

5''-(4-Chlorobenzylidene)-4'-(4-chlorophenyl)-5-fluoro-1',1''-dimethylindoline-3-spiro-2'-pyrrolidine-3'-spiro-3''-piperidine-2,4''-dione

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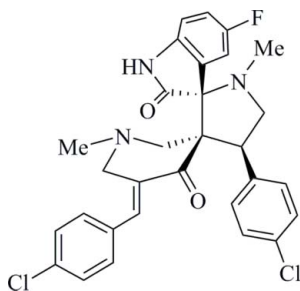
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.036; wR factor = 0.104; data-to-parameter ratio = 13.1.

The piperidine ring of the title compound, $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{FN}_3\text{O}_2$, adopts a twisted chair conformation. The pyrrolidine ring has a twisted envelope structure with the N atom at the flap [displaced by 0.592 (3) Å]. The fluorooxindole, chlorophenyl and chlorobenzylidene groups are planar with r.m.s. deviations of 0.0348, 0.0048 and 0.0048 Å, respectively. The structure is stabilized by intermolecular N—H...O hydrogen bonds.

Related literature

For biological applications of 1,4-dihydropyridine derivatives, see: Jerom & Spencer (1988); Perumal *et al.* (2001); Hagenbach & Gysin (1952); Mobio *et al.* (1989); Katritzky & Fan (1990); Ganellin & Spickett (1965); El-Subbagh *et al.* (2000). For their use as synthetic intermediates in the preparation of various pharmaceuticals, see: Wang & Wuorola (1992). For their occurrence in natural products such as alkaloids, see: Angle & Breitenbucher (1995).



Experimental

Crystal data

$\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{FN}_3\text{O}_2$
 $M_r = 550.44$
 Monoclinic, $P2_1/n$
 $a = 16.694$ (3) Å
 $b = 8.705$ (4) Å
 $c = 18.474$ (3) Å
 $\beta = 103.27$ (4)°

$V = 2613.3$ (14) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.29$ mm⁻¹
 $T = 293$ K
 $0.23 \times 0.21 \times 0.18$ mm

Data collection

Nonius MACH3 diffractometer
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.936$, $T_{\max} = 0.950$
 5427 measured reflections

4581 independent reflections
 2891 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 3 standard reflections every 60 min
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.104$
 $S = 1.02$
 4581 reflections
 349 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| D—H...A | D—H | H...A | D...A | D—H...A |
|--------------------------|----------|----------|-----------|---------|
| N3—H1N...O1 ⁱ | 0.84 (3) | 2.50 (3) | 3.288 (3) | 157 (3) |

Symmetry code: (i) $x, y - 1, z$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZJ2003).

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supplementary materials

Acta Cryst. (2011). E67, o801-o802 [doi:10.1107/S1600536811007550]

5''-(4-Chlorobenzylidene)-4''-(4-chlorophenyl)-5-fluoro-1',1''-dimethylindoline-3-spiro-2'-pyrrolidine-3'-spiro-3''-piperidine-2,4''-dione

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Comment

In the family of heterocyclic compounds, nitrogen containing heterocycles especially substituted piperidin-4-ones have considerable importance due to their variety of biological properties such as analgesic (Jerom *et al.*, 1988), local anaesthetic (Perumal *et al.*, 2001; Hagenbach & Gysin, 1952), antimicrobial, bactericidal, fungicidal, herbicidal, anticancer, CNS stimulant and depressant activities (Mobio *et al.*, 1989; Katritzky & Fan, 1990; Ganellin & Spickett, 1965) and antiviral, antitumour (El-Subbagh *et al.*, 2000). Also they are important synthetic intermediates in the preparation of various pharmaceuticals (Wang & Wuorola, 1992) and widely prevalent in natural products such as alkaloids (Angle & Breitenbucher, 1995). Hence, the present X-ray crystallographic study of the title compound has been carried out to determine the conformation of the system.

The piperidine ring of the title compound, C₃₀H₂₆N₃O₂Cl₂F, adopts a twisted chair conformation (C8/C9/C10/C11/N1/C12). Pyrrolidine ring has the twisted envelope structure with N atom at the flap (0.592 (3) Å from the mean plane formed by the atoms C10/C14/C23/C24) and this orientation may be influenced by the intramolecular C23—H23A...O2 hydrogen bond (Table 1).

Fluoroindole, the chlorophenyl and chlorophenylmethylidene groups are planar as confirmed by the values of the r.m.s. deviation (0.0348 Å, 0.0048 Å and 0.0048 Å), respectively, from the mean planes of the above groups. Fluoroindole is inclined with the plane of chlorophenyl by 33.99 (2)° and 55.56 (2)° with the mean plane of chlorophenylmethylidene. The sum of the bond angles around N1 atom (334.22°) of the piperidine ring in the molecule is in accordance with the *sp*² hybridization. Further, the structure is stabilized by intermolecular N—H...O hydrogen bond and intramolecular C—H...O hydrogen bonds.

