# 5-Chloro-5″-(4-chlorobenzylidene)-4′-(4-chlorophenyl)-1″-ethyl-1′-methyldispiro-[indoline-3,2′-pyrrolidine-3′,3″-piperidine]-2,4″-dione

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Two spiro links are found in the title compound, $C_{31}H_{28}Cl_3N_3O_2$, one connecting the piperidine and pyrrolidine rings, and the other connecting the pyrrolidine ring and indole residue. The piperidine ring adopts a half-chair conformation, in which the C atom connected to the spiro-C atom lies 0.741 (3) Å out of the plane of the remaining five atoms (r.m.s. deviation = 0.053 Å). The pyrrolidine ring has an envelope conformation with the flap atom being the methylene C atom. Centrosymmetric eight-membered {···HNCO}$_2$ amide dimers are the most significant feature of the crystal packing. These are connected into layers parallel to ($\bar{1}$20) by C—H···O and $\pi$–$\pi$ interactions between pyrrolidine-bound benzene rings [inter-centroid distance = 3.8348 (15) Å]. Slipped face-to-face interactions between the edges of pyrrolidine-bound benzene [shortest C···C separation = 3.484 (4) Å] connect the layers into a three-dimensional architecture.

## Related literature

For the biological activity of related spiropyrrolidine analogues, see: Girgis *et al.* (2012); Kumar *et al.* (2008). For related structural studies, see: Farag *et al.* (2013). For the synthesis of the precursor molecule, see Al-Omary *et al.* (2012).
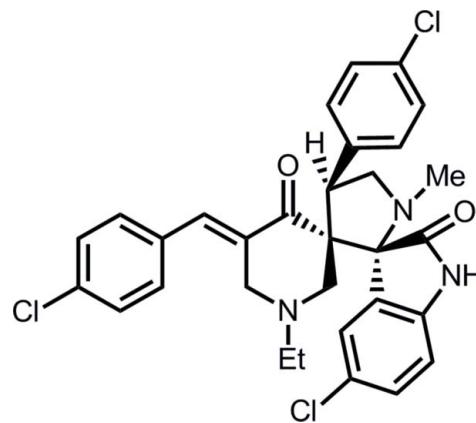
## Experimental

### Crystal data

| | |
|---|---|
| $C_{31}H_{28}Cl_3N_3O_2$ | $\gamma$ = 114.893 (1)° |
| $M_r$ = 580.91 | $V$ = 1443.77 (6) Å$^3$ |
| Triclinic, $P\bar{1}$ | $Z$ = 2 |
| $a$ = 11.1901 (2) Å | Mo $K\alpha$ radiation |
| $b$ = 11.6434 (3) Å | $\mu$ = 0.35 mm$^{-1}$ |
| $c$ = 12.4270 (3) Å | $T$ = 293 K |
| $\alpha$ = 99.477 (2)° | 1.02 × 0.53 × 0.37 mm |
| $\beta$ = 90.235 (2)° | |

### Data collection

| | |
|---|---|
| Nonius 590 KappaCCD diffractometer | 11344 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | 6482 independent reflections |
| $T_{min}$ = 0.880, $T_{max}$ = 0.994 | 4260 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.043 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.057 | 354 parameters |
| $wR(F^2)$ = 0.160 | H-atom parameters constrained |
| $S$ = 1.00 | $\Delta\rho_{max}$ = 0.72 e Å$^{-3}$ |
| 6482 reflections | $\Delta\rho_{min}$ = −0.73 e Å$^{-3}$ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3n···O2$^i$ | 0.86 | 2.03 | 2.883 (3) | 170 |
| C31—H31···O1$^{ii}$ | 0.93 | 2.47 | 3.160 (4) | 131 |

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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# organic compounds

## References

Al-Omary, F. A. M., Hassan, G. S., El-Messery, S. M. & El-Subbagh, H. I. (2012). *Eur. J. Med. Chem.* **47**, 65–72.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Farag, I. S. A., Girgis, A. S., Ramadan, A. A., Moustafa, A. M. & Tiekink, E. R. T. (2013). *Acta Cryst.* E70, o22–o23.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Girgis, A. S., Tala, S. R., Oliferenko, P. V., Oliferenko, A. A. & Katritzky, A. R. (2012). *Eur. J. Med. Chem.* **50**, 1–8.
Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Kumar, R. R., Perumal, S., Senthilkumar, P., Yoeeswair, P. & Sriram, D. (2008). *J. Med. Chem.* **51**, 5731–5735.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

# supporting information

## 5-Chloro-5″-(4-chlorobenzylidene)-4′-(4-chlorophenyl)-1″-ethyl-1′-methyl-dispiro[indoline-3,2′-pyrrolidine-3′,3″-piperidine]-2,4″-dione

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### S1. Experimental

#### S1.1. Synthesis and crystallization

A mixture of equimolar amounts of 3*E*,5*E*-1-ethyl-3,5-bis({4-chlorophenyl)methylidene)-4-piperidone (5 mmol), prepared by a literature procedure (Al-Omary *et al.*, 2012), 5-chloroisatin and sarcosine in absolute ethanol (25 ml) was boiled under reflux (TLC monitoring). The separated solid was collected and crystallized from *n*-butanol affording (I) as pale-yellow blocks. Reaction time 9 h. *M*.pt: 494–496 K. Yield 76%. Anal. Calcd. for $C_{31}H_{28}Cl_3N_3O_2$ (580.95): C, 64.09; H, 4.86; N, 7.23. Found: C, 64.28; H, 5.02; N, 7.31. IR: $v_{max}$/cm$^{-1}$: 3167 (N—H); 1689 (C=O); 1591, 1480 (C=C).

