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# Crystal structure of 3′-(1*H*-indole-3-carbonyl)-1′-methyl-2-oxo-4′-(4-oxo-4*H*-chromen-3-yl)spiro[indoline-3,2′-pyrrolidine]-3′-carbonitrile

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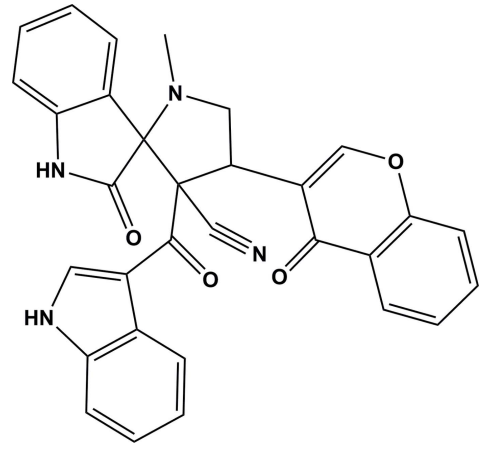
In the title compound, $C_{31}H_{22}N_4O_4$, the pyrrolidine ring adopts a twist conformation on the N—$CH_2$ bond. The indolin-2-one and the 1*H*-indole rings are nearly planar (r.m.s. deviations = 0.06 and 0.011 Å, respectively) and are inclined to one another by 34.19 (9)°. The chromene ring system is also nearly planar (r.m.s. deviation = 0.029 Å). It is almost normal to the 1*H*-indole ring system, with a dihedral angle of 88.71 (8)°, and is inclined to the indolin-2-one ring system by 72.76 (8)°. In the crystal, molecules are linked *via* N—H···O hydrogen bonds, forming slabs parallel to $(10\overline{1})$. The slabs are linked by C—H···O hydrogen bonds, forming a three-dimensional structure.

**Keywords:** crystal structure; indole; pyrrolidine; chromen; spiro; carbonitrile; hydrogen bonding.

**CCDC reference**: 1433172

## 1. Related literature

For the biological activities of indole derivatives, see: Macor *et al.* (1992); Andreani *et al.* (2001); Quetin-Leclercq (1994); Mukhopadhyay *et al.* (1981); Singh *et al.* (2000). For the structure of a very similar compound, see: Ramesh *et al.* (2009).




## 2. Experimental

### 2.1. Crystal data

$C_{31}H_{22}N_4O_4$
$M_r$ = 514.53
Monoclinic, $P2_1/n$
$a$ = 13.0401 (5) Å
$b$ = 14.9139 (6) Å
$c$ = 13.7161 (5) Å
$\beta$ = 112.603 (2)°
$V$ = 2462.60 (16) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 K
0.35 × 0.30 × 0.30 mm

### 2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min}$ = 0.969, $T_{max}$ = 0.974
16591 measured reflections
4341 independent reflections
3234 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.132
$S$ = 1.04
4329 reflections
353 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3$A$···O4$^{i}$ | 0.86 | 2.14 | 2.967 (3) | 161 |
| N4—H4$A$···O3$^{ii}$ | 0.86 | 2.06 | 2.866 (3) | 156 |
| C29—H29···O2$^{iii}$ | 0.93 | 2.59 | 3.267 (3) | 131 |

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

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: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5215).

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# supporting information

*Acta Cryst.* (2015). E**71**, o898–o899 [https://doi.org/10.1107/S2056989015020174]

## Crystal structure of 3′-(1*H*-indole-3-carbonyl)-1′-methyl-2-oxo-4′-(4-oxo-4*H*-chromen-3-yl)spiro[indoline-3,2′-pyrrolidine]-3′-carbonitrile

**M. P. Savithri, R. Raja, D. Kathirvelan, B. S. R. Reddy and A. SubbiahPandi**

### S1. Structural commentary

The chemistry of indole has been of increasing interest, since several compounds of this type possess diverse biological activities (Macor *et al.*, 1992). These derivatives exhibit antibacterial, antifungal (Singh *et al.*, 2000) and antitumour activities (Andreani *et al.*, 2001). Some of the indole alkaloids extracted from plants possess interesting cytotoxic and antiparasitic properties (Quetin-Leclercq, 1994; Mukhopadhyay *et al.*, 1981).

The geometric parameters of the title molecule (Fig. 1) agree well with those reported for a similar compound, 1′-methyl-2,2″-dioxoindoline-3-spiro-2′-pyrrolidine-3′-spiro-3″-indoline-4′,4′-dicarbonitrile (Ramesh *et al.*, 2009). The pyrrolidine ring (N2/C10/C11/C13/C21) adopts a twist conformation on bond N2—C21: puckering parameters and the asymmetry parameters for this ring are $q_2$ = 0.411 (2) Å, $\varphi_2$ = 160.3 (3)° nd ΔCs(C11) = 1.3 (2)°. Both indole rings, (N3/24–31) and (N4/C13—C20), are planar [maximum deviations of 0.013 Å for C27 and 0.080 (1) Å for C13 in the two rings] and are oriented at a dihedral angle of 34.19 (9)°. The sum of the bond angles around atom N2 of the central pyrrolidine ring is 337° as expected for $sp^3$ hybridization.