Experimental

A mixture of 1-methyl-3,5-bis[(*E*)-chlorobenzylidene]tetrahydro-4 (1*H*)-pyridin-ones (1 mmol), 5-fluoroisatin (1 mmol) and sarcosine in methanol (10 ml) was refluxed for 30 min. After completion of the reaction as evident from TLC, the mixture was poured into water (50 ml). The precipitated solid was filtered and washed with water to obtain the pure product. The product was dissolved in methanol and allowed to evaporate at room temperature. Transparent, needle-shaped, colourless crystals of small sizes (8 x 2 x 2 mm³) were obtained in a period of about a week. Yield: 94%; *M.p.*: 224 °C

Refinement

H atoms were placed at calculated positions and allowed to ride on their carrier atoms with C—H = 0.93–0.97 Å, and *U*_{iso} = 1.2*U*_{eq}(C) for CH₂ and CH groups and *U*_{iso} = 1.5*U*_{eq}(C) for CH₃ group. The N-bound H atom is located in a difference Fourier map and its positional parameters were refined.

Figures

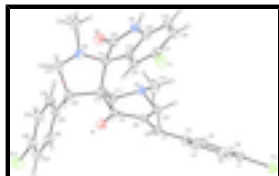


Fig. 1. The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

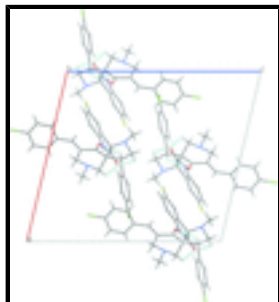


Fig. 2. Packing diagram

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Crystal data

$C_{30}H_{26}Cl_2FN_3O_2$

$M_r = 550.44$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 16.694 (3) \text{ \AA}$

$b = 8.705 (4) \text{ \AA}$

$c = 18.474 (3) \text{ \AA}$

$\beta = 103.27 (4)^\circ$

$V = 2613.3 (14) \text{ \AA}^3$

$Z = 4$

$F(000) = 1144$

$D_x = 1.399 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 2-25^\circ$

$\mu = 0.29 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Block, colourless

$0.23 \times 0.21 \times 0.18 \text{ mm}$

Data collection

Nonius MACH3
diffractometer

Radiation source: fine-focus sealed tube

graphite

$\omega-2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.936$, $T_{\max} = 0.950$

5427 measured reflections

4581 independent reflections

2891 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.3^\circ$

$h = 0 \rightarrow 19$

$k = -1 \rightarrow 10$

$l = -21 \rightarrow 21$

3 standard reflections every 60 min

intensity decay: none

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.104$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.02$ | $w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.726P]$ |
| 4581 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 349 parameters | $(\Delta/\sigma)_{\max} = 0.001$ |
| 0 restraints | $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$ |

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|---------------|--------------|--------------|----------------------------------|
| C11 | 0.15668 (5) | 0.37573 (8) | 0.72167 (3) | 0.0831 (2) |
| C12 | -0.36431 (5) | 0.61752 (10) | 0.00265 (4) | 0.0919 (3) |
| N1 | -0.05322 (10) | 0.13961 (19) | 0.27962 (9) | 0.0464 (4) |
| O1 | 0.07132 (10) | 0.52336 (18) | 0.24553 (8) | 0.0613 (4) |
| C8 | 0.03804 (12) | 0.3538 (2) | 0.33420 (11) | 0.0419 (5) |
| F1 | 0.32228 (9) | 0.21475 (19) | 0.36806 (8) | 0.0808 (5) |
| N3 | 0.05530 (14) | -0.1040 (2) | 0.21711 (12) | 0.0603 (6) |
| C12 | -0.02137 (13) | 0.2314 (2) | 0.34544 (11) | 0.0473 (5) |
| H12A | 0.0060 | 0.1641 | 0.3854 | 0.057* |
| H12B | -0.0671 | 0.2797 | 0.3608 | 0.057* |
| C9 | 0.03991 (12) | 0.4022 (2) | 0.25700 (11) | 0.0435 (5) |
| O2 | -0.05184 (11) | -0.0289 (2) | 0.12232 (10) | 0.0724 (5) |
| N2 | 0.08528 (11) | 0.2056 (2) | 0.11641 (9) | 0.0524 (5) |
| C20 | 0.12500 (14) | -0.0377 (3) | 0.26298 (13) | 0.0511 (6) |
| C15 | 0.12839 (13) | 0.1176 (2) | 0.24568 (11) | 0.0448 (5) |
| C5 | 0.04926 (13) | 0.3405 (3) | 0.50697 (12) | 0.0521 (6) |
| H5 | 0.0001 | 0.3012 | 0.4789 | 0.063* |

