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# Ethyl 3-[7-(*N*-acetyl-4-methoxybenzenesulfonamido)-3-chloro-2*H*-indazol-2-yl]propionate

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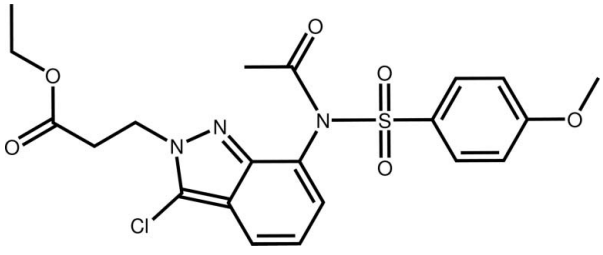
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.003 Å; disorder in main residue; $R$ factor = 0.043; $wR$ factor = 0.123; data-to-parameter ratio = 22.5.

In the title compound, $C_{21}H_{22}ClN_3O_6S$, the fused five- and six-membered ring rings are almost perpendicular to the planes through the atoms forming the acetyl and the propionic ester groups, as indicated by the dihedral angles of 80.3 (2) and 88.3 (7)°, respectively. The dihedral angle between the indazole system and the 4-methoxybenzenesulfonyl group is 13.76 (6)°. The carbonyl O atom is split over two positions in a 0.60 (5):0.40 (5) ratio. In the crystal, molecules are linked by C—H···O and C—H···N interactions into a three-dimensional network.

## Related literature

For the biological activity of sulfonamides, see: Lohou *et al.* (2012); Salerno *et al.* (2012); Kaltenbach *et al.* (2003); Thangadurai *et al.* (2012); Abbassi *et al.* (2012). For similar compounds, see: Abbassi *et al.* (2013); Chicha *et al.* (2013).



## Experimental

### Crystal data

$C_{21}H_{22}ClN_3O_6S$
$M_r$ = 479.93
Triclinic, $P\overline{1}$
$a$ = 9.1442 (3) Å
$b$ = 9.4376 (4) Å
$c$ = 14.0931 (6) Å
$\alpha$ = 108.262 (2)°
$\beta$ = 96.017 (2)°
$\gamma$ = 103.313 (2)°
$V$ = 1103.12 (8) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.31 mm$^{-1}$
$T$ = 296 K
0.38 × 0.32 × 0.27 mm

### Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.700, $T_{max}$ = 0.746
26786 measured reflections
6725 independent reflections
4687 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.123
$S$ = 1.02
6725 reflections
299 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.34 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2—H2$A$···O4$^{i}$ | 0.97 | 2.58 | 3.438 (3) | 148 |
| C21—H21$A$···O2$B^{ii}$ | 0.96 | 2.44 | 3.273 (7) | 144 |
| C21—H21$A$···O2$A^{ii}$ | 0.96 | 2.60 | 3.43 (2) | 145 |
| C2—H2$B$···O6$^{iii}$ | 0.97 | 2.71 | 3.510 (3) | 140 |
| C14—H14$C$···N2$^{iv}$ | 0.96 | 2.55 | 3.501 (2) | 173 |
| C14—H14$B$···O5$^{v}$ | 0.96 | 2.45 | 3.348 (2) | 155 |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; 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); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

The authors thank the Unit of Support for Technical and Scientific Research (UATRS, CNRST) for the X-ray measurements.

Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5294).

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# supporting information

*Acta Cryst.* (2014). E**70**, o307–o308 [doi:10.1107/S1600536814003183]

## Ethyl 3-[7-(*N*-acetyl-4-methoxybenzenesulfonamido)-3-chloro-2*H*-indazol-2-yl]propionate

**Assoman Kouakou, El Mostapha Rakib, Najat Abbassi, Mohamed Saadi and Lahcen El Ammari**

### S1. Structural commentary

The indazole ring system is recognized to be a highly effective pharmacophore in medicinal chemistry as well as being the core of important nitrogen-containing heterocycles that show a broad range of biological activities, such as nitric oxide syntheses and HIV protease inhibitors, anti-inflammatory and anti-cancer agents, and serotonin 5-HT3 receptor antagonists (Lohou *et al.*, 2012; Salerno *et al.*, 2012; Kaltenbach *et al.*, 2003; Thangadurai *et al.*, 2012; Abbassi *et al.*, 2012). The present work is a continuation of the investigation of the sulfonamide derivatives published recently by our team (Abbassi, *et al.*, 2013; Chicha, *et al.*, 2013).