In the crystal, molecules are linked by N—H···O hydrogen bonds forming slabs parallel to $(10\bar{1})$. The slabs are linked via C—H···O hydrogen bonds forming a three-dimensional structure (Table 1 and Fig. 2).

### S2. Synthesis and crystallization

A mixture of isatin2a-f (1.0 mmol), sarcosine3 (1.1 mmol) and (*E*)-2-(1*H*-indole -3-carbonyl)-3-(4-oxo-4*H*-chromen-3-yl)acrylonitrile 1 (1.2 mmol) in methanol was stirred at room temperature for 120 min. The solid precipitated during the reaction mixture was filtered and dried under vacuum to obtain spirooxindoles5a-f in crude form. The resulting crude product was purified by flash column chromatography (mesh 100–200) using hexane/EtOAC (7:3). The solid single product was finally recrystallized from ethanol, giving title compound in good yield as colourless block-like crystals.

### S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. N and C-bound H atoms were positioned geometrically (N—H = 0.86 Å, C–H = 0.93–0.98 Å) and allowed to ride on their parent atoms, with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H atoms and 1.2$U_{eq}$(N,C) for other H atoms.

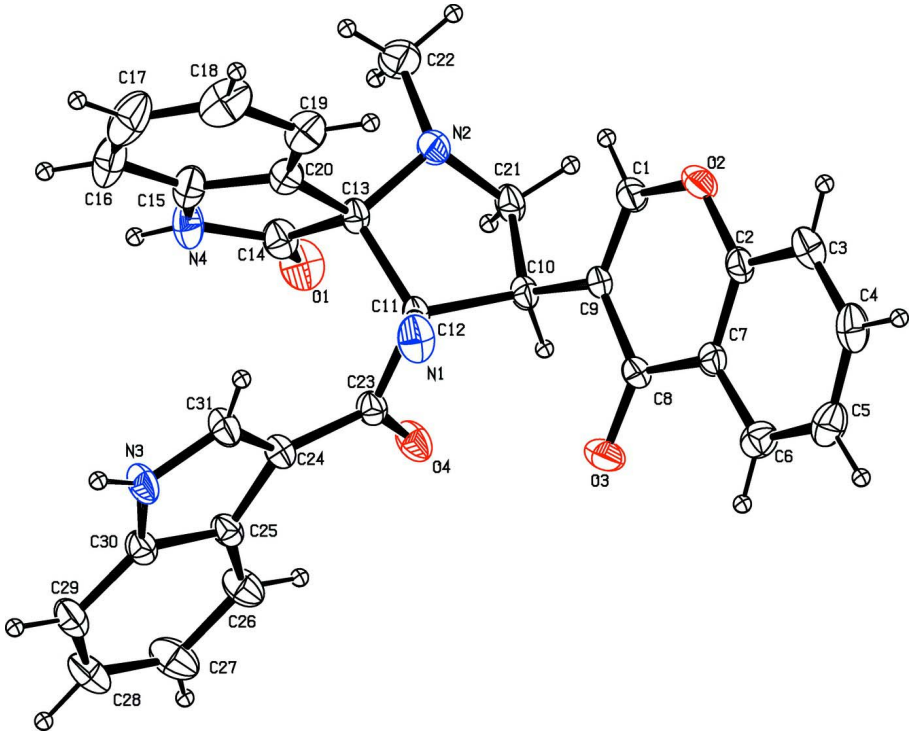


**Figure 1**

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

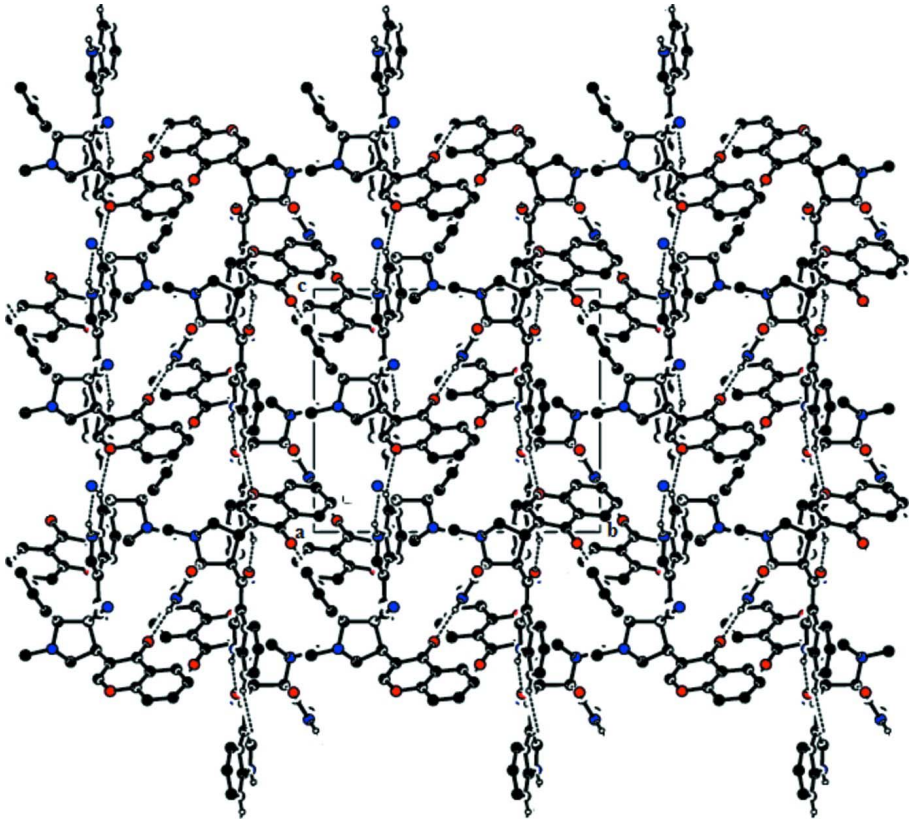

**Figure 2**

A view along the *b* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1).

**3′-(1*H*-Indole-3-carbonyl)-1′-methyl-2-oxo-4′-(4-oxo-4*H*-chromen-3-yl)spiro[indoline-3,2′-pyrrolidine]-3′-carbonitrile**

*Crystal data*

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$M_r$ = 514.53
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Hall symbol: -P 2ybn
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$b$ = 14.9139 (6) Å
$c$ = 13.7161 (5) Å
$\beta$ = 112.603 (2)°
$V$ = 2462.60 (16) Å$^3$
$Z$ = 4
$F(000)$ = 1072
$D_x$ = 1.388 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4241 reflections
$\theta$ = 1.8–25.0°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 K
Block, colourless