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| | | | | |
|------|---------------|-------------|--------------|------------|
| C10 | -0.00213 (12) | 0.2963 (2) | 0.19252 (11) | 0.0420 (5) |
| C11 | -0.07990 (13) | 0.2364 (2) | 0.21440 (11) | 0.0459 (5) |
| H11A | -0.1125 | 0.3216 | 0.2256 | 0.055* |
| H11B | -0.1132 | 0.1776 | 0.1739 | 0.055* |
| C4 | 0.10401 (13) | 0.4086 (2) | 0.47049 (11) | 0.0451 (5) |
| C17 | 0.25566 (14) | 0.1306 (3) | 0.33291 (13) | 0.0570 (6) |
| C25 | -0.10489 (14) | 0.4406 (2) | 0.08703 (11) | 0.0475 (5) |
| C28 | -0.26410 (16) | 0.5504 (3) | 0.03646 (13) | 0.0592 (6) |
| C24 | -0.01808 (13) | 0.3837 (3) | 0.11635 (11) | 0.0487 (5) |
| H24 | 0.0175 | 0.4746 | 0.1241 | 0.058* |
| C14 | 0.05642 (13) | 0.1582 (2) | 0.18243 (11) | 0.0464 (5) |
| C16 | 0.19562 (13) | 0.2034 (3) | 0.28079 (12) | 0.0503 (5) |
| H16 | 0.2002 | 0.3068 | 0.2696 | 0.060* |
| C26 | -0.12471 (17) | 0.5925 (3) | 0.09730 (13) | 0.0588 (6) |
| H26 | -0.0836 | 0.6590 | 0.1214 | 0.071* |
| C1 | 0.13761 (16) | 0.3869 (3) | 0.62522 (12) | 0.0577 (6) |
| C3 | 0.17622 (15) | 0.4682 (3) | 0.51528 (13) | 0.0566 (6) |
| H3 | 0.2138 | 0.5169 | 0.4929 | 0.068* |
| C7 | 0.09049 (13) | 0.4260 (3) | 0.38996 (12) | 0.0468 (5) |
| H7 | 0.1237 | 0.4993 | 0.3747 | 0.056* |
| C21 | 0.01022 (16) | -0.0003 (3) | 0.16971 (14) | 0.0549 (6) |
| C18 | 0.25207 (16) | -0.0208 (3) | 0.35107 (13) | 0.0630 (7) |
| H18 | 0.2942 | -0.0649 | 0.3868 | 0.076* |
| C6 | 0.06523 (15) | 0.3289 (3) | 0.58344 (12) | 0.0562 (6) |
| H6 | 0.0274 | 0.2823 | 0.6064 | 0.067* |
| C23 | 0.01550 (14) | 0.2770 (3) | 0.06552 (12) | 0.0587 (6) |
| H23A | -0.0251 | 0.2010 | 0.0429 | 0.070* |
| H23B | 0.0330 | 0.3337 | 0.0267 | 0.070* |
| C19 | 0.18501 (16) | -0.1081 (3) | 0.31565 (13) | 0.0611 (6) |
| H19 | 0.1809 | -0.2113 | 0.3273 | 0.073* |
| C30 | -0.16798 (15) | 0.3466 (3) | 0.04937 (13) | 0.0584 (6) |
| H30 | -0.1566 | 0.2444 | 0.0410 | 0.070* |
| C29 | -0.24709 (15) | 0.4006 (3) | 0.02398 (14) | 0.0625 (7) |
| H29 | -0.2884 | 0.3358 | -0.0014 | 0.075* |
| C27 | -0.20378 (18) | 0.6475 (3) | 0.07271 (14) | 0.0682 (7) |
| H27 | -0.2159 | 0.7495 | 0.0807 | 0.082* |
| C2 | 0.19346 (16) | 0.4570 (3) | 0.59173 (14) | 0.0636 (7) |
| H2 | 0.2423 | 0.4964 | 0.6203 | 0.076* |
| C13 | -0.11773 (16) | 0.0373 (3) | 0.29201 (14) | 0.0723 (8) |
| H13A | -0.0963 | -0.0271 | 0.3342 | 0.087* |
| H13B | -0.1368 | -0.0255 | 0.2488 | 0.087* |
| H13C | -0.1627 | 0.0970 | 0.3012 | 0.087* |
| C22 | 0.12756 (17) | 0.0882 (3) | 0.08263 (14) | 0.0740 (8) |
| H22A | 0.0902 | 0.0055 | 0.0647 | 0.089* |
| H22B | 0.1737 | 0.0497 | 0.1191 | 0.089* |
| H22C | 0.1465 | 0.1322 | 0.0419 | 0.089* |
| H1N | 0.0456 (17) | -0.198 (3) | 0.2158 (15) | 0.082 (9)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C11 | 0.1218 (6) | 0.0714 (4) | 0.0461 (3) | -0.0034 (4) | -0.0010 (4) | -0.0014 (3) |
| C12 | 0.0795 (5) | 0.1069 (6) | 0.0911 (5) | 0.0369 (5) | 0.0232 (4) | 0.0095 (5) |
| N1 | 0.0503 (10) | 0.0402 (10) | 0.0473 (10) | -0.0088 (8) | 0.0085 (8) | 0.0028 (8) |
| O1 | 0.0828 (12) | 0.0474 (9) | 0.0543 (10) | -0.0240 (9) | 0.0167 (8) | -0.0025 (8) |
| C8 | 0.0432 (11) | 0.0390 (11) | 0.0447 (11) | 0.0002 (10) | 0.0124 (9) | -0.0023 (10) |
| F1 | 0.0623 (9) | 0.0975 (12) | 0.0743 (9) | -0.0097 (9) | -0.0015 (7) | 0.0029 (9) |
