Crystal structure and Hirshfeld surface analysis of ethyl (3E)-5-(4-chlorophenyl)-3-[(4-chlorophenyl)formamid]imino]-7-methyl-2H,3H,5H-[1,3]thiazolo[3,2-a]pyrimidine-6-carboxylate

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In the title molecule, C_{23}H_{20}Cl_{2}N_{4}O_{3}S, the thiazole ring is planar while the pyrimidine unit fused to it adopts a screw-boat conformation. In the crystal, thick sheets parallel to the bc plane are formed by N—H/C1/C1/C1N, C—H/C1/C1/C1N and C—H/C1/C1/C1O hydrogen bonds together with /C25–/C25 interactions between the formamido carbonyl groups and the thiazole rings. Hirshfeld surface analysis indicates that the most important contributions to the crystal packing are from H/C1/C1/C1H (30.9%), Cl/C1/C1/C1H/H/C1/C1/C1Cl (20.7%), C/C1/C1/C1H/H/C1/C1/C1C (16.8%) and O/H/H/C1/C1/O (11.4%) interactions.

1. Chemical context

Several compounds bearing 1,3,4-oxadiazole have been reported to exhibit significant anticancer activities (Yadagiri et al., 2015; Valente et al., 2014; El-Din et al., 2015). On the other hand, pyrimidine-based compounds have shown significant activity against cancer and tumor cells (Tolba et al., 2022). Compounds combining the pharmacophores dihydro-pyrimidine and 1,3,4-oxadiazole have been prepared with the aim of developing potent anticancer agents (Ragab et al., 2017). The target hybrids have been synthesized through condensation of 6-methyl-4-aryl-1,2,3,4-tetrahydropyrimidine-2(1H)-thione derivatives and 2-(chloromethyl)-5-aryl-1,3,4-oxadiazole derivatives and screened for their in vitro cytotoxic activity against 60 cancer cell lines according to NCI (USA) protocols (Skehan et al., 1990). Unexpectedly, an intramolecular cyclization and ring opening of 1,3,4-oxadiazole has occurred and the title compound was chosen as an example of this series for further structural elucidation through X-ray crystallography.
2. Structural commentary

In the title compound, (Fig. 1), the thiazole ring is planar (r.m.s. deviation of the fitted atoms = 0.001 Å) and the C11–C16 and C18–C23 benzene rings are inclined to it by 88.95 (8)° and 11.47 (7)°, respectively. The pyrimidine ring (C1/C2/C3/C4/C5/C6) exhibits a screw-boat conformation with puckering parameters (Cremer & Pople, 1975) of $Q(2) = 0.2383$ (15) Å and $\theta(2) = 188.4$ (4)°. This ring is folded about the C1–N1 axis by 19.9 (1)°. The torsion angles about the bonds of the N'-methylideneformohydradizide link between the chlorophenyl ring and the 2,3-dihydro-5H-[1,3]thiazolo[3,2-a]pyrimidine ring system are: N2–C6=N3–N4 = –177.82 (12)°, C6=N3=N4=C17 = –171.54 (13)° and N3–N4–C17–C18 = –175.14 (12)°. The stereochemistry about the imine function C6=N3 is E.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, a combination of N4–H4⋯N1 and C5–H5B⋯N1 hydrogen bonds (Table 1) form helical chains extending along the b-axis direction (Fig. 2). The chains are connected by C5–H5A⋯O3, C15–H15⋯O3 and C8–H8B⋯Cl hydrogen bonds as well as centrosymmetrically related π-interactions between the C17=N3 carbonyl groups and the thiazole rings [O3⋯Cg1 = 3.0299 (14) Å, C17⋯Cg1 = 3.4656 (16) Å, C17=N3⋯Cg1 = 100.48 (10)°; Table 2 and

![Figure 2](image2.png)

Figure 2

A portion of the hydrogen-bonded chain viewed along the c-axis direction. N⋯H⋯N, and C⋯H⋯N hydrogen bonds are shown. H atoms not involved in these interactions have been omitted for clarity.

![Figure 3](image3.png)

Figure 3

Detail of the C⋯H⋯O and C⋯H⋯Cl hydrogen bonds and the π-interactions down the b-axis. H atoms not involved in these interactions have been omitted for clarity.