0.35 × 0.30 × 0.30 mm

*Data collection*

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min}$ = 0.969, $T_{max}$ = 0.974
16591 measured reflections
4341 independent reflections
3234 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.030
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 1.8°
$h$ = −14→15
$k$ = −17→17
$l$ = −16→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.132
$S$ = 1.04
4329 reflections
353 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
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 1.2814P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e 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 (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.2880 (2) | 0.25426 (16) | −0.10673 (17) | 0.0378 (6) |
| H1 | 0.2737 | 0.3152 | −0.1193 | 0.045* |
| C2 | 0.36735 (18) | 0.12268 (16) | −0.14083 (15) | 0.0353 (5) |
| C3 | 0.4277 (2) | 0.08350 (19) | −0.19416 (18) | 0.0467 (6) |
| H3 | 0.4542 | 0.1178 | −0.2361 | 0.056* |
| C4 | 0.4468 (2) | −0.00645 (19) | −0.18327 (19) | 0.0517 (7) |
| H4 | 0.4867 | −0.0338 | −0.2186 | 0.062* |
| C5 | 0.4078 (2) | −0.05821 (18) | −0.1203 (2) | 0.0498 (7) |
| H5 | 0.4201 | −0.1198 | −0.1153 | 0.060* |
| C6 | 0.35133 (19) | −0.01845 (17) | −0.06596 (19) | 0.0427 (6) |
| H6 | 0.3269 | −0.0529 | −0.0226 | 0.051* |
| C7 | 0.33001 (17) | 0.07404 (15) | −0.07526 (15) | 0.0325 (5) |
| C8 | 0.27094 (18) | 0.11941 (15) | −0.01806 (15) | 0.0340 (5) |
| C9 | 0.24912 (18) | 0.21424 (15) | −0.04083 (15) | 0.0307 (5) |
| C10 | 0.18396 (18) | 0.26261 (15) | 0.01285 (15) | 0.0321 (5) |
| H10 | 0.1243 | 0.2227 | 0.0130 | 0.039* |
| C11 | 0.25597 (17) | 0.28881 (15) | 0.13121 (15) | 0.0298 (5) |
| C12 | 0.3687 (2) | 0.25089 (15) | 0.16436 (16) | 0.0338 (5) |
| C13 | 0.26070 (17) | 0.39617 (15) | 0.13015 (15) | 0.0315 (5) |
| C14 | 0.1881 (2) | 0.43664 (17) | 0.18886 (18) | 0.0424 (6) |
| C15 | 0.3657 (2) | 0.48427 (17) | 0.27711 (19) | 0.0464 (6) |
| C16 | 0.4568 (3) | 0.52655 (19) | 0.3503 (2) | 0.0641 (9) |

