	C19—C14—C15	118.22 (16)
N1—C1—C2	102.96 (9)	C19—C14—C13	117.33 (14)
C12—C1—C2	117.43 (10)	C15—C14—C13	124.44 (17)
C6—C1—C2	111.50 (10)	C16—C15—C14	120.0 (2)
C20—C2—C13	106.66 (11)	C16—C15—H15	120.0
C20—C2—C3	110.37 (10)	C14—C15—H15	120.0
C13—C2—C3	112.93 (10)	C17—C16—C15	120.2 (2)
C20—C2—C1	108.58 (10)	C17—C16—H16	119.9
C13—C2—C1	114.63 (10)	C15—C16—H16	119.9
C3—C2—C1	103.64 (9)	C16—C17—C18	121.2 (2)
C21—C3—C4	116.52 (11)	C16—C17—H17	119.4
C21—C3—C2	115.59 (10)	C18—C17—H17	119.4
C4—C3—C2	103.51 (10)	C17—C18—C19	117.7 (2)
C21—C3—H3	106.9	C17—C18—H18	121.2
C4—C3—H3	106.9	C19—C18—H18	121.2
C2—C3—H3	106.9	C14—C19—C18	122.66 (18)
N1—C4—C3	102.26 (11)	C14—C19—O2	120.77 (13)
N1—C4—H4A	111.3	C18—C19—O2	116.53 (18)
C3—C4—H4A	111.3	O3—C20—O2	117.19 (13)
N1—C4—H4B	111.3	O3—C20—C2	125.69 (13)
C3—C4—H4B	111.3	O2—C20—C2	117.12 (12)
H4A—C4—H4B	109.2	C26—C21—C22	116.83 (14)
N1—C5—H5A	109.5	C26—C21—C3	122.78 (13)
N1—C5—H5B	109.5	C22—C21—C3	120.39 (12)
H5A—C5—H5B	109.5	C21—C22—C23	121.36 (15)
N1—C5—H5C	109.5	C21—C22—H22	119.3
H5A—C5—H5C	109.5	C23—C22—H22	119.3
H5B—C5—H5C	109.5	C24—C23—C22	121.72 (16)
O1—C6—N2	125.79 (12)	C24—C23—H23	119.1
O1—C6—C1	125.78 (11)	C22—C23—H23	119.1
N2—C6—C1	108.39 (11)	C23—C24—C25	117.01 (15)
C8—C7—C12	122.44 (13)	C23—C24—C27	122.04 (18)
C8—C7—N2	127.98 (13)	C25—C24—C27	120.95 (18)