The molecule of the title compound is built up from fused five- and six-membered rings linked to an acetyl-(4-methoxy-benzenesulfonyl)-amino group and to a propionic ethyl ester as shown in Fig. 1. The indazole ring system makes dihedral angles of 80.3 (2) and 88.3 (7)°, with the two planes through the atoms forming the acetyl (O3C13C14) and the propionic ester (O1O2C3C4C5) groups, respectively. The plane through the 4-methoxy-benzenesulfonyl group is nearly parallel to the indazole ring system, as indicated by the dihedral angle of 13.76 (6)°. In the crystal, the molecules are linked by C—H···O and C—H···N interactions to form a three-dimensional network (Fig. 2 and Table 1).

### S2. Synthesis and crystallization

Ethyl 3-(3-chloro-7-nitro-2*H*-indazol-2-yl)propanoate (1.48 mmol) was added to a mixture of indium powder (850 mg, 7.43 mmol) and acetic acid (8.35 ml, 150 mmol) in ethanol (5 ml). The reaction mixture was stirred at 333 K for 6 h. After reduction, the starting material disappeared, and the solution was allowed to cool. The pH was made slightly basic (pH 7–8) by addition of 5% aqueous potassium bicarbonate before extraction with ethyl acetate. The organic phase was washed with brine and dried over magnesium sulfate. The solvent was removed to afford the amine, which was immediately dissolved in pyridine (5 ml) and then reacted with 4-methoxybenzenesulfonyl chloride (1.25 mmol) at room temperature for 24 h. After the reaction mixture was concentrated *in vacuo*, the resulting residue was purified by flash chromatography (eluted with ethyl acetate: Hexane 2:8). The title compound was recrystallized from ethanol (Yield: 44%; M.pt: 394 K).

### S3. Refinement

H atoms were located in a difference map and treated as riding with C–H = 0.96 Å, 0.97 Å and 0.93 Å for methyl-, methylene- and aromatic-H, respectively, and with $U_{iso}$(H) = 1.5 $U_{eq}$ for methyl-H and $U_{iso}$(H) = 1.2 $U_{eq}$ for methylene- and aromatic-H. The ester-O atom was rfined over two positions, O2A and O2B, in a 40:60 ratio.