#### S1.2. Refinement

The C-bound H atoms were geometrically placed (C—H = 0.93–0.98 Å) and refined as riding with $U_{iso}$(H) = 1.2–1.5$U_{eq}$(C). The N-bound H-atom was treated similarly with N—H = 0.86 Å, and with $U_{iso}$(H) = 1.2$U_{eq}$(N).

### S2. Results and discussion

Spiropyrrolidine derivatives are known to have biological activity and the basic sketal structure has been well established by X-ray crystallography (Kumar *et al.* 2008). In continuation of our biological and crystallographic studies of such derivatives (Girgis *et al.* 2012; Farag *et al.* 2013), the title compound, (I), was synthesised and characterised crystallographically.

Two spiro links exist in (I), Fig. 1, namely where the piperidine and pyrrolidine rings are connected at C1, and where the pyrrolidine ring and indole residue are connected at C6. The phenylmethylidene and pyrrolidine-bound aryl residues are connected to the piperidine ring at positions C4 and C8, respectively. The conformation about the C4=C11 double bond is *E*. The *sp*$^3$ character of the piperidine-N1 atom is confirmed by the sum of the angles about this atom, *i.e.* 335 °. The piperidine ring adopts a half-chair conformation where the C2 atom lies 0.741 (3) Å out of the plane of the remaining five atoms (r.m.s. deviation = 0.0527 Å). The C6 and C8 atoms occupy axial and equatorial positions with respect to the piperidine ring, the phenylmethylidene residue occupies an equatorial position, and the N-bound methyl substituent is equatorial. The pyrrolidine ring has an envelope conformation with the flap atom being the C7 atom which lies 0.607 (4) Å out of the plane of the remaining four atoms (r.m.s. deviation = 0.0536 Å).

Centrosymmetric eight-membered {⋯HNCO}$_2$ synthons are found in the crystal structure of (I), Table 1. The carbonyl-O1 atom also participates in other significant intermolecular interactions, forming (pyrrolidine-bound benzene)C—H⋯O1 interactions with centrosymmetrically related dimers to form 14-membered {⋯HC$_5$O}$_2$ synthons leading to supra-molecular chains, Table 1. The chains are connected into a layer approximately parallel to (-1 2 0) by π—π, face-to-face, interactions [inter-centroid distance = 3.8348 (15) Å for symmetry operation: 1-*x*, 1-*y*, 1-*z*] between centrosymmetrically

related methylidene-benzene rings (Fig. 2). The closest interactions between layers appear to be slipped face-to-face interactions between the edges (atoms C28 and C29) of pyrrolidine-bound benzene rings with the shortest separation being 3.484 (4) Å for C28···C28$^i$ (symmetry operation $i$: -$x$, -1-$z$, 1-$z$); see Fig. 3.
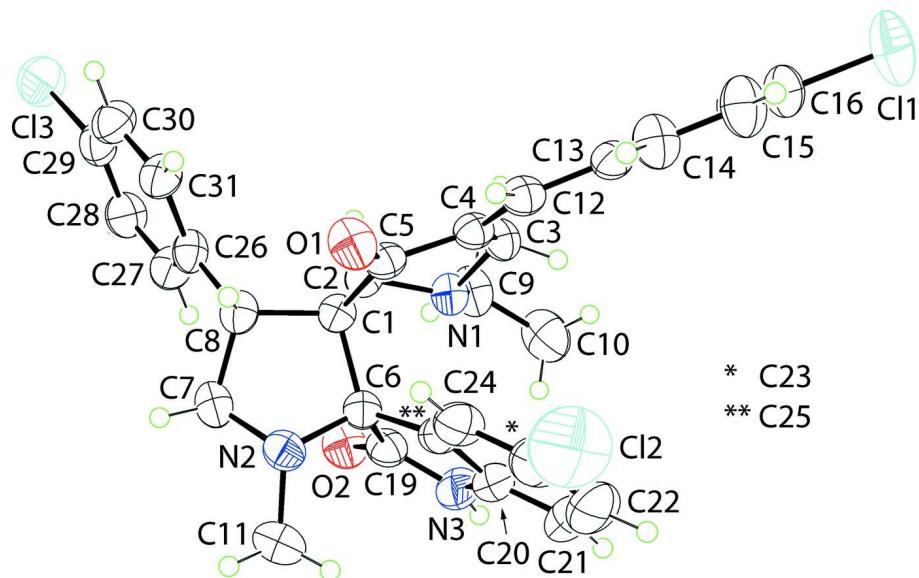