C12—C7—N2	109.56 (11)	C24—C25—C26	121.77 (16)
C7—C8—C9	117.18 (16)	C24—C25—H25	119.1
C7—C8—H8	121.4	C26—C25—H25	119.1
C9—C8—H8	121.4	C21—C26—C25	121.29 (16)
C10—C9—C8	121.34 (15)	C21—C26—H26	119.4
C10—C9—H9	119.3	C25—C26—H26	119.4
C8—C9—H9	119.3	C24—C27—H27A	109.5
C9—C10—C11	121.08 (15)	C24—C27—H27B	109.5
C9—C10—H10	119.5	H27A—C27—H27B	109.5
C11—C10—H10	119.5	C24—C27—H27C	109.5
C12—C11—C10	118.15 (15)	H27A—C27—H27C	109.5
C12—C11—H11	120.9	H27B—C27—H27C	109.5
C10—C11—H11	120.9	C4—N1—C5	115.16 (11)
C11—C12—C7	119.70 (12)	C4—N1—C1	107.14 (10)
C11—C12—C1	130.64 (12)	C5—N1—C1	115.52 (11)
C7—C12—C1	109.60 (10)	C6—N2—C7	111.83 (11)
C14—C13—C2	109.89 (12)	C6—N2—H2	124.1
C14—C13—H13A	109.7	C7—N2—H2	124.1
C2—C13—H13A	109.7	C20—O2—C19	121.05 (12)
C14—C13—H13B	109.7		
N1—C1—C2—C20	107.25 (11)	C13—C14—C15—C16	-179.46 (17)
C12—C1—C2—C20	-16.07 (14)	C14—C15—C16—C17	1.2 (3)
C6—C1—C2—C20	-131.25 (11)	C15—C16—C17—C18	-1.0 (4)
N1—C1—C2—C13	-133.62 (11)	C16—C17—C18—C19	0.2 (4)
C12—C1—C2—C13	103.06 (13)	C15—C14—C19—C18	-0.3 (2)
C6—C1—C2—C13	-12.12 (15)	C13—C14—C19—C18	178.73 (15)
N1—C1—C2—C3	-10.10 (11)	C15—C14—C19—O2	177.45 (14)
C12—C1—C2—C3	-133.42 (11)	C13—C14—C19—O2	-3.5 (2)
C6—C1—C2—C3	111.40 (11)	C17—C18—C19—C14	0.5 (3)
C20—C2—C3—C21	98.57 (13)	C17—C18—C19—O2	-177.40 (18)
C13—C2—C3—C21	-20.72 (15)	C13—C2—C20—O3	138.05 (15)
C1—C2—C3—C21	-145.34 (11)	C3—C2—C20—O3	15.04 (19)
C20—C2—C3—C4	-132.81 (11)	C1—C2—C20—O3	-97.92 (16)
C13—C2—C3—C4	107.91 (13)	C13—C2—C20—O2	-42.67 (15)
C1—C2—C3—C4	-16.72 (12)	C3—C2—C20—O2	-165.68 (11)
C21—C3—C4—N1	166.01 (10)	C1—C2—C20—O2	81.35 (14)
C2—C3—C4—N1	37.96 (13)	C4—C3—C21—C26	-22.73 (19)
N1—C1—C6—O1	55.83 (18)	C2—C3—C21—C26	99.17 (16)
C12—C1—C6—O1	175.18 (14)	C4—C3—C21—C22	156.91 (13)
C2—C1—C6—O1	-59.61 (18)	C2—C3—C21—C22	-81.19 (16)
N1—C1—C6—N2	-122.03 (12)	C26—C21—C22—C23	-0.4 (2)
C12—C1—C6—N2	-2.69 (13)	C3—C21—C22—C23	179.90 (14)
C2—C1—C6—N2	122.52 (12)	C21—C22—C23—C24	1.4 (3)
C12—C7—C8—C9	1.1 (2)	C22—C23—C24—C25	-1.0 (3)
N2—C7—C8—C9	-176.91 (14)	C22—C23—C24—C27	179.71 (17)
C7—C8—C9—C10	1.5 (2)	C23—C24—C25—C26	-0.4 (3)
C8—C9—C10—C11	-1.7 (3)	C27—C24—C25—C26	178.90 (18)
C9—C10—C11—C12	-0.7 (2)	C22—C21—C26—C25	-1.0 (2)
C10—C11—C12—C7	3.2 (2)	C3—C21—C26—C25	178.70 (15)

## supplementary materials

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C10—C11—C12—C1	-179.77 (13)	C24—C25—C26—C21	1.4 (3)
C8—C7—C12—C11	-3.5 (2)	C3—C4—N1—C5	-177.27 (12)
N2—C7—C12—C11	174.86 (12)	C3—C4—N1—C1	-47.26 (13)
C8—C7—C12—C1	178.92 (13)	C12—C1—N1—C4	162.40 (10)
N2—C7—C12—C1	-2.76 (14)	C6—C1—N1—C4	-85.00 (12)
N1—C1—C12—C11	-53.82 (18)	C2—C1—N1—C4	35.44 (12)
C6—C1—C12—C11	-174.04 (13)	C12—C1—N1—C5	-67.79 (14)
C2—C1—C12—C11	64.87 (18)	C6—C1—N1—C5	44.80 (15)
N1—C1—C12—C7	123.46 (11)	C2—C1—N1—C5	165.25 (11)
C6—C1—C12—C7	3.23 (13)	O1—C6—N2—C7	-176.60 (14)
C2—C1—C12—C7	-117.86 (11)	C1—C6—N2—C7	1.27 (15)
C20—C2—C13—C14	57.15 (15)	C8—C7—N2—C6	179.11 (14)
C3—C2—C13—C14	178.55 (11)	C12—C7—N2—C6	0.90 (16)
C1—C2—C13—C14	-63.05 (16)	O3—C20—O2—C19	-176.49 (13)
C2—C13—C14—C19	-36.75 (18)	C2—C20—O2—C19	4.17 (18)
C2—C13—C14—C15	142.23 (15)	C14—C19—O2—C20	21.8 (2)
C19—C14—C15—C16	-0.5 (3)	C18—C19—O2—C20	-160.33 (14)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 $\cdots$ O1 <sup>i</sup>	0.86	2.02	2.874 (1)	174.
C5—H5B $\cdots$ O3 <sup>ii</sup>	0.96	2.59	3.407 (2)	143.