Table 1

| Contact | Distance (Å) | Symmetry operation |
|---------|--------------|--------------------|
| C1⋯H10B | 2.96         | $x, -1 + y, z$     |
| H4⋯N1   | 2.16         | $1 - x, 1 - y, 1 - z$ |
| H5⋯O3   | 2.54         | $x, 1 - y, 1 + z$ |
| H13⋯Cl2 | 2.91         | $1 - x, -y, 1 - z$ |
| H5A⋯O3  | 2.53         | $1 - x, 1 - y, 1 - z$ |
| H20⋯H9B | 2.53         | $1 + x, 1 + y, 1 + z$ |
| H9A⋯H9A | 2.43         | $x, -1 + y, 1 - z$ |

Table 2

Summary of short interatomic contacts (Å) in the title compound.

Table 1

| Contact | Distance (Å) | Symmetry operation |
|---------|--------------|--------------------|
| C1⋯H10B | 2.96         | $x, -1 + y, z$     |
| H4⋯N1   | 2.16         | $1 - x, 1 - y, 1 - z$ |
| H5⋯O3   | 2.54         | $x, 1 - y, 1 + z$ |
| H13⋯Cl2 | 2.91         | $1 - x, -y, 1 - z$ |
| H5A⋯O3  | 2.53         | $1 - x, 1 - y, 1 - z$ |
| H20⋯H9B | 2.53         | $1 + x, 1 + y, 1 + z$ |
| H9A⋯H9A | 2.43         | $x, -1 + y, 1 - z$ |

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plots (Fig. 6) reveals that H···H (30.9%), Cl···H/H···Cl (20.7%), C···H/H···C (16.8%) and O···H/H···O (11.4%) interactions make the greatest contributions to the surface contacts. The remaining contributions for the title compound are from N···H/H···N, S···H/H···S, S···C/C···S, N···C/C···N, S···N/N···S, C···C, Cl···O/O···Cl, O···C/C···O, N···N, Cl···Cl, S···O/O···S, O···N/N···O and Cl···C/C···Cl contacts, which are each less than 4.5% and have a negligible effect on the packing. The percentage contributions of all interactions are given in Table 3.

4. Database survey

A search of the Cambridge Structural Database (CSD Version 5.39; Groom et al., 2016) for similar structures with the 2,3-dihydro-5H-[1,3]thiazolo[3,2-a]pyrimidine ring system showed

| Contact          | Percentage contribution |
|------------------|-------------------------|
| H···H            | 30.9                    |
| Cl···H/H···Cl    | 20.7                    |
| C···H/H···C      | 16.8                    |
| O···H/H···O      | 11.4                    |
| N···H/H···N      | 4.5                     |
| S···H/H···S      | 3.4                     |
| S···C/C···S      | 2.9                     |
| N···C/C···N      | 1.4                     |
| S···N/N···S      | 1.4                     |
| C···C           | 2.8                     |
| Cl···O/O···Cl    | 0.9                     |
| O···C/C···O     | 0.9                     |
| N···N          | 0.8                     |
| Cl···Cl        | 0.4                     |
| S···O/O···S      | 0.3                     |
| O···N/N···O     | 0.2                     |
| Cl···C/C···Cl  | 0.1                     |

Figure 4
Packing viewed along the a-axis direction with intermolecular interactions shown as in Fig. 2.

Figure 5
(a) Front view and (b) back view of the three-dimensional Hirshfeld surface of the title compound plotted over dnorm in the range −0.4486 to +1.3171 a.u.

Figure 6
Two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b) H···H, (c) Cl···H/H···Cl, (d) C···H/H···C and (e) O···H/H···O interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.
the three closest are those of \( \text{rac}-(2\text{'S},2\text{'R},4\text{'R},5\text{'R},6\text{'R},-)\text{-ethyl 4\text{-methoxycarbonyl}-5\text{''}- (4\text{-methoxyphenyl})-1,7\text{-dimethyl-2,3\text{''}-dioxo-2\text{''}-dihydropyrimidine-3\text{''}-spiro-2\text{''}-thiazolo[3,2-a]pyrimidine-6\text{''}-carboxylate \ [CSD refcode PONWUL (I); Hou et al., 2009], 3-(4-fluorophenyl)2-sulfanyliden-5-(trifluoromethyl)-2,3-dihydropyrazino[1,3][thiazolo[4,5-d]pyrimidine-7(6H)-one toluene solvate [WEGSUA (II); Becan et al., 2022] and 7-ethylamino-3-phenyl-5-(trifluoromethyl)-1,3,4-tetrahydropyrazino[2,3-a]pyrimidine system. Two molecules are connected into a dimer by two N–H ⋅⋅⋅ O hydrogen bonds, forming an \( R_2^2(8) \) graph-set motif.