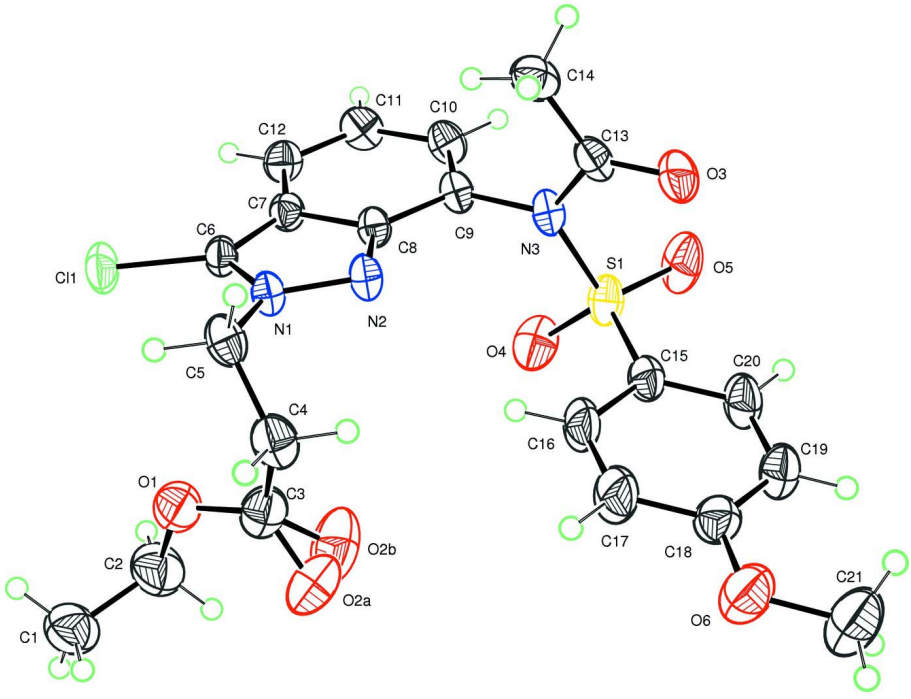


**Figure 1**

Plot of the molecule of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

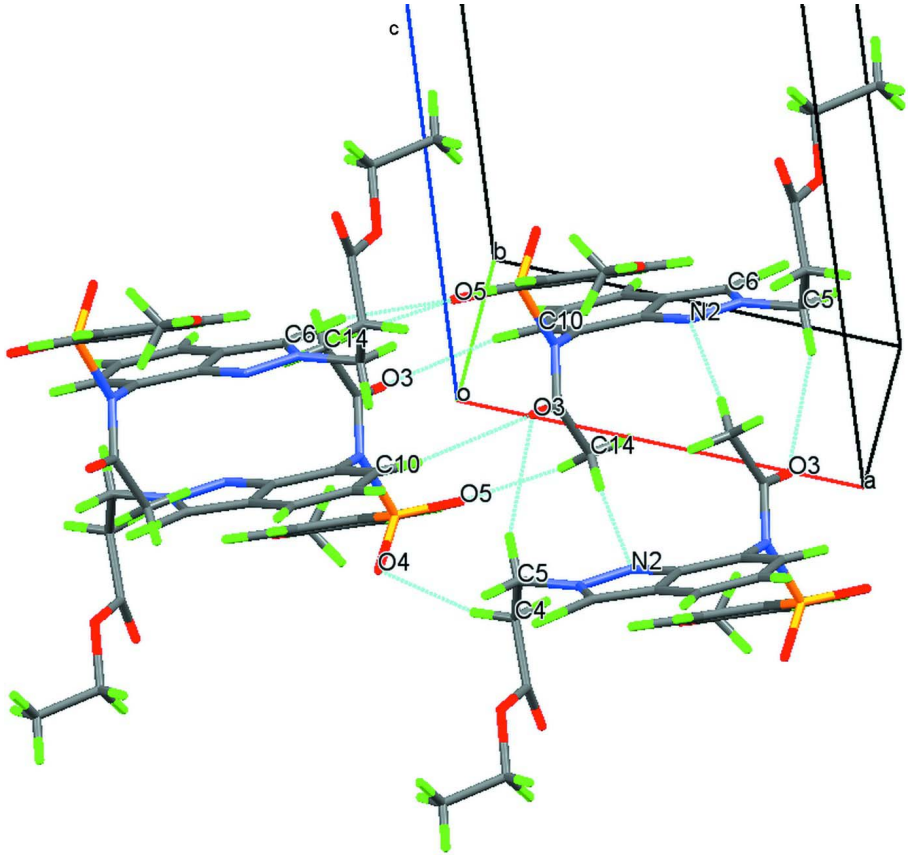


**Figure 2**

Partial crystal packing for the title compound showing hydrogen bonds as dashed lines.

## Ethyl 3-[7-(*N*-acetyl-4-methoxybenzenesulfonamido)-3-chloro-2*H*-indazol-2-yl]propionate

*Crystal data*

$C_{21}H_{22}ClN_3O_6S$
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$\alpha = 108.262$ (2)°
$\beta = 96.017$ (2)°
$\gamma = 103.313$ (2)°
$V = 1103.12$ (8) Å$^3$
$Z = 2$
$F(000) = 500$
$D_x = 1.445$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6725 reflections
$\theta = 2.4$–30.5°
$\mu = 0.31$ mm$^{-1}$
$T = 296$ K
Block, colourless
0.38 × 0.32 × 0.27 mm