| N3 | 0.0734 (15) | 0.0359 (11) | 0.0717 (14) | -0.0051 (11) | 0.0170 (11) | -0.0048 (11) |
| C12 | 0.0506 (12) | 0.0472 (13) | 0.0442 (12) | -0.0026 (11) | 0.0113 (10) | 0.0036 (10) |
| C9 | 0.0455 (12) | 0.0373 (12) | 0.0486 (12) | -0.0024 (10) | 0.0127 (10) | -0.0008 (10) |
| O2 | 0.0784 (12) | 0.0592 (11) | 0.0723 (11) | -0.0169 (10) | 0.0025 (10) | -0.0181 (9) |
| N2 | 0.0589 (11) | 0.0572 (12) | 0.0434 (10) | -0.0002 (10) | 0.0162 (9) | -0.0012 (9) |
| C20 | 0.0606 (15) | 0.0426 (12) | 0.0537 (13) | 0.0031 (12) | 0.0205 (12) | -0.0020 (11) |
| C15 | 0.0500 (12) | 0.0434 (12) | 0.0432 (11) | -0.0005 (11) | 0.0154 (10) | -0.0017 (10) |
| C5 | 0.0487 (13) | 0.0594 (15) | 0.0467 (13) | 0.0006 (11) | 0.0077 (10) | -0.0037 (11) |
| C10 | 0.0478 (12) | 0.0371 (11) | 0.0413 (11) | -0.0046 (10) | 0.0104 (9) | -0.0008 (9) |
| C11 | 0.0487 (12) | 0.0422 (12) | 0.0459 (12) | -0.0047 (10) | 0.0086 (10) | 0.0018 (10) |
| C4 | 0.0475 (12) | 0.0403 (12) | 0.0463 (12) | 0.0032 (10) | 0.0082 (10) | -0.0038 (10) |
| C17 | 0.0491 (14) | 0.0706 (17) | 0.0517 (13) | -0.0016 (13) | 0.0125 (11) | -0.0044 (13) |
| C25 | 0.0652 (14) | 0.0380 (12) | 0.0396 (11) | -0.0039 (11) | 0.0125 (11) | 0.0057 (9) |
| C28 | 0.0681 (16) | 0.0607 (16) | 0.0515 (14) | 0.0134 (14) | 0.0193 (12) | 0.0090 (12) |
| C24 | 0.0575 (13) | 0.0437 (12) | 0.0442 (12) | -0.0103 (11) | 0.0101 (10) | 0.0011 (10) |
| C14 | 0.0555 (13) | 0.0399 (12) | 0.0442 (12) | -0.0048 (10) | 0.0124 (10) | -0.0037 (10) |
| C16 | 0.0539 (13) | 0.0502 (13) | 0.0493 (12) | -0.0017 (12) | 0.0173 (11) | -0.0004 (11) |
| C26 | 0.0792 (17) | 0.0440 (13) | 0.0509 (13) | -0.0030 (13) | 0.0103 (12) | -0.0024 (11) |
| C1 | 0.0786 (17) | 0.0429 (13) | 0.0457 (12) | 0.0062 (13) | 0.0019 (12) | -0.0018 (11) |
| C3 | 0.0594 (15) | 0.0506 (13) | 0.0575 (15) | -0.0081 (12) | 0.0087 (12) | -0.0037 (12) |
| C7 | 0.0472 (12) | 0.0440 (12) | 0.0508 (13) | -0.0016 (10) | 0.0142 (10) | -0.0016 (10) |
| C21 | 0.0652 (16) | 0.0441 (14) | 0.0570 (14) | -0.0068 (12) | 0.0172 (13) | -0.0107 (12) |
| C18 | 0.0652 (16) | 0.0706 (18) | 0.0539 (14) | 0.0174 (14) | 0.0151 (12) | 0.0086 (13) |
| C6 | 0.0616 (15) | 0.0574 (15) | 0.0500 (13) | 0.0031 (12) | 0.0137 (12) | 0.0013 (12) |
| C23 | 0.0654 (15) | 0.0668 (16) | 0.0437 (12) | -0.0009 (13) | 0.0123 (11) | 0.0007 (12) |
| C19 | 0.0769 (17) | 0.0476 (14) | 0.0632 (15) | 0.0096 (14) | 0.0250 (13) | 0.0059 (13) |
| C30 | 0.0679 (16) | 0.0395 (13) | 0.0615 (14) | -0.0006 (12) | 0.0015 (12) | 0.0005 (11) |
| C29 | 0.0621 (16) | 0.0540 (15) | 0.0657 (15) | -0.0020 (13) | 0.0029 (13) | 0.0061 (13) |
| C27 | 0.095 (2) | 0.0495 (15) | 0.0602 (15) | 0.0153 (15) | 0.0188 (15) | -0.0031 (13) |
| C2 | 0.0702 (16) | 0.0525 (14) | 0.0582 (15) | -0.0077 (13) | -0.0056 (13) | -0.0046 (12) |
| C13 | 0.0798 (18) | 0.0659 (17) | 0.0662 (16) | -0.0311 (15) | 0.0068 (14) | 0.0128 (14) |
| C22 | 0.0839 (19) | 0.0835 (19) | 0.0605 (15) | 0.0118 (16) | 0.0286 (14) | -0.0052 (14) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|---------|-----------|---------|-----------|
| C11—C1 | 1.739 (2) | C17—C16 | 1.375 (3) |
| C12—C28 | 1.746 (3) | C25—C26 | 1.386 (3) |
| N1—C12 | 1.450 (3) | C25—C30 | 1.388 (3) |
| N1—C11 | 1.454 (3) | C25—C24 | 1.510 (3) |