**Figure 1**

The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.
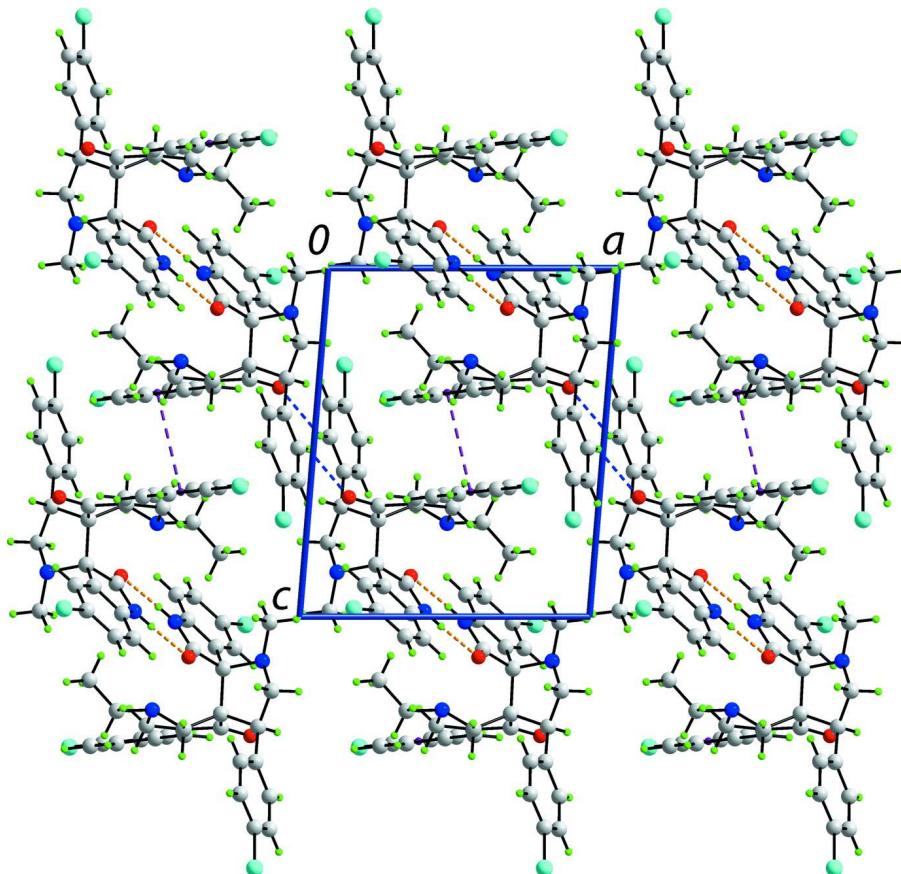
**Figure 2**

A view of the supramolecular layer in the *ac* plane in the crystal structure of (I). The N—H⋯O, C—H⋯O and π—π interactions are shown as orange, blue and purple dashed lines, respectively.
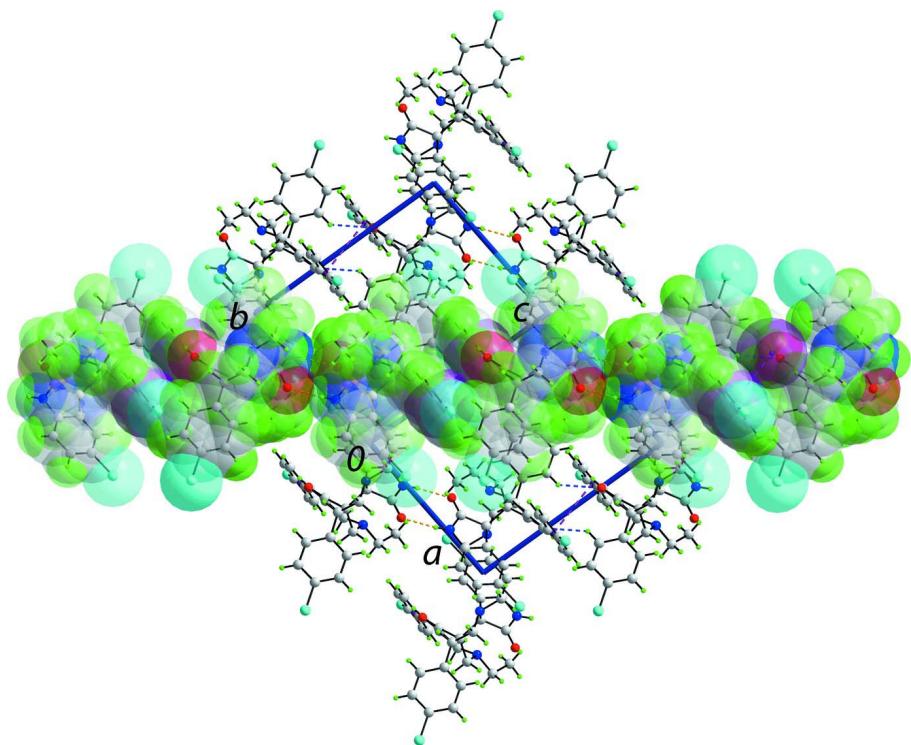
**Figure 3**

A view of the unit-cell contents in (I). One layer has been highlighted in space-filling mode. The N—H···O, C—H···O and π—π interactions are shown as orange, blue and purple dashed lines, respectively.

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*Crystal data*

| | |
|---|---|
| $C_{31}H_{28}Cl_3N_3O_2$ | $Z = 2$ |
| $M_r = 580.91$ | $F(000) = 604$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.336$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 11.1901$ (2) Å | Cell parameters from 7513 reflections |
| $b = 11.6434$ (3) Å | $\theta = 2.9$–27.9° |
| $c = 12.4270$ (3) Å | $\mu = 0.35$ mm$^{-1}$ |
| $\alpha = 99.477$ (2)° | $T = 293$ K |
| $\beta = 90.235$ (2)° | Block, pale-yellow |
| $\gamma = 114.893$ (1)° | $1.02 \times 0.53 \times 0.37$ mm |
| $V = 1443.77$ (6) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Nonius 590 KappaCCD diffractometer | 11344 measured reflections |
| Radiation source: fine-focus sealed tube | 6482 independent reflections |
| Graphite monochromator | 4260 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.043$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$ |
| | $h = -12 \rightarrow 14$ |
| | $k = -15 \rightarrow 14$ |
| $T_{min} = 0.880$, $T_{max} = 0.994$ | $l = -16 \rightarrow 15$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.057$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.160$ | |
| $S = 1.00$ | H-atom parameters constrained |
| 6482 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.8473P]$ |
| 354 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 0.72$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.73$ e Å$^{-3}$ |