*Data collection*

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.700$, $T_{max} = 0.746$
26786 measured reflections
6725 independent reflections
4687 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 30.5°$, $\theta_{min} = 2.4°$
$h = -13\rightarrow13$
$k = -13\rightarrow12$
$l = -19\rightarrow20$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.123$
$S = 1.02$
6725 reflections
299 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
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.2297P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å$^{-3}$
$\Delta\rho_{min} = -0.34$ 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* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| C1 | 1.0486 (3) | 0.8525 (3) | 0.54237 (17) | 0.0722 (6) | |
| H1A | 1.0445 | 0.9308 | 0.6042 | 0.108* | |
| H1B | 1.0923 | 0.9013 | 0.4975 | 0.108* | |
| H1C | 1.1106 | 0.7903 | 0.5579 | 0.108* | |
| C2 | 0.8924 (3) | 0.7528 (3) | 0.49251 (17) | 0.0745 (6) | |
| H2A | 0.8474 | 0.7029 | 0.5373 | 0.089* | |
| H2B | 0.8285 | 0.8150 | 0.4774 | 0.089* | |
| C3 | 0.8483 (2) | 0.4891 (2) | 0.38663 (16) | 0.0538 (4) | |
| C4 | 0.8705 (2) | 0.3834 (2) | 0.28825 (15) | 0.0522 (4) | |
| H4A | 0.8013 | 0.2809 | 0.2726 | 0.063* | |
| H4B | 0.9742 | 0.3743 | 0.2970 | 0.063* | |
| C5 | 0.84382 (17) | 0.43617 (19) | 0.19883 (13) | 0.0449 (4) | |
| H5A | 0.9164 | 0.5362 | 0.2122 | 0.054* | |
| H5B | 0.8617 | 0.3625 | 0.1387 | 0.054* | |
| C6 | 0.64292 (16) | 0.56845 (16) | 0.16545 (11) | 0.0358 (3) | |
| C7 | 0.48449 (16) | 0.52038 (16) | 0.13433 (11) | 0.0345 (3) | |
| C8 | 0.44533 (15) | 0.36588 (15) | 0.13440 (11) | 0.0327 (3) | |
| C9 | 0.28989 (16) | 0.27675 (16) | 0.10605 (11) | 0.0355 (3) | |
| C10 | 0.18252 (17) | 0.34113 (19) | 0.07555 (13) | 0.0435 (4) | |
| H10 | 0.0804 | 0.2829 | 0.0551 | 0.052* | |
| C11 | 0.2236 (2) | 0.4947 (2) | 0.07452 (13) | 0.0477 (4) | |
| H11 | 0.1477 | 0.5347 | 0.0529 | 0.057* | |
| C12 | 0.37178 (19) | 0.58583 (18) | 0.10434 (12) | 0.0429 (3) | |
| H12 | 0.3973 | 0.6873 | 0.1048 | 0.051* | |
| C13 | 0.25249 (17) | −0.01017 (17) | 0.03603 (12) | 0.0423 (3) | |