supplementary materials

| | | | |
|---------------|-------------|-------------|-------------|
| N1—C13 | 1.456 (3) | C28—C29 | 1.366 (3) |
| O1—C9 | 1.218 (2) | C28—C27 | 1.367 (4) |
| C8—C7 | 1.345 (3) | C24—C23 | 1.517 (3) |
| C8—C9 | 1.494 (3) | C24—H24 | 0.9800 |
| C8—C12 | 1.502 (3) | C14—C21 | 1.572 (3) |
| F1—C17 | 1.365 (3) | C16—H16 | 0.9300 |
| N3—C21 | 1.358 (3) | C26—C27 | 1.379 (3) |
| N3—C20 | 1.397 (3) | C26—H26 | 0.9300 |
| N3—H1N | 0.84 (3) | C1—C6 | 1.372 (3) |
| C12—H12A | 0.9700 | C1—C2 | 1.374 (4) |
| C12—H12B | 0.9700 | C3—C2 | 1.379 (3) |
| C9—C10 | 1.542 (3) | C3—H3 | 0.9300 |
| O2—C21 | 1.219 (3) | C7—H7 | 0.9300 |
| N2—C23 | 1.457 (3) | C18—C19 | 1.387 (3) |
| N2—C22 | 1.461 (3) | C18—H18 | 0.9300 |
| N2—C14 | 1.469 (3) | C6—H6 | 0.9300 |
| C20—C19 | 1.371 (3) | C23—H23A | 0.9700 |
| C20—C15 | 1.393 (3) | C23—H23B | 0.9700 |
| C15—C16 | 1.380 (3) | C19—H19 | 0.9300 |
| C15—C14 | 1.513 (3) | C30—C29 | 1.379 (3) |
| C5—C6 | 1.380 (3) | C30—H30 | 0.9300 |
| C5—C4 | 1.387 (3) | C29—H29 | 0.9300 |
| C5—H5 | 0.9300 | C27—H27 | 0.9300 |
| C10—C11 | 1.537 (3) | C2—H2 | 0.9300 |
| C10—C24 | 1.568 (3) | C13—H13A | 0.9600 |
| C10—C14 | 1.587 (3) | C13—H13B | 0.9600 |
| C11—H11A | 0.9700 | C13—H13C | 0.9600 |
| C11—H11B | 0.9700 | C22—H22A | 0.9600 |
| C4—C3 | 1.396 (3) | C22—H22B | 0.9600 |
| C4—C7 | 1.461 (3) | C22—H22C | 0.9600 |
| C17—C18 | 1.364 (4) | | |
| C12—N1—C11 | 111.05 (16) | C15—C14—C21 | 100.68 (17) |
| C12—N1—C13 | 110.34 (18) | N2—C14—C10 | 102.30 (16) |
| C11—N1—C13 | 112.83 (17) | C15—C14—C10 | 119.19 (17) |
| C7—C8—C9 | 116.53 (19) | C21—C14—C10 | 112.84 (17) |
| C7—C8—C12 | 124.05 (19) | C17—C16—C15 | 117.6 (2) |
| C9—C8—C12 | 119.41 (17) | C17—C16—H16 | 121.2 |
| C21—N3—C20 | 112.2 (2) | C15—C16—H16 | 121.2 |
| C21—N3—H1N | 123.9 (19) | C27—C26—C25 | 121.8 (2) |
| C20—N3—H1N | 123.5 (19) | C27—C26—H26 | 119.1 |
| N1—C12—C8 | 113.68 (17) | C25—C26—H26 | 119.1 |
| N1—C12—H12A | 108.8 | C6—C1—C2 | 120.7 (2) |
| C8—C12—H12A | 108.8 | C6—C1—C11 | 119.1 (2) |
| N1—C12—H12B | 108.8 | C2—C1—C11 | 120.16 (19) |
| C8—C12—H12B | 108.8 | C2—C3—C4 | 122.0 (2) |
| H12A—C12—H12B | 107.7 | C2—C3—H3 | 119.0 |
| O1—C9—C8 | 120.96 (19) | C4—C3—H3 | 119.0 |
| O1—C9—C10 | 121.42 (19) | C8—C7—C4 | 130.8 (2) |
| C8—C9—C10 | 117.59 (18) | C8—C7—H7 | 114.6 |