*Special details*

**Geometry**. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.75652 (9) | 0.88544 (7) | 0.62569 (9) | 0.0843 (3) |
| Cl2 | 0.18456 (16) | 0.46678 (12) | 0.97683 (11) | 0.1288 (5) |
| Cl3 | 0.08381 (9) | −0.48680 (8) | 0.27827 (7) | 0.0746 (3) |
| O1 | 0.13605 (17) | 0.13409 (17) | 0.65765 (16) | 0.0535 (5) |
| O2 | 0.37169 (18) | −0.08975 (17) | 0.88375 (15) | 0.0527 (5) |
| N1 | 0.48196 (18) | 0.11736 (18) | 0.73216 (16) | 0.0388 (4) |
| N2 | 0.11620 (19) | −0.05244 (19) | 0.87264 (16) | 0.0433 (5) |
| N3 | 0.4280 (2) | 0.1109 (2) | 0.98503 (17) | 0.0524 (5) |
| H3n | 0.4902 | 0.1139 | 1.0278 | 0.063* |
| C1 | 0.2438 (2) | 0.0150 (2) | 0.72095 (18) | 0.0352 (5) |
| C2 | 0.3678 (2) | 0.0046 (2) | 0.67812 (19) | 0.0388 (5) |
| H2A | 0.3713 | −0.0728 | 0.6938 | 0.047* |
| H2B | 0.3663 | 0.0006 | 0.5995 | 0.047* |
| C3 | 0.4971 (2) | 0.2310 (2) | 0.6878 (2) | 0.0427 (5) |
| H3A | 0.5315 | 0.2262 | 0.6165 | 0.051* |
| H3B | 0.5614 | 0.3072 | 0.7354 | 0.051* |
| C4 | 0.3699 (2) | 0.2447 (2) | 0.67642 (18) | 0.0381 (5) |
| C5 | 0.2403 (2) | 0.1327 (2) | 0.68197 (18) | 0.0375 (5) |
| C6 | 0.2491 (2) | 0.0382 (2) | 0.85091 (18) | 0.0370 (5) |
| C7 | 0.0761 (3) | −0.1661 (2) | 0.7874 (2) | 0.0485 (6) |
| H7A | −0.0180 | −0.2201 | 0.7849 | 0.058* |
| H7B | 0.1242 | −0.2164 | 0.7981 | 0.058* |
| C8 | 0.1119 (2) | −0.1086 (2) | 0.68402 (19) | 0.0407 (5) |
| H8 | 0.0449 | −0.0790 | 0.6682 | 0.049* |
| C9 | 0.6045 (3) | 0.0993 (3) | 0.7295 (3) | 0.0542 (7) |