| | | | | |
|---|---|---|---|---|
| H16 | 0.4530 | 0.5548 | 0.4093 | 0.077* |
| C17 | 0.5530 (3) | 0.5251 (2) | 0.3323 (3) | 0.0734 (10) |
| H17 | 0.6159 | 0.5529 | 0.3804 | 0.088* |
| C18 | 0.5596 (2) | 0.4835 (2) | 0.2449 (3) | 0.0683 (9) |
| H18 | 0.6256 | 0.4856 | 0.2338 | 0.082* |
| C19 | 0.4675 (2) | 0.43842 (19) | 0.1731 (2) | 0.0507 (7) |
| H19 | 0.4715 | 0.4095 | 0.1146 | 0.061* |
| C20 | 0.37124 (19) | 0.43801 (16) | 0.19138 (17) | 0.0378 (6) |
| C21 | 0.13173 (19) | 0.35150 (16) | −0.03531 (16) | 0.0382 (6) |
| H21A | 0.1129 | 0.3522 | −0.1110 | 0.046* |
| H21B | 0.0653 | 0.3635 | −0.0217 | 0.046* |
| C22 | 0.1867 (2) | 0.50981 (18) | −0.0085 (2) | 0.0581 (8) |
| H22A | 0.1694 | 0.5195 | −0.0823 | 0.087* |
| H22B | 0.2473 | 0.5479 | 0.0325 | 0.087* |
| H22C | 0.1227 | 0.5236 | 0.0073 | 0.087* |
| C23 | 0.19977 (18) | 0.25368 (15) | 0.20664 (16) | 0.0331 (5) |
| C24 | 0.25979 (18) | 0.25638 (15) | 0.32050 (16) | 0.0339 (5) |
| C25 | 0.21092 (18) | 0.23643 (15) | 0.39638 (16) | 0.0338 (5) |
| C26 | 0.1073 (2) | 0.20842 (18) | 0.39024 (19) | 0.0472 (6) |
| H26 | 0.0500 | 0.1987 | 0.3251 | 0.057* |
| C27 | 0.0911 (2) | 0.1953 (2) | 0.4831 (2) | 0.0603 (8) |
| H27 | 0.0222 | 0.1757 | 0.4799 | 0.072* |
| C28 | 0.1754 (2) | 0.2107 (2) | 0.5811 (2) | 0.0555 (7) |
| H28 | 0.1615 | 0.2020 | 0.6421 | 0.067* |
| C29 | 0.2784 (2) | 0.23842 (17) | 0.58952 (18) | 0.0456 (6) |
| H29 | 0.3350 | 0.2487 | 0.6549 | 0.055* |
| C30 | 0.29469 (19) | 0.25050 (16) | 0.49630 (16) | 0.0359 (5) |
| C31 | 0.36911 (19) | 0.27949 (17) | 0.37844 (17) | 0.0412 (6) |
| H31 | 0.4208 | 0.2950 | 0.3499 | 0.049* |
| N1 | 0.45588 (18) | 0.22200 (15) | 0.18987 (16) | 0.0502 (6) |
| N2 | 0.21796 (16) | 0.41585 (13) | 0.01775 (13) | 0.0390 (5) |
| N3 | 0.38947 (16) | 0.27611 (14) | 0.48210 (14) | 0.0430 (5) |
| H3A | 0.4522 | 0.2881 | 0.5320 | 0.052* |
| N4 | 0.25757 (18) | 0.48177 (15) | 0.27375 (16) | 0.0521 (6) |
| H4A | 0.2375 | 0.5062 | 0.3204 | 0.063* |
| O1 | 0.08831 (15) | 0.42855 (14) | 0.16214 (15) | 0.0609 (5) |
| O2 | 0.34652 (14) | 0.21307 (11) | −0.15668 (12) | 0.0435 (4) |
| O3 | 0.24130 (15) | 0.08041 (11) | 0.04650 (13) | 0.0511 (5) |
| O4 | 0.10336 (13) | 0.22832 (12) | 0.16760 (12) | 0.0457 (4) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0488 (14) | 0.0357 (13) | 0.0302 (11) | 0.0036 (11) | 0.0165 (11) | −0.0004 (10) |
| C2 | 0.0390 (13) | 0.0396 (14) | 0.0232 (10) | 0.0015 (11) | 0.0072 (9) | −0.0036 (9) |
| C3 | 0.0508 (15) | 0.0603 (18) | 0.0311 (12) | 0.0063 (13) | 0.0180 (11) | −0.0023 (11) |
| C4 | 0.0495 (16) | 0.0614 (19) | 0.0413 (14) | 0.0121 (14) | 0.0144 (12) | −0.0139 (13) |
| C5 | 0.0469 (15) | 0.0412 (15) | 0.0549 (15) | 0.0063 (12) | 0.0124 (13) | −0.0107 (12) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C6 | 0.0378 (14) | 0.0402 (15) | 0.0454 (14) | −0.0025 (11) | 0.0108 (11) | −0.0007 (11) |
| C7 | 0.0338 (12) | 0.0348 (13) | 0.0242 (10) | −0.0015 (10) | 0.0060 (9) | −0.0028 (9) |