| | | | | | |
|---|---|---|---|---|---|
| C14 | 0.3172 (2) | 0.01302 (19) | −0.05230 (13) | 0.0488 (4) | |
| H14A | 0.4034 | 0.1038 | −0.0286 | 0.073* | |
| H14B | 0.2405 | 0.0264 | −0.0981 | 0.073* | |
| H14C | 0.3494 | −0.0761 | −0.0872 | 0.073* | |
| C15 | 0.28344 (17) | 0.00934 (18) | 0.26812 (12) | 0.0426 (3) | |
| C16 | 0.4413 (2) | 0.0666 (2) | 0.29788 (16) | 0.0613 (5) | |
| H16 | 0.4928 | 0.1571 | 0.2887 | 0.074* | |
| C17 | 0.5205 (2) | −0.0119 (3) | 0.34089 (19) | 0.0711 (6) | |
| H17 | 0.6266 | 0.0248 | 0.3596 | 0.085* | |
| C18 | 0.4447 (2) | −0.1454 (2) | 0.35699 (14) | 0.0516 (4) | |
| C19 | 0.2880 (2) | −0.2002 (2) | 0.32867 (15) | 0.0548 (4) | |
| H19 | 0.2360 | −0.2887 | 0.3400 | 0.066* | |
| C20 | 0.20833 (19) | −0.1236 (2) | 0.28343 (16) | 0.0552 (5) | |
| H20 | 0.1025 | −0.1620 | 0.2630 | 0.066* | |
| C21 | 0.4639 (3) | −0.3534 (3) | 0.4150 (2) | 0.0850 (7) | |
| H21A | 0.3928 | −0.3336 | 0.4597 | 0.127* | |
| H21B | 0.5405 | −0.3892 | 0.4452 | 0.127* | |
| H21C | 0.4103 | −0.4315 | 0.3510 | 0.127* | |
| N1 | 0.68752 (13) | 0.44938 (14) | 0.17929 (9) | 0.0359 (3) | |
| N2 | 0.56842 (13) | 0.32172 (13) | 0.16155 (10) | 0.0366 (3) | |
| N3 | 0.24731 (14) | 0.12398 (13) | 0.11297 (10) | 0.0388 (3) | |
| O1 | 0.90147 (18) | 0.63540 (16) | 0.39826 (10) | 0.0687 (4) | |
| O2A | 0.827 (4) | 0.460 (2) | 0.4645 (11) | 0.074 (4) | 0.40 (5) |
| O2B | 0.763 (3) | 0.4365 (10) | 0.433 (2) | 0.097 (5) | 0.60 (5) |
| O3 | 0.20543 (16) | −0.13637 (13) | 0.04358 (10) | 0.0594 (3) | |
| O4 | 0.21707 (17) | 0.26817 (15) | 0.28507 (11) | 0.0632 (4) | |
| O5 | 0.02109 (13) | 0.02348 (18) | 0.18811 (13) | 0.0709 (4) | |
| O6 | 0.53520 (17) | −0.21420 (19) | 0.39901 (13) | 0.0750 (4) | |
| S1 | 0.17842 (4) | 0.11051 (5) | 0.21770 (4) | 0.04718 (12) | |
| Cl1 | 0.76852 (5) | 0.74258 (5) | 0.18505 (4) | 0.05352 (13) | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0799 (15) | 0.0598 (12) | 0.0636 (13) | 0.0125 (11) | −0.0014 (11) | 0.0131 (10) |
| C2 | 0.0808 (15) | 0.0679 (14) | 0.0560 (12) | 0.0081 (11) | 0.0137 (11) | 0.0050 (10) |
| C3 | 0.0460 (9) | 0.0567 (11) | 0.0697 (12) | 0.0192 (8) | 0.0124 (8) | 0.0329 (9) |
| C4 | 0.0395 (8) | 0.0446 (9) | 0.0715 (12) | 0.0145 (7) | 0.0029 (8) | 0.0193 (8) |
| C5 | 0.0288 (7) | 0.0433 (8) | 0.0569 (10) | 0.0070 (6) | 0.0096 (6) | 0.0117 (7) |
| C6 | 0.0376 (7) | 0.0283 (7) | 0.0378 (7) | 0.0020 (5) | 0.0082 (6) | 0.0115 (5) |
| C7 | 0.0369 (7) | 0.0280 (6) | 0.0366 (7) | 0.0069 (5) | 0.0079 (6) | 0.0099 (5) |
| C8 | 0.0319 (7) | 0.0262 (6) | 0.0379 (7) | 0.0070 (5) | 0.0084 (5) | 0.0088 (5) |
| C9 | 0.0305 (6) | 0.0278 (6) | 0.0434 (8) | 0.0054 (5) | 0.0076 (6) | 0.0078 (5) |
| C10 | 0.0316 (7) | 0.0413 (8) | 0.0528 (9) | 0.0101 (6) | 0.0055 (6) | 0.0106 (7) |
| C11 | 0.0443 (9) | 0.0453 (9) | 0.0557 (10) | 0.0208 (7) | 0.0054 (7) | 0.0159 (7) |
| C12 | 0.0506 (9) | 0.0329 (7) | 0.0484 (9) | 0.0156 (6) | 0.0094 (7) | 0.0157 (6) |
| C13 | 0.0380 (8) | 0.0296 (7) | 0.0484 (9) | 0.0052 (6) | −0.0055 (6) | 0.0063 (6) |