| | | | |
|---|---|---|---|
| H9A | 0.6395 | 0.1114 | 0.6589 | 0.065* |
| H9B | 0.5841 | 0.0116 | 0.7373 | 0.065* |
| C10 | 0.7081 (3) | 0.1904 (3) | 0.8178 (3) | 0.0718 (9) |
| H10A | 0.7305 | 0.2774 | 0.8095 | 0.108* |
| H10B | 0.7854 | 0.1743 | 0.8125 | 0.108* |
| H10C | 0.6747 | 0.1778 | 0.8880 | 0.108* |
| C11 | 0.1021 (3) | −0.0799 (3) | 0.9836 (2) | 0.0609 (7) |
| H11A | 0.0106 | −0.1300 | 0.9925 | 0.091* |
| H11B | 0.1349 | −0.0004 | 1.0355 | 0.091* |
| H11C | 0.1517 | −0.1274 | 0.9959 | 0.091* |
| C12 | 0.3628 (3) | 0.3537 (2) | 0.66025 (19) | 0.0424 (5) |
| H12 | 0.2769 | 0.3464 | 0.6538 | 0.051* |
| C13 | 0.4638 (2) | 0.4803 (2) | 0.65098 (18) | 0.0405 (5) |
| C14 | 0.4248 (3) | 0.5800 (3) | 0.6556 (2) | 0.0534 (7) |
| H14 | 0.3366 | 0.5627 | 0.6642 | 0.064* |
| C15 | 0.5127 (3) | 0.7033 (3) | 0.6478 (3) | 0.0611 (8) |
| H15 | 0.4839 | 0.7679 | 0.6510 | 0.073* |
| C16 | 0.6433 (3) | 0.7303 (2) | 0.6353 (2) | 0.0537 (7) |
| C17 | 0.6857 (3) | 0.6346 (3) | 0.6289 (2) | 0.0538 (7) |
| H17 | 0.7740 | 0.6528 | 0.6198 | 0.065* |
| C18 | 0.5963 (3) | 0.5111 (2) | 0.6361 (2) | 0.0497 (6) |
| H18 | 0.6255 | 0.4466 | 0.6309 | 0.060* |
| C19 | 0.3588 (2) | 0.0111 (2) | 0.9046 (2) | 0.0441 (6) |
| C20 | 0.3866 (3) | 0.2094 (3) | 0.9908 (2) | 0.0519 (6) |
| C21 | 0.4321 (4) | 0.3248 (3) | 1.0627 (3) | 0.0784 (10) |
| H21 | 0.5032 | 0.3489 | 1.1138 | 0.094* |
| C22 | 0.3694 (5) | 0.4044 (3) | 1.0570 (3) | 0.0883 (12) |
| H22 | 0.3992 | 0.4836 | 1.1040 | 0.106* |
| C23 | 0.2635 (4) | 0.3662 (3) | 0.9821 (3) | 0.0741 (10) |
| C24 | 0.2167 (3) | 0.2502 (3) | 0.9093 (2) | 0.0527 (7) |
| H24 | 0.1443 | 0.2256 | 0.8594 | 0.063* |
| C25 | 0.2810 (2) | 0.1722 (2) | 0.91300 (19) | 0.0427 (6) |
| C26 | 0.1113 (2) | −0.2007 (2) | 0.5831 (2) | 0.0407 (5) |
| C27 | 0.1627 (3) | −0.2913 (2) | 0.5846 (2) | 0.0485 (6) |
| H27 | 0.2025 | −0.2933 | 0.6496 | 0.058* |
| C28 | 0.1555 (3) | −0.3778 (2) | 0.4911 (2) | 0.0518 (6) |
| H28 | 0.1906 | −0.4371 | 0.4932 | 0.062* |
| C29 | 0.0960 (3) | −0.3750 (2) | 0.3951 (2) | 0.0501 (6) |
| C30 | 0.0446 (3) | −0.2871 (3) | 0.3903 (2) | 0.0530 (6) |
| H30 | 0.0049 | −0.2858 | 0.3249 | 0.064* |
| C31 | 0.0529 (3) | −0.2008 (2) | 0.4842 (2) | 0.0479 (6) |
| H31 | 0.0184 | −0.1412 | 0.4810 | 0.057* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0726 (5) | 0.0396 (4) | 0.1372 (8) | 0.0211 (4) | 0.0221 (5) | 0.0141 (4) |
| Cl2 | 0.1991 (14) | 0.0931 (8) | 0.1389 (10) | 0.1089 (9) | 0.0425 (9) | 0.0100 (7) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Cl3 | 0.0954 (6) | 0.0525 (4) | 0.0640 (5) | 0.0258 (4) | 0.0110 (4) | −0.0047 (3) |
| O1 | 0.0433 (10) | 0.0552 (11) | 0.0732 (12) | 0.0273 (9) | −0.0027 (9) | 0.0251 (9) |
| O2 | 0.0540 (11) | 0.0530 (11) | 0.0630 (11) | 0.0307 (9) | −0.0014 (9) | 0.0207 (9) |
| N1 | 0.0349 (10) | 0.0363 (10) | 0.0505 (11) | 0.0202 (9) | 0.0005 (8) | 0.0086 (9) |
| N2 | 0.0421 (11) | 0.0459 (12) | 0.0451 (11) | 0.0204 (10) | 0.0071 (9) | 0.0121 (9) |
| N3 | 0.0534 (13) | 0.0570 (14) | 0.0457 (12) | 0.0222 (11) | −0.0104 (10) | 0.0108 (11) |
| C1 | 0.0361 (12) | 0.0351 (11) | 0.0389 (12) | 0.0194 (10) | 0.0001 (9) | 0.0066 (9) |
| C2 | 0.0422 (13) | 0.0370 (12) | 0.0413 (13) | 0.0218 (11) | 0.0008 (10) | 0.0048 (10) |
| C3 | 0.0439 (13) | 0.0359 (12) | 0.0521 (14) | 0.0196 (11) | 0.0036 (11) | 0.0113 (11) |
| C4 | 0.0454 (13) | 0.0388 (12) | 0.0351 (12) | 0.0223 (11) | 0.0018 (10) | 0.0087 (10) |
| C5 | 0.0426 (13) | 0.0408 (12) | 0.0340 (11) | 0.0224 (11) | −0.0001 (9) | 0.0074 (10) |
| C6 | 0.0375 (12) | 0.0370 (12) | 0.0397 (12) | 0.0182 (10) | 0.0004 (9) | 0.0091 (10) |
| C7 | 0.0411 (14) | 0.0407 (13) | 0.0587 (16) | 0.0120 (11) | 0.0032 (11) | 0.0114 (12) |
| C8 | 0.0367 (12) | 0.0389 (12) | 0.0485 (14) | 0.0185 (10) | −0.0033 (10) | 0.0064 (10) |
| C9 | 0.0404 (14) | 0.0482 (15) | 0.0819 (19) | 0.0249 (12) | 0.0036 (13) | 0.0162 (14) |
| C10 | 0.0414 (16) | 0.083 (2) | 0.094 (2) | 0.0232 (16) | 0.0001 (15) | 0.0325 (19) |
| C11 | 0.0635 (18) | 0.0696 (19) | 0.0572 (17) | 0.0301 (16) | 0.0193 (14) | 0.0268 (15) |
| C12 | 0.0490 (14) | 0.0449 (13) | 0.0405 (13) | 0.0261 (12) | 0.0026 (10) | 0.0102 (11) |
| C13 | 0.0508 (14) | 0.0392 (12) | 0.0368 (12) | 0.0242 (11) | −0.0013 (10) | 0.0072 (10) |
| C14 | 0.0502 (15) | 0.0458 (15) | 0.0723 (18) | 0.0274 (13) | 0.0013 (13) | 0.0133 (13) |
| C15 | 0.0601 (18) | 0.0401 (15) | 0.089 (2) | 0.0278 (14) | 0.0019 (15) | 0.0099 (14) |
| C16 | 0.0580 (17) | 0.0357 (13) | 0.0656 (17) | 0.0194 (12) | 0.0047 (13) | 0.0063 (12) |
| C17 | 0.0545 (16) | 0.0475 (15) | 0.0666 (17) | 0.0278 (13) | 0.0118 (13) | 0.0129 (13) |
| C18 | 0.0603 (16) | 0.0436 (14) | 0.0569 (16) | 0.0315 (13) | 0.0118 (13) | 0.0141 (12) |
| C19 | 0.0434 (14) | 0.0485 (14) | 0.0446 (14) | 0.0207 (12) | 0.0012 (11) | 0.0164 (12) |
| C20 | 0.0623 (17) | 0.0486 (15) | 0.0371 (13) | 0.0167 (13) | 0.0002 (12) | 0.0064 (11) |
| C21 | 0.105 (3) | 0.062 (2) | 0.0463 (17) | 0.020 (2) | −0.0093 (17) | −0.0034 (15) |
| C22 | 0.141 (4) | 0.054 (2) | 0.057 (2) | 0.036 (2) | 0.013 (2) | −0.0079 (16) |
| C23 | 0.118 (3) | 0.0525 (18) | 0.063 (2) | 0.047 (2) | 0.028 (2) | 0.0078 (15) |
| C24 | 0.0703 (18) | 0.0499 (15) | 0.0479 (15) | 0.0344 (14) | 0.0157 (13) | 0.0105 (12) |
| C25 | 0.0527 (15) | 0.0417 (13) | 0.0361 (12) | 0.0216 (12) | 0.0068 (10) | 0.0086 (10) |
| C26 | 0.0357 (12) | 0.0341 (12) | 0.0507 (14) | 0.0142 (10) | −0.0038 (10) | 0.0058 (10) |
| C27 | 0.0516 (15) | 0.0440 (14) | 0.0542 (15) | 0.0248 (12) | −0.0038 (12) | 0.0089 (12) |
| C28 | 0.0580 (16) | 0.0399 (14) | 0.0613 (17) | 0.0250 (13) | 0.0053 (13) | 0.0077 (12) |
| C29 | 0.0508 (15) | 0.0379 (13) | 0.0527 (15) | 0.0122 (12) | 0.0064 (12) | 0.0033 (11) |
| C30 | 0.0546 (16) | 0.0544 (16) | 0.0486 (15) | 0.0230 (13) | −0.0057 (12) | 0.0068 (12) |
| C31 | 0.0478 (14) | 0.0469 (14) | 0.0524 (15) | 0.0241 (12) | −0.0056 (11) | 0.0079 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C16 | 1.740 (3) | C10—H10B | 0.9600 |
| Cl2—C23 | 1.747 (3) | C10—H10C | 0.9600 |
| Cl3—C29 | 1.745 (3) | C11—H11A | 0.9600 |
| O1—C5 | 1.211 (3) | C11—H11B | 0.9600 |
| O2—C19 | 1.229 (3) | C11—H11C | 0.9600 |
| N1—C2 | 1.448 (3) | C12—C13 | 1.456 (3) |
| N1—C3 | 1.461 (3) | C12—H12 | 0.9300 |
| N1—C9 | 1.472 (3) | C13—C18 | 1.392 (4) |