Compound (II) crystallizes as a semi-solvate in the triclinic space group \( P\bar{T} \). The asymmetric unit is composed of one molecule in the lactam form and half of a toluene molecule. In the crystal structure of (II), the molecules are linked into a centrosymmetric dimer by N–H ⋅⋅⋅ O hydrogen bonds. Such dimers are further linked via rather weak C–H ⋅⋅⋅ S and C–H ⋅⋅⋅ F interactions. In addition, aromatic π–π stacking interactions are also observed.

Compound (III) crystallizes in the \( P2_1/n \) space group with one molecule in the asymmetric unit. Both the thiazolo-pyrimidine and the phenyl rings are flat and subtend a dihedral angle of 70.8 (1)° to each other. In the crystal of (III), N–H ⋅⋅⋅ S hydrogen bonds link the molecules into zigzag chains running along the \( b \)-axis direction. The interchain contacts are provided by weak C–H ⋅⋅⋅ S and C–H ⋅⋅⋅ F bonds while C–H ⋅⋅⋅ π and π–π interactions generate the three-dimensional network.

5. Synthesis and crystallization

A mixture of ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2 mmol), 2-(chloromethyl)-5-(4-chlorophenyl)-1,3,4-oxadiazole (2 mmol), potassium iodide (2 mmol) and triethyl amine (2 mmol), was refluxed for 4h in absolute ethanol (20 mL). The reaction mixture was poured onto crushed ice (40 g) and acidified with acetic acid (2 mL). The deposited precipitate was filtered off, washed with cold water, dried and crystallized from a methanol/DMF mixture 4:1 (v/v).

Yield: 80%; melting point: 477–779 K; IR (KBr, \( \nu_{\max }/\text{cm}^{-1} \): 3402, 3174, 1708, 1693, 1651, \( ^1{H} \) NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 10.82 (s, 1H, NH), 7.85 (d, \( J = 8.3 \) Hz, 2H, Ar–H), 7.57 (d, \( J = 8.4 \) Hz, 2H, Ar–H), 7.41 (dd, \( J = 8.8, 8.4 \) Hz, 4H, Ar–H), 6.10 (s, 1H, C4–H), 4.46 (d, \( J = 17.4 \) Hz, 1H, S–CH2), 4.36 (d, \( J = 17.4 \) Hz, 1H, S–CH2), 4.03 (q, \( J = 5.2 \) Hz, 2H, CH2–CH3), 2.34 (s, 3H, C6–CH3), 1.12 (t, \( J = 7.1 \) Hz, 3H, CH3–CH3).

\( ^1{C} \) NMR (100 MHz, DMSO-\( d_6 \)) \( \delta \) 167.02, 162.17, 153.72, 153.44, 139.52, 136.36, 132.78, 132.16, 129.82, 129.55, 128.41, 128.30, 105.37, 59.85, 54.69, 28.11, 22.66, 13.97. Analysis calculated for \( \text{C}_{23}\text{H}_{20}\text{Cl}_{2}\text{N}_{4}\text{O}_{3}\text{S} \) (503.40): C 54.88, H 4.00, N 11.13. Found: C 55.13, H 3.94, N 11.36.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. Only the hydrogen atoms of the methyl group attached to C10 were included as riding contributions in idealized positions since independent refinement of them led to an unsatisfactory geometry for this methyl group. All the remaining C and N-bound hydrogen atoms were found in difference-Fourier maps and they were refined freely.

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Crystal structure and Hirshfeld surface analysis of ethyl (3E)-5-(4-chlorophenyl)-3-[[{4-chlorophenyl}formamido]imino]-7-methyl-2H,3H,5H-[1,3]thiazolo[3,2-a]pyrimidine-6-carboxylate

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Computing details

Data collection: APEX3 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/1 (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2020).