| C8 | 0.0406 (13) | 0.0360 (13) | 0.0226 (10) | −0.0039 (10) | 0.0091 (9) | 0.0006 (9) |
| C9 | 0.0364 (12) | 0.0328 (12) | 0.0193 (10) | −0.0038 (10) | 0.0069 (9) | −0.0030 (9) |
| C10 | 0.0319 (12) | 0.0381 (13) | 0.0229 (10) | −0.0020 (10) | 0.0068 (9) | −0.0032 (9) |
| C11 | 0.0288 (11) | 0.0360 (13) | 0.0213 (10) | 0.0038 (10) | 0.0061 (9) | −0.0026 (9) |
| C12 | 0.0371 (13) | 0.0382 (14) | 0.0242 (10) | 0.0036 (11) | 0.0098 (10) | −0.0052 (9) |
| C13 | 0.0305 (11) | 0.0347 (13) | 0.0260 (10) | 0.0049 (10) | 0.0074 (9) | −0.0026 (9) |
| C14 | 0.0425 (15) | 0.0451 (15) | 0.0397 (13) | 0.0098 (12) | 0.0160 (11) | −0.0009 (11) |
| C15 | 0.0494 (16) | 0.0387 (14) | 0.0400 (13) | 0.0073 (12) | 0.0046 (11) | −0.0077 (11) |
| C16 | 0.063 (2) | 0.0510 (18) | 0.0545 (17) | 0.0071 (15) | −0.0035 (15) | −0.0207 (13) |
| C17 | 0.0541 (19) | 0.0541 (19) | 0.083 (2) | −0.0019 (15) | −0.0054 (16) | −0.0189 (17) |
| C18 | 0.0353 (15) | 0.063 (2) | 0.095 (2) | −0.0018 (14) | 0.0114 (15) | 0.0006 (18) |
| C19 | 0.0374 (14) | 0.0514 (17) | 0.0585 (16) | −0.0003 (12) | 0.0133 (12) | −0.0029 (13) |
| C20 | 0.0346 (13) | 0.0354 (13) | 0.0372 (12) | 0.0033 (11) | 0.0070 (10) | 0.0001 (10) |
| C21 | 0.0389 (13) | 0.0449 (15) | 0.0240 (11) | 0.0047 (11) | 0.0045 (10) | −0.0018 (10) |
| C22 | 0.0685 (19) | 0.0431 (16) | 0.0476 (15) | 0.0043 (14) | 0.0055 (13) | 0.0095 (12) |
| C23 | 0.0322 (13) | 0.0363 (13) | 0.0273 (11) | 0.0027 (10) | 0.0076 (10) | 0.0001 (9) |
| C24 | 0.0347 (13) | 0.0396 (14) | 0.0260 (11) | 0.0013 (10) | 0.0100 (10) | 0.0009 (9) |
| C25 | 0.0369 (13) | 0.0367 (13) | 0.0262 (11) | 0.0080 (10) | 0.0104 (9) | 0.0054 (9) |
| C26 | 0.0372 (14) | 0.0653 (18) | 0.0364 (13) | 0.0044 (13) | 0.0112 (11) | 0.0117 (12) |
| C27 | 0.0465 (16) | 0.087 (2) | 0.0538 (17) | 0.0042 (15) | 0.0263 (14) | 0.0180 (15) |
| C28 | 0.0637 (18) | 0.074 (2) | 0.0369 (14) | 0.0116 (15) | 0.0283 (13) | 0.0134 (13) |
| C29 | 0.0552 (16) | 0.0538 (16) | 0.0269 (11) | 0.0094 (13) | 0.0148 (11) | 0.0038 (11) |
| C30 | 0.0390 (13) | 0.0385 (14) | 0.0283 (11) | 0.0065 (11) | 0.0109 (10) | 0.0022 (9) |
| C31 | 0.0377 (13) | 0.0580 (16) | 0.0263 (11) | −0.0042 (12) | 0.0105 (10) | −0.0017 (10) |
| N1 | 0.0426 (13) | 0.0590 (15) | 0.0451 (12) | 0.0159 (11) | 0.0126 (10) | −0.0065 (10) |
| N2 | 0.0431 (11) | 0.0376 (11) | 0.0290 (9) | 0.0023 (9) | 0.0058 (8) | 0.0027 (8) |
| N3 | 0.0371 (11) | 0.0631 (14) | 0.0225 (9) | −0.0068 (10) | 0.0044 (8) | −0.0026 (9) |
| N4 | 0.0581 (14) | 0.0577 (14) | 0.0411 (12) | 0.0102 (11) | 0.0196 (11) | −0.0165 (10) |
| O1 | 0.0446 (12) | 0.0786 (14) | 0.0649 (12) | 0.0107 (10) | 0.0269 (9) | −0.0055 (10) |
| O2 | 0.0595 (11) | 0.0454 (11) | 0.0336 (8) | 0.0034 (8) | 0.0269 (8) | 0.0051 (7) |
| O3 | 0.0732 (12) | 0.0463 (11) | 0.0445 (9) | 0.0007 (9) | 0.0344 (9) | 0.0102 (8) |
| O4 | 0.0334 (9) | 0.0706 (12) | 0.0293 (8) | −0.0076 (9) | 0.0080 (7) | 0.0009 (8) |