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| N2—C7 | 1.453 (3) | C13—C14 | 1.395 (3) |
| N2—C11 | 1.461 (3) | C14—C15 | 1.377 (4) |
| N2—C6 | 1.475 (3) | C14—H14 | 0.9300 |
| N3—C19 | 1.343 (3) | C15—C16 | 1.375 (4) |
| N3—C20 | 1.398 (3) | C15—H15 | 0.9300 |
| N3—H3n | 0.8600 | C16—C17 | 1.375 (4) |
| C1—C2 | 1.532 (3) | C17—C18 | 1.382 (4) |
| C1—C5 | 1.543 (3) | C17—H17 | 0.9300 |
| C1—C8 | 1.565 (3) | C18—H18 | 0.9300 |
| C1—C6 | 1.589 (3) | C20—C21 | 1.373 (4) |
| C2—H2A | 0.9700 | C20—C25 | 1.393 (4) |
| C2—H2B | 0.9700 | C21—C22 | 1.387 (5) |
| C3—C4 | 1.506 (3) | C21—H21 | 0.9300 |
| C3—H3A | 0.9700 | C22—C23 | 1.371 (5) |
| C3—H3B | 0.9700 | C22—H22 | 0.9300 |
| C4—C12 | 1.351 (3) | C23—C24 | 1.384 (4) |
| C4—C5 | 1.499 (3) | C24—C25 | 1.381 (3) |
| C6—C25 | 1.514 (3) | C24—H24 | 0.9300 |
| C6—C19 | 1.561 (3) | C26—C31 | 1.389 (3) |
| C7—C8 | 1.524 (3) | C26—C27 | 1.401 (3) |
| C7—H7A | 0.9700 | C27—C28 | 1.384 (4) |
| C7—H7B | 0.9700 | C27—H27 | 0.9300 |
| C8—C26 | 1.508 (3) | C28—C29 | 1.376 (4) |
| C8—H8 | 0.9800 | C28—H28 | 0.9300 |
| C9—C10 | 1.498 (4) | C29—C30 | 1.378 (4) |
| C9—H9A | 0.9700 | C30—C31 | 1.384 (4) |
| C9—H9B | 0.9700 | C30—H30 | 0.9300 |
| C10—H10A | 0.9600 | C31—H31 | 0.9300 |
| | | | |
| C2—N1—C3 | 110.85 (18) | H11A—C11—H11B | 109.5 |
| C2—N1—C9 | 113.09 (19) | N2—C11—H11C | 109.5 |
| C3—N1—C9 | 111.41 (19) | H11A—C11—H11C | 109.5 |
| C7—N2—C11 | 114.2 (2) | H11B—C11—H11C | 109.5 |
| C7—N2—C6 | 106.79 (18) | C4—C12—C13 | 132.3 (2) |
| C11—N2—C6 | 115.8 (2) | C4—C12—H12 | 113.9 |
| C19—N3—C20 | 111.8 (2) | C13—C12—H12 | 113.9 |
| C19—N3—H3n | 124.1 | C18—C13—C14 | 116.6 (2) |
| C20—N3—H3n | 124.1 | C18—C13—C12 | 125.9 (2) |
| C2—C1—C5 | 106.00 (18) | C14—C13—C12 | 117.5 (2) |
| C2—C1—C8 | 114.65 (18) | C15—C14—C13 | 122.0 (3) |
| C5—C1—C8 | 111.33 (17) | C15—C14—H14 | 119.0 |
| C2—C1—C6 | 112.13 (17) | C13—C14—H14 | 119.0 |
| C5—C1—C6 | 108.72 (17) | C16—C15—C14 | 119.6 (2) |
| C8—C1—C6 | 103.98 (17) | C16—C15—H15 | 120.2 |
| N1—C2—C1 | 107.91 (18) | C14—C15—H15 | 120.2 |
| N1—C2—H2A | 110.1 | C15—C16—C17 | 120.3 (3) |
| C1—C2—H2A | 110.1 | C15—C16—Cl1 | 120.5 (2) |
| N1—C2—H2B | 110.1 | C17—C16—Cl1 | 119.2 (2) |