Ethyl (3E)-5-(4-chlorophenyl)-3-[[{4-chlorophenyl}formamido]imino]-7-methyl-2H,3H,5H-[1,3]thiazolo[3,2-a]pyrimidine-6-carboxylate

Crystal data

\[ C_{23}H_{20}Cl_2N_4O_3S \]  \( M_r = 503.39 \)

Monoclinic, \( P_2_1/c \)

\( a = 14.8117 (18) \) Å

\( b = 10.7086 (13) \) Å

\( c = 15.1887 (19) \) Å

\( \beta = 112.417 (3) ^\circ \)

\( V = 2227.1 (5) \) Å\(^3\)

\( Z = 4 \)

\( F(000) = 1040 \)

\( D_{\alpha} = 1.501 \) Mg m\(^{-3}\)

Cu Kα radiation, \( \lambda = 1.54178 \) Å

Cell parameters from 9966 reflections

\( \theta = 3.2–74.6^\circ \)

\( \mu = 3.80 \) mm\(^{-1}\)

\( T = 150 \) K

Plate, pale yellow

\( 0.21 \times 0.18 \times 0.08 \) mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer

Radiation source: INCOATEC \( \mu \)S micro–focus source

Mirror monochromator

Detector resolution: 10.4167 pixels mm\(^{-1}\)

\( \omega \) scans

Absorption correction: numerical

(SADABS; Krause et al., 2015)

\( T_{\text{min}} = 0.59, T_{\text{max}} = 0.76 \)

16958 measured reflections

4497 independent reflections

4000 reflections with \( I > 2\sigma(I) \)

\( R_{\text{int}} = 0.031 \)

\( \theta_{\text{max}} = 74.6^\circ, \theta_{\text{min}} = 3.2^\circ \)

\( h = -18 \rightarrow 17 \)

\( k = -13 \rightarrow 12 \)

\( l = -18 \rightarrow 18 \)
Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.082$
$S = 1.05$
4497 reflections
367 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 1.0281P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.23$ e Å$^{-3}$
$\Delta\rho_{\text{min}} = -0.35$ e Å$^{-3}$

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. The hydrogen atoms attached to C10 were included as riding contributions in idealized positions since independent refinement of them led to an unsatisfactory geometry for this methyl group.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

| Atom | x    | y    | z    | $U_{iso}/U_{eq}$ |
|------|------|------|------|------------------|
| Cl1  | 0.17142 (3) | 0.13315 (4) | 0.78029 (3) | 0.03577 (12) |
| Cl2  | 0.88333 (3) | -0.06239 (4) | 0.59045 (3) | 0.03541 (12) |
| S1   | 0.54003 (3) | 0.68437 (3) | 0.77522 (3) | 0.02275 (10) |
| O1   | 0.06386 (8) | 0.72960 (11) | 0.49406 (8) | 0.0282 (3) |
| O2   | 0.12796 (7) | 0.58575 (10) | 0.42622 (7) | 0.0214 (2) |
| O3   | 0.46040 (8) | 0.25187 (11) | 0.44901 (8) | 0.0277 (3) |
| N1   | 0.35416 (9) | 0.75804 (11) | 0.71116 (9) | 0.0191 (3) |
| N2   | 0.39614 (8) | 0.58809 (11) | 0.63452 (9) | 0.0167 (2) |
| N3   | 0.45875 (9) | 0.42363 (11) | 0.57852 (9) | 0.0182 (2) |
| N4   | 0.54188 (9) | 0.35323 (11) | 0.58917 (9) | 0.0185 (3) |
| H4   | 0.5851 (16) | 0.339 (2) | 0.6478 (16) | 0.034 (5)* |
| C1   | 0.29435 (10) | 0.54883 (13) | 0.58144 (10) | 0.0164 (3) |
| H1   | 0.2883 (13) | 0.5261 (17) | 0.5176 (13) | 0.020 (4)* |
| C2   | 0.22891 (10) | 0.60608 (13) | 0.57591 (10) | 0.0174 (3) |
| C3   | 0.25829 (11) | 0.75263 (14) | 0.64191 (10) | 0.0187 (3) |
| C4   | 0.41675 (10) | 0.68010 (13) | 0.70116 (10) | 0.0173 (3) |
| C5   | 0.56960 (11) | 0.55753 (14) | 0.71172 (12) | 0.0222 (3) |
| H5A  | 0.6126 (14) | 0.5860 (18) | 0.6802 (14) | 0.026 (5)* |
| H5B  | 0.6020 (14) | 0.490 (2) | 0.7563 (14) | 0.030 (5)* |
| C6   | 0.47481 (10) | 0.51442 (13) | 0.63687 (10) | 0.0171 (3) |
| C7   | 0.13182 (10) | 0.66442 (14) | 0.49758 (10) | 0.0187 (3) |
| C8   | 0.03585 (11) | 0.58383 (16) | 0.34410 (11) | 0.0242 (3) |
| H8A  | 0.0046 (14) | 0.6678 (18) | 0.3345 (13) | 0.025 (5)* |
### Atomic displacement parameters (Å²)