*Geometric parameters (Å, º)*

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|---|---|---|---|
| C1—C9 | 1.335 (3) | C16—H16 | 0.9300 |
| C1—O2 | 1.353 (3) | C17—C18 | 1.381 (5) |
| C1—H1 | 0.9300 | C17—H17 | 0.9300 |
| C2—O2 | 1.376 (3) | C18—C19 | 1.398 (4) |
| C2—C7 | 1.382 (3) | C18—H18 | 0.9300 |
| C2—C3 | 1.392 (3) | C19—C20 | 1.372 (3) |
| C3—C4 | 1.362 (4) | C19—H19 | 0.9300 |
| C3—H3 | 0.9300 | C21—N2 | 1.444 (3) |
| C4—C5 | 1.392 (4) | C21—H21A | 0.9700 |
| C4—H4 | 0.9300 | C21—H21B | 0.9700 |
| C5—C6 | 1.369 (3) | C22—N2 | 1.465 (3) |

| | | | |
|---|---|---|---|
| C5—H5 | 0.9300 | C22—H22A | 0.9600 |
| C6—C7 | 1.403 (3) | C22—H22B | 0.9600 |
| C6—H6 | 0.9300 | C22—H22C | 0.9600 |
| C7—C8 | 1.460 (3) | C23—O4 | 1.222 (3) |
| C8—O3 | 1.239 (3) | C23—C24 | 1.454 (3) |
| C8—C9 | 1.453 (3) | C24—C31 | 1.383 (3) |
| C9—C10 | 1.505 (3) | C24—C25 | 1.445 (3) |
| C10—C21 | 1.521 (3) | C25—C26 | 1.385 (3) |
| C10—C11 | 1.581 (3) | C25—C30 | 1.402 (3) |
| C10—H10 | 0.9800 | C26—C27 | 1.383 (3) |
| C11—C12 | 1.474 (3) | C26—H26 | 0.9300 |
| C11—C23 | 1.570 (3) | C27—C28 | 1.390 (4) |
| C11—C13 | 1.603 (3) | C27—H27 | 0.9300 |
| C12—N1 | 1.138 (3) | C28—C29 | 1.367 (4) |
| C13—N2 | 1.454 (3) | C28—H28 | 0.9300 |
| C13—C20 | 1.497 (3) | C29—C30 | 1.386 (3) |
| C13—C14 | 1.580 (3) | C29—H29 | 0.9300 |
| C14—O1 | 1.214 (3) | C30—N3 | 1.377 (3) |
| C14—N4 | 1.349 (3) | C31—N3 | 1.343 (3) |
| C15—C16 | 1.378 (4) | C31—H31 | 0.9300 |
| C15—C20 | 1.389 (3) | N3—H3A | 0.8600 |
| C15—N4 | 1.393 (3) | N4—H4A | 0.8600 |
| C16—C17 | 1.369 (4) | | |

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| C9—C1—O2 | 125.1 (2) | C17—C18—C19 | 120.3 (3) |
| C9—C1—H1 | 117.5 | C17—C18—H18 | 119.9 |
| O2—C1—H1 | 117.5 | C19—C18—H18 | 119.9 |
| O2—C2—C7 | 121.33 (19) | C20—C19—C18 | 118.2 (3) |
| O2—C2—C3 | 116.4 (2) | C20—C19—H19 | 120.9 |
| C7—C2—C3 | 122.2 (2) | C18—C19—H19 | 120.9 |
| C4—C3—C2 | 118.2 (2) | C19—C20—C15 | 120.1 (2) |
| C4—C3—H3 | 120.9 | C19—C20—C13 | 130.6 (2) |
| C2—C3—H3 | 120.9 | C15—C20—C13 | 109.3 (2) |
| C3—C4—C5 | 121.3 (2) | N2—C21—C10 | 103.20 (17) |
| C3—C4—H4 | 119.4 | N2—C21—H21A | 111.1 |
| C5—C4—H4 | 119.4 | C10—C21—H21A | 111.1 |
| C6—C5—C4 | 119.9 (2) | N2—C21—H21B | 111.1 |
| C6—C5—H5 | 120.0 | C10—C21—H21B | 111.1 |
| C4—C5—H5 | 120.0 | H21A—C21—H21B | 109.1 |
| C5—C6—C7 | 120.4 (2) | N2—C22—H22A | 109.5 |
| C5—C6—H6 | 119.8 | N2—C22—H22B | 109.5 |
| C7—C6—H6 | 119.8 | H22A—C22—H22B | 109.5 |
| C2—C7—C6 | 117.9 (2) | N2—C22—H22C | 109.5 |
| C2—C7—C8 | 119.8 (2) | H22A—C22—H22C | 109.5 |
| C6—C7—C8 | 122.3 (2) | H22B—C22—H22C | 109.5 |
| O3—C8—C9 | 121.4 (2) | O4—C23—C24 | 121.2 (2) |
| O3—C8—C7 | 122.7 (2) | O4—C23—C11 | 118.47 (18) |
| C9—C8—C7 | 115.85 (18) | C24—C23—C11 | 120.25 (19) |