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| C1—C2—H2B | 110.1 | C16—C17—C18 | 119.5 (3) |
| H2A—C2—H2B | 108.4 | C16—C17—H17 | 120.3 |
| N1—C3—C4 | 113.32 (19) | C18—C17—H17 | 120.3 |
| N1—C3—H3A | 108.9 | C17—C18—C13 | 122.0 (2) |
| C4—C3—H3A | 108.9 | C17—C18—H18 | 119.0 |
| N1—C3—H3B | 108.9 | C13—C18—H18 | 119.0 |
| C4—C3—H3B | 108.9 | O2—C19—N3 | 125.4 (2) |
| H3A—C3—H3B | 107.7 | O2—C19—C6 | 125.6 (2) |
| C12—C4—C5 | 115.8 (2) | N3—C19—C6 | 108.6 (2) |
| C12—C4—C3 | 124.2 (2) | C21—C20—C25 | 121.6 (3) |
| C5—C4—C3 | 120.06 (19) | C21—C20—N3 | 128.8 (3) |
| O1—C5—C4 | 121.7 (2) | C25—C20—N3 | 109.6 (2) |
| O1—C5—C1 | 120.7 (2) | C20—C21—C22 | 118.4 (3) |
| C4—C5—C1 | 117.58 (18) | C20—C21—H21 | 120.8 |
| N2—C6—C25 | 110.00 (19) | C22—C21—H21 | 120.8 |
| N2—C6—C19 | 111.18 (18) | C23—C22—C21 | 119.9 (3) |
| C25—C6—C19 | 100.62 (19) | C23—C22—H22 | 120.0 |
| N2—C6—C1 | 103.23 (17) | C21—C22—H22 | 120.0 |
| C25—C6—C1 | 118.74 (17) | C22—C23—C24 | 122.3 (3) |
| C19—C6—C1 | 113.26 (18) | C22—C23—Cl2 | 119.4 (3) |
| N2—C7—C8 | 102.53 (19) | C24—C23—Cl2 | 118.3 (3) |
| N2—C7—H7A | 111.3 | C25—C24—C23 | 117.9 (3) |
| C8—C7—H7A | 111.3 | C25—C24—H24 | 121.1 |
| N2—C7—H7B | 111.3 | C23—C24—H24 | 121.1 |
| C8—C7—H7B | 111.3 | C24—C25—C20 | 119.9 (2) |
| H7A—C7—H7B | 109.2 | C24—C25—C6 | 130.6 (2) |
| C26—C8—C7 | 115.4 (2) | C20—C25—C6 | 109.2 (2) |
| C26—C8—C1 | 117.06 (19) | C31—C26—C27 | 117.5 (2) |
| C7—C8—C1 | 103.79 (18) | C31—C26—C8 | 119.5 (2) |
| C26—C8—H8 | 106.6 | C27—C26—C8 | 122.9 (2) |
| C7—C8—H8 | 106.6 | C28—C27—C26 | 121.3 (2) |
| C1—C8—H8 | 106.6 | C28—C27—H27 | 119.4 |
| N1—C9—C10 | 112.9 (2) | C26—C27—H27 | 119.4 |
| N1—C9—H9A | 109.0 | C29—C28—C27 | 119.2 (2) |
| C10—C9—H9A | 109.0 | C29—C28—H28 | 120.4 |
| N1—C9—H9B | 109.0 | C27—C28—H28 | 120.4 |
| C10—C9—H9B | 109.0 | C28—C29—C30 | 121.1 (2) |
| H9A—C9—H9B | 107.8 | C28—C29—Cl3 | 119.0 (2) |
| C9—C10—H10A | 109.5 | C30—C29—Cl3 | 119.8 (2) |
| C9—C10—H10B | 109.5 | C29—C30—C31 | 119.1 (2) |
| H10A—C10—H10B | 109.5 | C29—C30—H30 | 120.5 |
| C9—C10—H10C | 109.5 | C31—C30—H30 | 120.5 |
| H10A—C10—H10C | 109.5 | C30—C31—C26 | 121.8 (2) |
| H10B—C10—H10C | 109.5 | C30—C31—H31 | 119.1 |
| N2—C11—H11A | 109.5 | C26—C31—H31 | 119.1 |
| N2—C11—H11B | 109.5 | | |
| | | | |
| C3—N1—C2—C1 | −74.5 (2) | C13—C14—C15—C16 | −0.1 (5) |