|   | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| C11 | 0.0475 (3) | 0.0231 (2) | 0.0488 (3) | −0.00518 (16) | 0.0318 (2) | 0.00199 (17) |
| C12 | 0.0330 (2) | 0.0397 (2) | 0.0294 (2) | 0.01712 (17) | 0.00721 (18) | −0.00225 (17) |
| S1  | 0.01551 (18) | 0.02385 (19) | 0.02288 (19) | −0.00037 (13) | 0.00060 (15) | −0.00508 (14) |
| O1  | 0.0180 (5) | 0.0331 (6) | 0.0285 (6) | 0.0073 (4) | 0.0032 (5) | −0.0054 (5) |
| O2  | 0.0141 (5) | 0.0247 (5) | 0.0197 (5) | 0.0017 (4) | 0.0002 (4) | −0.0039 (4) |
| O3  | 0.0221 (6) | 0.0340 (6) | 0.0211 (6) | 0.0022 (5) | 0.0016 (5) | −0.0051 (5) |
| N1  | 0.0173 (6) | 0.0195 (6) | 0.0184 (6) | −0.0006 (5) | 0.0043 (5) | −0.0012 (5) |
| N2  | 0.0127 (6) | 0.0167 (6) | 0.0181 (6) | −0.0003 (4) | 0.0030 (5) | −0.0006 (5) |
| N3  | 0.0155 (6) | 0.0189 (6) | 0.0192 (6) | 0.0023 (5) | 0.0053 (5) | 0.0022 (5) |
| N4  | 0.0156 (6) | 0.0200 (6) | 0.0177 (6) | 0.0037 (5) | 0.0037 (5) | 0.0006 (5) |
| C1  | 0.0124 (6) | 0.0184 (7) | 0.0155 (7) | −0.0002 (5) | 0.0020 (5) | −0.0013 (5) |
| C2  | 0.0149 (7) | 0.0178 (7) | 0.0181 (7) | 0.0008 (5) | 0.0046 (6) | 0.0012 (5) |
| C3  | 0.0174 (7) | 0.0198 (7) | 0.0180 (7) | 0.0001 (5) | 0.0058 (6) | 0.0018 (5) |
| C4  | 0.0167 (7) | 0.0171 (7) | 0.0163 (7) | −0.0021 (5) | 0.0044 (6) | 0.0011 (5) |
### Geometric parameters (Å, °)