| C14 | 0.0582 (10) | 0.0387 (8) | 0.0445 (9) | 0.0178 (7) | 0.0012 (7) | 0.0072 (7) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C15 | 0.0344 (7) | 0.0408 (8) | 0.0494 (9) | 0.0031 (6) | 0.0109 (6) | 0.0155 (7) |
| C16 | 0.0376 (9) | 0.0613 (12) | 0.0818 (14) | −0.0078 (8) | 0.0013 (9) | 0.0393 (10) |
| C17 | 0.0359 (9) | 0.0798 (15) | 0.0981 (16) | −0.0058 (9) | −0.0025 (9) | 0.0521 (13) |
| C18 | 0.0457 (9) | 0.0578 (11) | 0.0535 (10) | 0.0098 (8) | 0.0101 (7) | 0.0253 (8) |
| C19 | 0.0460 (9) | 0.0487 (10) | 0.0719 (12) | 0.0050 (7) | 0.0163 (8) | 0.0282 (9) |
| C20 | 0.0339 (8) | 0.0500 (10) | 0.0798 (13) | 0.0009 (7) | 0.0107 (8) | 0.0277 (9) |
| C21 | 0.0747 (15) | 0.0906 (18) | 0.117 (2) | 0.0263 (13) | 0.0257 (14) | 0.0693 (16) |
| N1 | 0.0290 (6) | 0.0305 (6) | 0.0447 (7) | 0.0029 (4) | 0.0062 (5) | 0.0124 (5) |
| N2 | 0.0291 (6) | 0.0274 (6) | 0.0511 (7) | 0.0045 (4) | 0.0076 (5) | 0.0130 (5) |
| N3 | 0.0328 (6) | 0.0280 (6) | 0.0501 (7) | 0.0027 (5) | 0.0085 (5) | 0.0102 (5) |
| O1 | 0.0901 (11) | 0.0518 (8) | 0.0469 (7) | −0.0014 (7) | 0.0122 (7) | 0.0092 (6) |
| O2A | 0.090 (8) | 0.069 (5) | 0.079 (5) | 0.023 (5) | 0.029 (5) | 0.044 (3) |
| O2B | 0.106 (9) | 0.078 (3) | 0.117 (9) | 0.013 (4) | 0.069 (8) | 0.041 (4) |
| O3 | 0.0734 (9) | 0.0294 (6) | 0.0623 (8) | 0.0020 (5) | −0.0003 (6) | 0.0112 (5) |
| O4 | 0.0792 (9) | 0.0511 (7) | 0.0686 (8) | 0.0254 (7) | 0.0410 (7) | 0.0198 (6) |
| O5 | 0.0303 (6) | 0.0794 (10) | 0.1197 (12) | 0.0092 (6) | 0.0205 (7) | 0.0597 (9) |
| O6 | 0.0554 (8) | 0.0882 (11) | 0.0985 (12) | 0.0154 (7) | 0.0105 (8) | 0.0603 (10) |
| S1 | 0.03440 (19) | 0.0441 (2) | 0.0676 (3) | 0.00900 (16) | 0.02084 (18) | 0.02352 (19) |
| Cl1 | 0.0495 (2) | 0.0355 (2) | 0.0679 (3) | −0.00609 (16) | 0.00440 (19) | 0.02249 (18) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.475 (3) | C11—H11 | 0.9300 |
| C1—H1A | 0.9600 | C12—H12 | 0.9300 |
| C1—H1B | 0.9600 | C13—O3 | 1.2116 (19) |
| C1—H1C | 0.9600 | C13—N3 | 1.3996 (19) |
| C2—O1 | 1.464 (2) | C13—C14 | 1.488 (2) |
| C2—H2A | 0.9700 | C14—H14A | 0.9600 |
| C2—H2B | 0.9700 | C14—H14B | 0.9600 |
| C3—O2B | 1.193 (6) | C14—H14C | 0.9600 |
| C3—O2A | 1.233 (10) | C15—C20 | 1.377 (2) |
| C3—O1 | 1.305 (2) | C15—C16 | 1.387 (2) |
| C3—C4 | 1.498 (3) | C15—S1 | 1.7446 (18) |
| C4—C5 | 1.510 (3) | C16—C17 | 1.370 (3) |
| C4—H4A | 0.9700 | C16—H16 | 0.9300 |
| C4—H4B | 0.9700 | C17—C18 | 1.389 (3) |
| C5—N1 | 1.4680 (19) | C17—H17 | 0.9300 |
| C5—H5A | 0.9700 | C18—O6 | 1.357 (2) |
| C5—H5B | 0.9700 | C18—C19 | 1.375 (2) |
| C6—N1 | 1.3413 (19) | C19—C20 | 1.377 (3) |
| C6—C7 | 1.392 (2) | C19—H19 | 0.9300 |
| C6—Cl1 | 1.6959 (14) | C20—H20 | 0.9300 |
| C7—C12 | 1.410 (2) | C21—O6 | 1.423 (3) |
| C7—C8 | 1.4194 (19) | C21—H21A | 0.9600 |
| C8—N2 | 1.3464 (18) | C21—H21B | 0.9600 |
| C8—C9 | 1.4168 (18) | C21—H21C | 0.9600 |
| C9—C10 | 1.367 (2) | N1—N2 | 1.3602 (15) |
| C9—N3 | 1.4412 (18) | N3—S1 | 1.6932 (14) |