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

Fig. 1

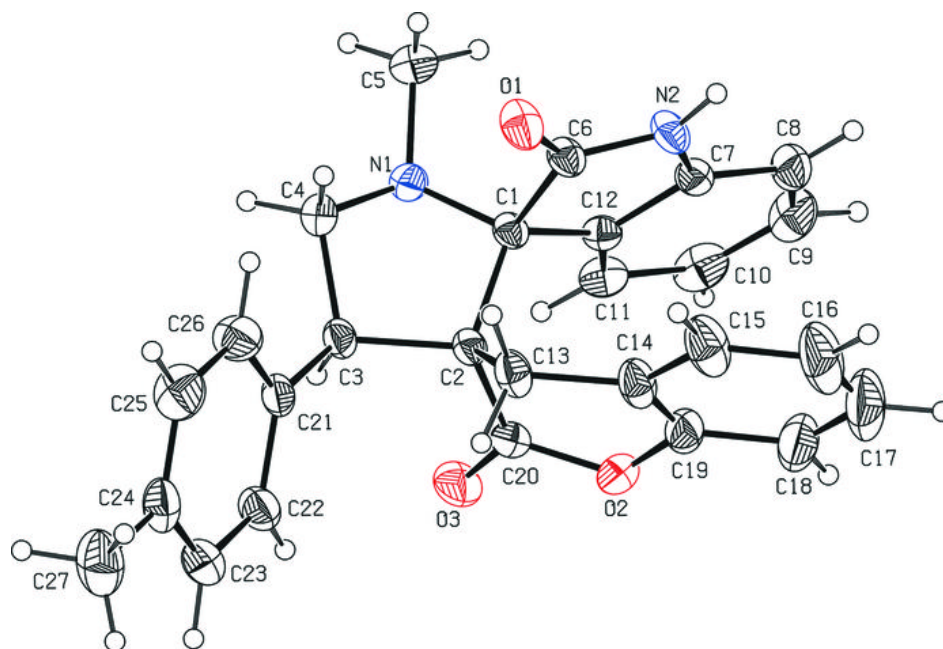


Fig. 2

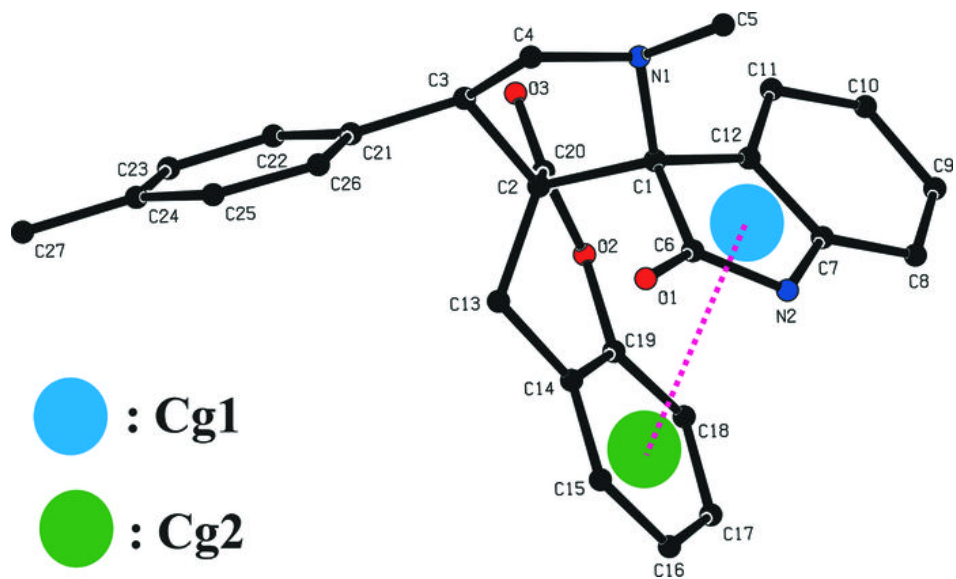


Fig. 3