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| C1—C9—C8 | 119.1 (2) | C31—C24—C25 | 106.26 (18) |
| C1—C9—C10 | 123.3 (2) | C31—C24—C23 | 129.4 (2) |
| C8—C9—C10 | 117.54 (18) | C25—C24—C23 | 124.3 (2) |
| C9—C10—C21 | 116.64 (18) | C26—C25—C30 | 118.7 (2) |
| C9—C10—C11 | 113.37 (17) | C26—C25—C24 | 135.1 (2) |
| C21—C10—C11 | 102.75 (16) | C30—C25—C24 | 106.2 (2) |
| C9—C10—H10 | 107.9 | C27—C26—C25 | 118.5 (2) |
| C21—C10—H10 | 107.9 | C27—C26—H26 | 120.7 |
| C11—C10—H10 | 107.9 | C25—C26—H26 | 120.7 |
| C12—C11—C23 | 109.35 (17) | C26—C27—C28 | 121.6 (3) |
| C12—C11—C10 | 110.51 (16) | C26—C27—H27 | 119.2 |
| C23—C11—C10 | 110.54 (17) | C28—C27—H27 | 119.2 |
| C12—C11—C13 | 110.41 (18) | C29—C28—C27 | 121.2 (2) |
| C23—C11—C13 | 111.63 (16) | C29—C28—H28 | 119.4 |
| C10—C11—C13 | 104.32 (16) | C27—C28—H28 | 119.4 |
| N1—C12—C11 | 179.7 (3) | C28—C29—C30 | 117.1 (2) |
| N2—C13—C20 | 113.88 (18) | C28—C29—H29 | 121.5 |
| N2—C13—C14 | 113.76 (17) | C30—C29—H29 | 121.5 |
| C20—C13—C14 | 101.03 (17) | N3—C30—C29 | 129.1 (2) |
| N2—C13—C11 | 102.17 (16) | N3—C30—C25 | 107.93 (19) |
| C20—C13—C11 | 116.32 (17) | C29—C30—C25 | 123.0 (2) |
| C14—C13—C11 | 110.14 (18) | N3—C31—C24 | 109.9 (2) |
| O1—C14—N4 | 126.6 (2) | N3—C31—H31 | 125.1 |
| O1—C14—C13 | 126.2 (2) | C24—C31—H31 | 125.1 |
| N4—C14—C13 | 107.2 (2) | C21—N2—C13 | 107.89 (17) |
| C16—C15—C20 | 122.2 (3) | C21—N2—C22 | 114.99 (19) |
| C16—C15—N4 | 127.9 (2) | C13—N2—C22 | 114.23 (18) |
| C20—C15—N4 | 109.9 (2) | C31—N3—C30 | 109.70 (19) |
| C17—C16—C15 | 117.0 (3) | C31—N3—H3A | 125.2 |
| C17—C16—H16 | 121.5 | C30—N3—H3A | 125.2 |
| C15—C16—H16 | 121.5 | C14—N4—C15 | 112.2 (2) |
| C16—C17—C18 | 122.1 (3) | C14—N4—H4A | 123.9 |
| C16—C17—H17 | 118.9 | C15—N4—H4A | 123.9 |
| C18—C17—H17 | 118.9 | C1—O2—C2 | 118.70 (17) |

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| O2—C2—C3—C4 | −177.9 (2) | N4—C15—C20—C19 | 174.1 (2) |
| C7—C2—C3—C4 | 2.2 (3) | C16—C15—C20—C13 | 177.2 (2) |
| C2—C3—C4—C5 | −0.3 (4) | N4—C15—C20—C13 | −4.1 (3) |
| C3—C4—C5—C6 | −1.6 (4) | N2—C13—C20—C19 | −49.2 (3) |
| C4—C5—C6—C7 | 1.6 (4) | C14—C13—C20—C19 | −171.6 (3) |
| O2—C2—C7—C6 | 177.87 (19) | C11—C13—C20—C19 | 69.2 (3) |
| C3—C2—C7—C6 | −2.1 (3) | N2—C13—C20—C15 | 128.8 (2) |
| O2—C2—C7—C8 | −2.4 (3) | C14—C13—C20—C15 | 6.4 (2) |
| C3—C2—C7—C8 | 177.6 (2) | C11—C13—C20—C15 | −112.8 (2) |
| C5—C6—C7—C2 | 0.2 (3) | C9—C10—C21—N2 | −89.1 (2) |
| C5—C6—C7—C8 | −179.5 (2) | C11—C10—C21—N2 | 35.6 (2) |
| C2—C7—C8—O3 | −175.6 (2) | C12—C11—C23—O4 | −135.8 (2) |
| C6—C7—C8—O3 | 4.1 (3) | C10—C11—C23—O4 | −13.9 (3) |