| | | | |
|---------------|--------------|-----------------|-------------|
| C23—N2—C22 | 114.55 (18) | C4—C7—H7 | 114.6 |
| C23—N2—C14 | 106.82 (16) | O2—C21—N3 | 125.6 (2) |
| C22—N2—C14 | 116.15 (19) | O2—C21—C14 | 126.4 (2) |
| C19—C20—C15 | 122.4 (2) | N3—C21—C14 | 107.9 (2) |
| C19—C20—N3 | 128.1 (2) | C17—C18—C19 | 119.3 (2) |
| C15—C20—N3 | 109.5 (2) | C17—C18—H18 | 120.3 |
| C16—C15—C20 | 119.3 (2) | C19—C18—H18 | 120.3 |
| C16—C15—C14 | 130.7 (2) | C1—C6—C5 | 119.1 (2) |
| C20—C15—C14 | 109.71 (19) | C1—C6—H6 | 120.4 |
| C6—C5—C4 | 122.3 (2) | C5—C6—H6 | 120.4 |
| C6—C5—H5 | 118.8 | N2—C23—C24 | 102.47 (17) |
| C4—C5—H5 | 118.8 | N2—C23—H23A | 111.3 |
| C11—C10—C9 | 105.19 (16) | C24—C23—H23A | 111.3 |
| C11—C10—C24 | 114.90 (17) | N2—C23—H23B | 111.3 |
| C9—C10—C24 | 110.89 (17) | C24—C23—H23B | 111.3 |
| C11—C10—C14 | 110.74 (16) | H23A—C23—H23B | 109.2 |
| C9—C10—C14 | 111.11 (16) | C20—C19—C18 | 118.0 (2) |
| C24—C10—C14 | 104.14 (16) | C20—C19—H19 | 121.0 |
| N1—C11—C10 | 107.35 (16) | C18—C19—H19 | 121.0 |
| N1—C11—H11A | 110.2 | C29—C30—C25 | 121.8 (2) |
| C10—C11—H11A | 110.2 | C29—C30—H30 | 119.1 |
| N1—C11—H11B | 110.2 | C25—C30—H30 | 119.1 |
| C10—C11—H11B | 110.2 | C28—C29—C30 | 119.2 (2) |
| H11A—C11—H11B | 108.5 | C28—C29—H29 | 120.4 |
| C5—C4—C3 | 116.5 (2) | C30—C29—H29 | 120.4 |
| C5—C4—C7 | 125.05 (19) | C28—C27—C26 | 119.2 (2) |
| C3—C4—C7 | 118.4 (2) | C28—C27—H27 | 120.4 |
| C18—C17—F1 | 118.6 (2) | C26—C27—H27 | 120.4 |
| C18—C17—C16 | 123.5 (2) | C1—C2—C3 | 119.3 (2) |
| F1—C17—C16 | 118.0 (2) | C1—C2—H2 | 120.4 |
| C26—C25—C30 | 117.0 (2) | C3—C2—H2 | 120.4 |
| C26—C25—C24 | 120.2 (2) | N1—C13—H13A | 109.5 |
| C30—C25—C24 | 122.8 (2) | N1—C13—H13B | 109.5 |
| C29—C28—C27 | 121.0 (2) | H13A—C13—H13B | 109.5 |
| C29—C28—C12 | 118.6 (2) | N1—C13—H13C | 109.5 |
| C27—C28—C12 | 120.4 (2) | H13A—C13—H13C | 109.5 |
| C25—C24—C23 | 116.08 (18) | H13B—C13—H13C | 109.5 |
| C25—C24—C10 | 115.64 (17) | N2—C22—H22A | 109.5 |
| C23—C24—C10 | 104.34 (17) | N2—C22—H22B | 109.5 |
| C25—C24—H24 | 106.7 | H22A—C22—H22B | 109.5 |
| C23—C24—H24 | 106.7 | N2—C22—H22C | 109.5 |
| C10—C24—H24 | 106.7 | H22A—C22—H22C | 109.5 |
| N2—C14—C15 | 110.68 (17) | H22B—C22—H22C | 109.5 |
| N2—C14—C21 | 111.43 (17) | | |
| C11—N1—C12—C8 | -46.9 (2) | C24—C10—C14—N2 | 15.56 (19) |
| C13—N1—C12—C8 | -172.82 (19) | C11—C10—C14—C15 | -98.0 (2) |
| C7—C8—C12—N1 | -162.6 (2) | C9—C10—C14—C15 | 18.5 (2) |
| C9—C8—C12—N1 | 18.2 (3) | C24—C10—C14—C15 | 137.96 (18) |
| C7—C8—C9—O1 | -17.5 (3) | C11—C10—C14—C21 | 19.7 (2) |