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| C9—N1—C2—C1 | 159.54 (19) | C14—C15—C16—C17 | 1.0 (5) |
| C5—C1—C2—N1 | 65.3 (2) | C14—C15—C16—Cl1 | −179.8 (2) |
| C8—C1—C2—N1 | −171.45 (17) | C15—C16—C17—C18 | −0.6 (4) |
| C6—C1—C2—N1 | −53.2 (2) | Cl1—C16—C17—C18 | −179.8 (2) |
| C2—N1—C3—C4 | 46.3 (3) | C16—C17—C18—C13 | −0.7 (4) |
| C9—N1—C3—C4 | 173.2 (2) | C14—C13—C18—C17 | 1.5 (4) |
| N1—C3—C4—C12 | 165.1 (2) | C12—C13—C18—C17 | −179.6 (2) |
| N1—C3—C4—C5 | −15.4 (3) | C20—N3—C19—O2 | −177.5 (2) |
| C12—C4—C5—O1 | 10.4 (3) | C20—N3—C19—C6 | −3.7 (3) |
| C3—C4—C5—O1 | −169.2 (2) | N2—C6—C19—O2 | 60.9 (3) |
| C12—C4—C5—C1 | −169.1 (2) | C25—C6—C19—O2 | 177.3 (2) |
| C3—C4—C5—C1 | 11.3 (3) | C1—C6—C19—O2 | −54.8 (3) |
| C2—C1—C5—O1 | 146.0 (2) | N2—C6—C19—N3 | −112.9 (2) |
| C8—C1—C5—O1 | 20.7 (3) | C25—C6—C19—N3 | 3.6 (2) |
| C6—C1—C5—O1 | −93.2 (3) | C1—C6—C19—N3 | 131.4 (2) |
| C2—C1—C5—C4 | −34.5 (3) | C19—N3—C20—C21 | 179.0 (3) |
| C8—C1—C5—C4 | −159.77 (19) | C19—N3—C20—C25 | 2.2 (3) |
| C6—C1—C5—C4 | 86.3 (2) | C25—C20—C21—C22 | 0.6 (5) |
| C7—N2—C6—C25 | 162.75 (18) | N3—C20—C21—C22 | −175.8 (3) |
| C11—N2—C6—C25 | −68.9 (3) | C20—C21—C22—C23 | 1.0 (5) |
| C7—N2—C6—C19 | −86.7 (2) | C21—C22—C23—C24 | −1.0 (5) |
| C11—N2—C6—C19 | 41.7 (3) | C21—C22—C23—Cl2 | 179.4 (3) |
| C7—N2—C6—C1 | 35.1 (2) | C22—C23—C24—C25 | −0.5 (5) |
| C11—N2—C6—C1 | 163.4 (2) | Cl2—C23—C24—C25 | 179.1 (2) |
| C2—C1—C6—N2 | −134.84 (18) | C23—C24—C25—C20 | 2.1 (4) |
| C5—C1—C6—N2 | 108.29 (19) | C23—C24—C25—C6 | 175.3 (3) |
| C8—C1—C6—N2 | −10.4 (2) | C21—C20—C25—C24 | −2.2 (4) |
| C2—C1—C6—C25 | 103.2 (2) | N3—C20—C25—C24 | 174.9 (2) |
| C5—C1—C6—C25 | −13.7 (3) | C21—C20—C25—C6 | −176.8 (3) |
| C8—C1—C6—C25 | −132.4 (2) | N3—C20—C25—C6 | 0.3 (3) |
| C2—C1—C6—C19 | −14.5 (3) | N2—C6—C25—C24 | −58.7 (3) |
| C5—C1—C6—C19 | −131.4 (2) | C19—C6—C25—C24 | −176.1 (2) |
| C8—C1—C6—C19 | 109.9 (2) | C1—C6—C25—C24 | 59.8 (3) |
| C11—N2—C7—C8 | −175.4 (2) | N2—C6—C25—C20 | 115.1 (2) |
| C6—N2—C7—C8 | −46.1 (2) | C19—C6—C25—C20 | −2.3 (2) |
| N2—C7—C8—C26 | 166.56 (19) | C1—C6—C25—C20 | −126.4 (2) |
| N2—C7—C8—C1 | 37.1 (2) | C7—C8—C26—C31 | 135.5 (2) |
| C2—C1—C8—C26 | −21.6 (3) | C1—C8—C26—C31 | −101.9 (3) |
| C5—C1—C8—C26 | 98.7 (2) | C7—C8—C26—C27 | −41.9 (3) |
| C6—C1—C8—C26 | −144.36 (19) | C1—C8—C26—C27 | 80.7 (3) |
| C2—C1—C8—C7 | 106.9 (2) | C31—C26—C27—C28 | −0.1 (4) |
| C5—C1—C8—C7 | −132.80 (19) | C8—C26—C27—C28 | 177.3 (2) |
| C6—C1—C8—C7 | −15.9 (2) | C26—C27—C28—C29 | −0.4 (4) |
| C2—N1—C9—C10 | −158.0 (2) | C27—C28—C29—C30 | 0.6 (4) |
| C3—N1—C9—C10 | 76.3 (3) | C27—C28—C29—Cl3 | −178.5 (2) |
| C5—C4—C12—C13 | 179.6 (2) | C28—C29—C30—C31 | −0.3 (4) |
| C3—C4—C12—C13 | −0.9 (4) | Cl3—C29—C30—C31 | 178.8 (2) |
| C4—C12—C13—C18 | 13.4 (4) | C29—C30—C31—C26 | −0.2 (4) |

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| C4—C12—C13—C14 | −167.7 (3) | C27—C26—C31—C30 | 0.4 (4) |
| C18—C13—C14—C15 | −1.1 (4) | C8—C26—C31—C30 | −177.2 (2) |
| C12—C13—C14—C15 | 179.9 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N3—H3n···O2[i] | 0.86 | 2.03 | 2.883 (3) | 170 |
| C31—H31···O1[ii] | 0.93 | 2.47 | 3.160 (4) | 131 |

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