|   | C1—C14 | C12—C21 | S1—C4 | S1—C5 | O1—C7 | N1—C4 | N2—C6 | N2—C1 | N3—C6 | N3—N4 | N4—C17 | N4—H4 | C1—C2 | C1—C11 | C1—H1 | C2—C3 | C2—C7 | C3—C10 | C5—C6 | C5—H5A | C5—H5B |
|---|--------|---------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|
|   | 1.7459 (16) | 1.7365 (16) | 1.7421 (15) | 1.8135 (16) | 1.2092 (18) | 1.2987 (19) | 1.3963 (18) | 1.4740 (17) | 1.2754 (19) | 1.3995 (17) | 1.3680 (19) | 0.89 (2) | 1.5228 (19) | 1.526 (2) | 0.970 (18) | 1.353 (2) | 1.477 (2) | 1.503 (2) | 1.503 (2) | 0.98 (2) | 0.98 (2) |
|   | C8—H8B | C9—H9A | C9—H9B | C9—H9C | C10—H10A | C11—C12 | C13—C14 | C13—C15 | C15—C16 | C15—H15 | C16—H16 | C17—C18 | C18—C19 | C18—C23 | C19—C20 | C19—H19 | C20—C21 | C20—H20 | C21—C22 | C22—C23 |    |
C8—C9 1.500 (2) C22—H22 0.95 (2)
C8—H8A 1.00 (2) C23—H23 0.95 (2)
C4—S1—C5 92.48 (7) H9A—C9—H9C 110.0 (18)
C7—O2—C8 115.69 (11) H9B—C9—H9C 107.6 (17)
C4—N1—C3 116.56 (12) C3—C10—H10A 109.5
C4—N2—C6 116.21 (12) C3—C10—H10B 109.5
C4—N2—C1 120.38 (12) H10A—C10—H10B 109.5
C6—N2—C1 121.49 (12) C3—C10—H10C 109.5
C6—N3—N4 114.05 (12) H10B—C10—H10C 109.5
C17—N4—N3 117.37 (12) C12—C11—C16 119.03 (14)
C17—N4—H4 117.6 (14) C12—C11—C1 120.47 (13)
N3—N4—H4 118.2 (13) C12—C11—C1 120.43 (13)
N2—C1—C2 107.61 (11) C11—C12—H12 119.8 (12)
N2—C1—C11 110.33 (11) C11—C12—H12 119.8 (12)
N2—C1—H1 107.7 (10) C13—C12—H12 119.5 (12)
C2—C1—C11 110.98 (11) H12—C13—C14 121.9 (12)
C2—C1—H1 111.0 (11) C13—C12—H12 119.5 (12)
C11—C1—H1 111.0 (11) C14—C13—C12 121.9 (12)
C3—C2—C7 121.09 (13) C2 — C14—C15 121.9 (12)
C3—C2—C1 120.89 (13) C2 — C14—C15 121.9 (12)
C7—C2—C1 118.01 (12) C2 — C14—C15 121.9 (12)
C2—C3—N1 122.05 (13) C15 — C14—C16 121.9 (12)
C2—C3—N1 122.05 (13) C15 — C14—C16 121.9 (12)
C2—C3—C7 125.34 (14) C14 — C15—C16 121.9 (12)
N1—C3—C10 112.60 (13) C16 — C15—C16 121.9 (12)
N1—C4—N2 112.77 (13) C16 — C15—C16 121.9 (12)
N1—C4—S1 121.79 (11) C15 — C16—C11 121.9 (12)
N2—C4—S1 121.79 (11) C15 — C16—C11 121.9 (12)
N2—C4—S1 121.79 (11) C15 — C16—C11 121.9 (12)
C6—C5—N3 106.67 (10) C11 — C16—C15 121.9 (12)
C6—C5—C5A 108.6 (11) C11 — C16—C15 121.9 (12)
S1—C5—N3 111.1 (11) O3 — C17—N4 123.67 (14)
S1—C5—C5A 111.1 (11) O3 — C17—N4 123.67 (14)
C6—C5—H5B 111.6 (12) N4 — C17—N4 145.0 (13)
S1—C5—H5B 111.6 (12) N4 — C17—N4 145.0 (13)
H5A—C5—H5B 109.7 (12) C19 — C18—C23 121.04 (14)
H5A—C5—H5B 109.7 (12) C19 — C18—C23 121.04 (14)
N3—C6—N2 118.70 (13) C23 — C18—C23 121.04 (14)
N3—C6—C5 129.25 (13) C23 — C18—C23 121.04 (14)
N2—C6—C5 129.25 (13) C20 — C19—C18 121.04 (14)
O1—C7—O2 122.84 (13) C18 — C19—C18 121.04 (14)
O1—C7—C2 126.15 (14) C18 — C19—C18 121.04 (14)
O2—C7—C2 110.99 (12) C21 — C20—C19 121.04 (14)
O2—C8—C9 110.25 (13) C21 — C20—C19 121.04 (14)
O2—C8—H8A 110.1 (11) C20 — C21—C22 121.04 (14)
C9—C8—H8A 111.8 (11) C20 — C21—C22 121.04 (14)
O2—C8—H8B 104.2 (11) C22 — C21—C22 121.04 (14)
C9—C8—H8B 112.8 (11) C22 — C21—C22 121.04 (14)
H8A—C8—H8B 107.4 (16) C23 — C22—C21 121.04 (14)
C8—C9—H9A 109.4 (13) C23 — C22—C21 121.04 (14)
C8—C9—H9B 110.2 (12) C22 — C23—C18 121.04 (14)

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### Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N4—H4···N1 | 0.89 (2) | 2.16 (2) | 3.0076 (18) | 158 (2) |
| C5—H5A···O3 | 0.98 (2) | 2.533 (19) | 3.081 (2) | 115.3 (14) |
| C5—H5B···N1 | 0.98 (2) | 2.57 (2) | 3.453 (2) | 150.1 (16) |