supplementary materials

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|-----------------|--------------|-----------------|--------------|
| C12—C8—C9—O1 | 161.9 (2) | C9—C10—C14—C21 | 136.27 (18) |
| C7—C8—C9—C10 | 164.77 (18) | C24—C10—C14—C21 | -104.29 (19) |
| C12—C8—C9—C10 | -15.9 (3) | C18—C17—C16—C15 | 0.3 (3) |
| C21—N3—C20—C19 | -178.2 (2) | F1—C17—C16—C15 | -179.82 (18) |
| C21—N3—C20—C15 | -0.7 (3) | C20—C15—C16—C17 | -1.4 (3) |
| C19—C20—C15—C16 | 2.2 (3) | C14—C15—C16—C17 | -174.3 (2) |
| N3—C20—C15—C16 | -175.45 (19) | C30—C25—C26—C27 | 1.3 (3) |
| C19—C20—C15—C14 | 176.5 (2) | C24—C25—C26—C27 | -178.5 (2) |
| N3—C20—C15—C14 | -1.1 (2) | C5—C4—C3—C2 | 1.5 (3) |
| O1—C9—C10—C11 | -139.5 (2) | C7—C4—C3—C2 | 179.8 (2) |
| C8—C9—C10—C11 | 38.2 (2) | C9—C8—C7—C4 | 179.3 (2) |
| O1—C9—C10—C24 | -14.7 (3) | C12—C8—C7—C4 | 0.0 (4) |
| C8—C9—C10—C24 | 163.01 (17) | C5—C4—C7—C8 | -18.4 (4) |
| O1—C9—C10—C14 | 100.6 (2) | C3—C4—C7—C8 | 163.5 (2) |
| C8—C9—C10—C14 | -81.7 (2) | C20—N3—C21—O2 | 177.5 (2) |
| C12—N1—C11—C10 | 74.2 (2) | C20—N3—C21—C14 | 2.2 (3) |
| C13—N1—C11—C10 | -161.35 (19) | N2—C14—C21—O2 | -60.5 (3) |
| C9—C10—C11—N1 | -66.3 (2) | C15—C14—C21—O2 | -177.9 (2) |
| C24—C10—C11—N1 | 171.46 (16) | C10—C14—C21—O2 | 54.0 (3) |
| C14—C10—C11—N1 | 53.8 (2) | N2—C14—C21—N3 | 114.7 (2) |
| C6—C5—C4—C3 | -1.2 (3) | C15—C14—C21—N3 | -2.7 (2) |
| C6—C5—C4—C7 | -179.3 (2) | C10—C14—C21—N3 | -130.82 (19) |
| C26—C25—C24—C23 | -138.5 (2) | F1—C17—C18—C19 | -179.7 (2) |
| C30—C25—C24—C23 | 41.7 (3) | C16—C17—C18—C19 | 0.2 (4) |
| C26—C25—C24—C10 | 98.8 (2) | C2—C1—C6—C5 | 0.5 (4) |
| C30—C25—C24—C10 | -81.1 (3) | C11—C1—C6—C5 | 178.68 (18) |
| C11—C10—C24—C25 | 18.4 (3) | C4—C5—C6—C1 | 0.2 (4) |
| C9—C10—C24—C25 | -100.7 (2) | C22—N2—C23—C24 | 176.68 (19) |
| C14—C10—C24—C25 | 139.74 (18) | C14—N2—C23—C24 | 46.6 (2) |
| C11—C10—C24—C23 | -110.3 (2) | C25—C24—C23—N2 | -162.38 (18) |
| C9—C10—C24—C23 | 130.57 (18) | C10—C24—C23—N2 | -33.9 (2) |
| C14—C10—C24—C23 | 11.0 (2) | C15—C20—C19—C18 | -1.7 (3) |
| C23—N2—C14—C15 | -166.58 (18) | N3—C20—C19—C18 | 175.5 (2) |
| C22—N2—C14—C15 | 64.2 (2) | C17—C18—C19—C20 | 0.5 (3) |
| C23—N2—C14—C21 | 82.3 (2) | C26—C25—C30—C29 | -0.8 (3) |
| C22—N2—C14—C21 | -46.9 (3) | C24—C25—C30—C29 | 179.1 (2) |
| C23—N2—C14—C10 | -38.6 (2) | C27—C28—C29—C30 | 0.9 (4) |
| C22—N2—C14—C10 | -167.77 (18) | C12—C28—C29—C30 | 179.04 (18) |
| C16—C15—C14—N2 | 57.8 (3) | C25—C30—C29—C28 | -0.3 (4) |
| C20—C15—C14—N2 | -115.70 (19) | C29—C28—C27—C26 | -0.4 (4) |
| C16—C15—C14—C21 | 175.7 (2) | C12—C28—C27—C26 | -178.46 (18) |
| C20—C15—C14—C21 | 2.3 (2) | C25—C26—C27—C28 | -0.8 (4) |
| C16—C15—C14—C10 | -60.4 (3) | C6—C1—C2—C3 | -0.2 (4) |
| C20—C15—C14—C10 | 126.16 (19) | C11—C1—C2—C3 | -178.34 (19) |
| C11—C10—C14—N2 | 139.59 (16) | C4—C3—C2—C1 | -0.9 (4) |
| C9—C10—C14—N2 | -103.89 (18) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| C11—H11B···O2 | 0.97 | 2.37 | 2.968 (3) | 119 |
| C23—H23A···O2 | 0.97 | 2.58 | 3.162 (3) | 119 |
| C24—H24···O1 | 0.98 | 2.26 | 2.787 (3) | 113 |
| N3—H1N···O1 ⁱ | 0.84 (3) | 2.50 (3) | 3.288 (3) | 157 (3) |