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|---|---|---|---|
| C10—C11 | 1.416 (2) | O4—S1 | 1.4292 (13) |
| C10—H10 | 0.9300 | O5—S1 | 1.4260 (13) |
| C11—C12 | 1.367 (2) | | |

| | | | |
|---|---|---|---|
| C2—C1—H1A | 109.5 | C7—C12—H12 | 121.2 |
| C2—C1—H1B | 109.5 | O3—C13—N3 | 120.00 (16) |
| H1A—C1—H1B | 109.5 | O3—C13—C14 | 123.63 (15) |
| C2—C1—H1C | 109.5 | N3—C13—C14 | 116.37 (13) |
| H1A—C1—H1C | 109.5 | C13—C14—H14A | 109.5 |
| H1B—C1—H1C | 109.5 | C13—C14—H14B | 109.5 |
| O1—C2—C1 | 108.42 (19) | H14A—C14—H14B | 109.5 |
| O1—C2—H2A | 110.0 | C13—C14—H14C | 109.5 |
| C1—C2—H2A | 110.0 | H14A—C14—H14C | 109.5 |
| O1—C2—H2B | 110.0 | H14B—C14—H14C | 109.5 |
| C1—C2—H2B | 110.0 | C20—C15—C16 | 119.85 (17) |
| H2A—C2—H2B | 108.4 | C20—C15—S1 | 119.72 (13) |
| O2B—C3—O2A | 30.9 (5) | C16—C15—S1 | 120.34 (13) |
| O2B—C3—O1 | 126.8 (4) | C17—C16—C15 | 119.22 (16) |
| O2A—C3—O1 | 116.2 (10) | C17—C16—H16 | 120.4 |
| O2B—C3—C4 | 119.1 (8) | C15—C16—H16 | 120.4 |
| O2A—C3—C4 | 128.4 (6) | C16—C17—C18 | 120.96 (17) |
| O1—C3—C4 | 112.24 (16) | C16—C17—H17 | 119.5 |
| C3—C4—C5 | 114.43 (15) | C18—C17—H17 | 119.5 |
| C3—C4—H4A | 108.7 | O6—C18—C19 | 124.74 (17) |
| C5—C4—H4A | 108.7 | O6—C18—C17 | 115.74 (16) |
| C3—C4—H4B | 108.7 | C19—C18—C17 | 119.50 (18) |
| C5—C4—H4B | 108.7 | C18—C19—C20 | 119.67 (16) |
| H4A—C4—H4B | 107.6 | C18—C19—H19 | 120.2 |
| N1—C5—C4 | 111.86 (13) | C20—C19—H19 | 120.2 |
| N1—C5—H5A | 109.2 | C19—C20—C15 | 120.77 (15) |
| C4—C5—H5A | 109.2 | C19—C20—H20 | 119.6 |
| N1—C5—H5B | 109.2 | C15—C20—H20 | 119.6 |
| C4—C5—H5B | 109.2 | O6—C21—H21A | 109.5 |
| H5A—C5—H5B | 107.9 | O6—C21—H21B | 109.5 |
| N1—C6—C7 | 108.02 (12) | H21A—C21—H21B | 109.5 |
| N1—C6—Cl1 | 122.44 (11) | O6—C21—H21C | 109.5 |
| C7—C6—Cl1 | 129.55 (12) | H21A—C21—H21C | 109.5 |
| C6—C7—C12 | 135.94 (14) | H21B—C21—H21C | 109.5 |
| C6—C7—C8 | 102.85 (13) | C6—N1—N2 | 112.93 (12) |
| C12—C7—C8 | 121.18 (13) | C6—N1—C5 | 128.36 (12) |
| N2—C8—C9 | 127.74 (13) | N2—N1—C5 | 118.31 (12) |
| N2—C8—C7 | 112.71 (12) | C8—N2—N1 | 103.47 (11) |
| C9—C8—C7 | 119.54 (13) | C13—N3—C9 | 123.30 (13) |
| C10—C9—C8 | 118.45 (13) | C13—N3—S1 | 120.09 (11) |
| C10—C9—N3 | 121.44 (13) | C9—N3—S1 | 116.51 (10) |
| C8—C9—N3 | 120.08 (13) | C3—O1—C2 | 118.52 (17) |
| C9—C10—C11 | 121.33 (14) | C18—O6—C21 | 118.14 (16) |
| C9—C10—H10 | 119.3 | O5—S1—O4 | 118.40 (9) |