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| C2—C7—C8—C9 | 4.0 (3) | C13—C11—C23—O4 | 101.7 (2) |
| C6—C7—C8—C9 | −176.31 (19) | C12—C11—C23—C24 | 47.7 (3) |
| O2—C1—C9—C8 | 0.8 (3) | C10—C11—C23—C24 | 169.53 (19) |
| O2—C1—C9—C10 | −179.79 (19) | C13—C11—C23—C24 | −74.8 (2) |
| O3—C8—C9—C1 | 176.4 (2) | O4—C23—C24—C31 | 177.3 (2) |
| C7—C8—C9—C1 | −3.2 (3) | C11—C23—C24—C31 | −6.3 (4) |
| O3—C8—C9—C10 | −3.0 (3) | O4—C23—C24—C25 | −4.6 (4) |
| C7—C8—C9—C10 | 177.35 (17) | C11—C23—C24—C25 | 171.8 (2) |
| C1—C9—C10—C21 | 18.8 (3) | C31—C24—C25—C26 | −178.7 (3) |
| C8—C9—C10—C21 | −161.80 (19) | C23—C24—C25—C26 | 2.8 (4) |
| C1—C9—C10—C11 | −100.3 (2) | C31—C24—C25—C30 | 1.0 (3) |
| C8—C9—C10—C11 | 79.1 (2) | C23—C24—C25—C30 | −177.5 (2) |
| C9—C10—C11—C12 | −5.8 (3) | C30—C25—C26—C27 | −0.2 (4) |
| C21—C10—C11—C12 | −132.58 (19) | C24—C25—C26—C27 | 179.5 (3) |
| C9—C10—C11—C23 | −127.01 (19) | C25—C26—C27—C28 | 0.9 (4) |
| C21—C10—C11—C23 | 106.2 (2) | C26—C27—C28—C29 | −0.8 (5) |
| C9—C10—C11—C13 | 112.85 (19) | C27—C28—C29—C30 | 0.1 (4) |
| C21—C10—C11—C13 | −13.9 (2) | C28—C29—C30—N3 | −178.7 (3) |
| C23—C11—C12—N1 | −139 (100) | C28—C29—C30—C25 | 0.6 (4) |
| C10—C11—C12—N1 | 99 (58) | C26—C25—C30—N3 | 178.9 (2) |
| C13—C11—C12—N1 | −16 (58) | C24—C25—C30—N3 | −0.9 (3) |
| C12—C11—C13—N2 | 106.58 (18) | C26—C25—C30—C29 | −0.6 (4) |
| C23—C11—C13—N2 | −131.55 (17) | C24—C25—C30—C29 | 179.6 (2) |
| C10—C11—C13—N2 | −12.2 (2) | C25—C24—C31—N3 | −0.7 (3) |
| C12—C11—C13—C20 | −18.1 (2) | C23—C24—C31—N3 | 177.7 (2) |
| C23—C11—C13—C20 | 103.8 (2) | C10—C21—N2—C13 | −47.0 (2) |
| C10—C11—C13—C20 | −136.82 (18) | C10—C21—N2—C22 | −175.8 (2) |
| C12—C11—C13—C14 | −132.21 (18) | C20—C13—N2—C21 | 162.61 (19) |
| C23—C11—C13—C14 | −10.3 (2) | C14—C13—N2—C21 | −82.3 (2) |
| C10—C11—C13—C14 | 109.05 (18) | C11—C13—N2—C21 | 36.3 (2) |
| N2—C13—C14—O1 | 50.7 (3) | C20—C13—N2—C22 | −68.2 (3) |
| C20—C13—C14—O1 | 173.2 (3) | C14—C13—N2—C22 | 46.9 (3) |
| C11—C13—C14—O1 | −63.3 (3) | C11—C13—N2—C22 | 165.5 (2) |
| N2—C13—C14—N4 | −129.2 (2) | C24—C31—N3—C30 | 0.2 (3) |
| C20—C13—C14—N4 | −6.7 (2) | C29—C30—N3—C31 | 179.9 (2) |
| C11—C13—C14—N4 | 116.8 (2) | C25—C30—N3—C31 | 0.5 (3) |
| C20—C15—C16—C17 | 3.2 (4) | O1—C14—N4—C15 | −175.1 (3) |
| N4—C15—C16—C17 | −175.2 (3) | C13—C14—N4—C15 | 4.9 (3) |
| C15—C16—C17—C18 | 0.2 (5) | C16—C15—N4—C14 | 177.9 (3) |
| C16—C17—C18—C19 | −2.2 (5) | C20—C15—N4—C14 | −0.7 (3) |
| C17—C18—C19—C20 | 0.9 (4) | C9—C1—O2—C2 | 1.0 (3) |
| C18—C19—C20—C15 | 2.3 (4) | C7—C2—O2—C1 | −0.1 (3) |
| C18—C19—C20—C13 | −179.9 (2) | C3—C2—O2—C1 | 179.87 (19) |
| C16—C15—C20—C19 | −4.5 (4) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*A*···O4$^{i}$ | 0.86 | 2.14 | 2.967 (3) | 161 |
| N4—H4*A*···O3$^{ii}$ | 0.86 | 2.06 | 2.866 (3) | 156 |
| C29—H29···O2$^{iii}$ | 0.93 | 2.59 | 3.267 (3) | 131 |

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