Symmetry codes: (i) *x*, *y*-1, *z*.

Fig. 1

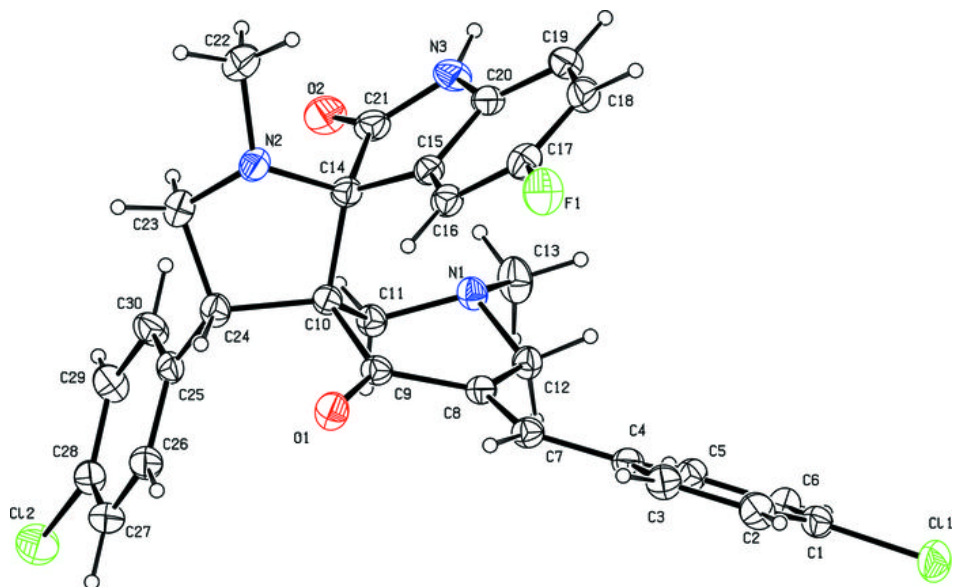


Fig. 2