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| Supporting Information |  |  |
|-----------------------|---|---|
| H9A—C9—H9B | 108.5 (17) | C22—C23—H23 | 118.2 (12) |
| C8—C9—H9C | 111.2 (12) | C18—C23—H23 | 121.1 (12) |
| C6—N3—N4—C17 | −171.54 (13) | C1—C2—C7—O1 | 162.79 (15) |
| C4—N2—C1—C2 | 28.34 (17) | C3—C2—C7—O2 | 162.47 (13) |
| C6—N2—C1—C2 | −168.05 (12) | C1—C2—C7—O2 | −18.75 (18) |
| C4—N2—C1—C11 | −92.88 (15) | C7—O2—C8—C9 | −91.73 (16) |
| C6—N2—C1—C11 | 70.74 (16) | N2—C1—C11—C12 | −142.35 (14) |
| N2—C1—C2—C3 | −25.06 (18) | C2—C1—C11—C12 | 98.47 (16) |
| C11—C1—C2—C3 | 95.74 (16) | N2—C1—C11—C16 | 40.59 (18) |
| C8—C9—H9C | 111.2 (12) | C1—C11—C12—C13 | −174.50 (14) |
| C6—N2—C4—N1 | −173.09 (13) | C11—C12—C13—C14 | 8.2 (2) |
| C1—N2—C4—N1 | 8.2 (2) | C12—C13—C14—C15 | −1.8 (2) |
| C6—N2—C4—S1 | 174.58 (10) | C1—C11—C12—C13 | −1.8 (2) |
| C1—N2—C4—S1 | −172.92 (14) | C12—C13—C14—C15 | 0.8 (2) |
| C4—N1—C3—C2 | −170.30 (13) | C12—C13—C14—C11 | 178.85 (12) |
| C3—N1—C4—N2 | −5.4 (2) | C1—C11—C12—C13 | −1.5 (2) |
| C3—N1—C4—S1 | 174.58 (10) | C12—C13—C14—C15 | −0.9 (2) |
| C4—N1—C3—C10 | −197.75 (14) | C1—C11—C12—C13 | 176.17 (13) |
| C6—N2—C4—N1 | −15.3 (2) | N3—N4—C17—O3 | 6.5 (2) |
| C6—N2—C4—S1 | 0.26 (16) | N3—N4—C17—C18 | −175.14 (12) |
| C1—N2—C4—S1 | 164.71 (10) | O3—C17—C18—C19 | 159.59 (15) |
| C5—S1—C4—N1 | −180.09 (13) | N4—C17—C18—C19 | −18.8 (2) |
| C5—S1—C4—N2 | 1.90 (11) | O3—C17—C18—C23 | −18.5 (2) |
| C4—S1—C5—C6 | −3.28 (11) | N4—C17—C18—C23 | 163.08 (13) |
| N4—N3—C6—N2 | −177.82 (12) | C23—C18—C19—C20 | −1.2 (2) |
| N4—N3—C6—C5 | 2.2 (2) | C17—C18—C19—C20 | −179.26 (14) |
| C4—N2—C6—N3 | 177.12 (13) | C18—C19—C20—C21 | 0.3 (2) |
| C1—N2—C6—N3 | 12.9 (2) | C19—C20—C21—C22 | 0.4 (2) |
| C4—N2—C6—C5 | −2.92 (18) | C19—C20—C21—C12 | −179.59 (12) |
| C1—N2—C6—C5 | −167.18 (13) | C20—C21—C22—C23 | −0.3 (2) |
| S1—C5—C6—N3 | −176.04 (13) | C12—C21—C22—C23 | 179.70 (13) |
| S1—C5—C6—N2 | 4.01 (15) | C21—C22—C23—C18 | −0.6 (2) |
| C8—O2—C7—O1 | −0.2 (2) | C19—C18—C23—C22 | 1.3 (2) |
| C8—O2—C7—C2 | −178.77 (12) | C17—C18—C23—C22 | 179.48 (14) |
| C3—C2—C7—O1 | −16.0 (2) |  |  |  |
|          |                |        |        |        |
|----------|----------------|--------|--------|--------|
| C8—H8B···Cl1^iii | 1.02 (2)       | 2.77 (2) | 3.4430 (17) | 123.1 (14) |
| C15—H15···O3^iv | 0.95 (2)       | 2.54 (2) | 3.1682 (19) | 124.5 (17) |

Symmetry codes: (i) −x+1, y−1/2, −z+3/2; (ii) −x+1, −y+1, −z+1; (iii) x, −y+1/2, z−1/2; (iv) x, −y+1/2, z+1/2.