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| C11—C10—H10 | 119.3 | O5—S1—N3 | 109.15 (8) |
| C12—C11—C10 | 121.85 (15) | O4—S1—N3 | 103.71 (7) |
| C12—C11—H11 | 119.1 | O5—S1—C15 | 109.27 (8) |
| C10—C11—H11 | 119.1 | O4—S1—C15 | 109.37 (9) |
| C11—C12—C7 | 117.60 (14) | N3—S1—C15 | 106.18 (7) |
| C11—C12—H12 | 121.2 | | |

| | | | |
|---|---|---|---|
| O2B—C3—C4—C5 | 126 (2) | C7—C6—N1—C5 | 171.20 (14) |
| O2A—C3—C4—C5 | 161.7 (19) | Cl1—C6—N1—C5 | −8.9 (2) |
| O1—C3—C4—C5 | −39.5 (2) | C4—C5—N1—C6 | 130.76 (16) |
| C3—C4—C5—N1 | −59.63 (19) | C4—C5—N1—N2 | −57.11 (18) |
| N1—C6—C7—C12 | −176.92 (16) | C9—C8—N2—N1 | 179.12 (14) |
| Cl1—C6—C7—C12 | 3.2 (3) | C7—C8—N2—N1 | 0.16 (16) |
| N1—C6—C7—C8 | 1.25 (15) | C6—N1—N2—C8 | 0.70 (16) |
| Cl1—C6—C7—C8 | −178.68 (12) | C5—N1—N2—C8 | −172.61 (13) |
| C6—C7—C8—N2 | −0.88 (16) | O3—C13—N3—C9 | −175.04 (14) |
| C12—C7—C8—N2 | 177.63 (13) | C14—C13—N3—C9 | 4.8 (2) |
| C6—C7—C8—C9 | −179.94 (13) | O3—C13—N3—S1 | 1.2 (2) |
| C12—C7—C8—C9 | −1.4 (2) | C14—C13—N3—S1 | −179.00 (11) |
| N2—C8—C9—C10 | −176.42 (14) | C10—C9—N3—C13 | 97.10 (18) |
| C7—C8—C9—C10 | 2.5 (2) | C8—C9—N3—C13 | −85.05 (18) |
| N2—C8—C9—N3 | 5.7 (2) | C10—C9—N3—S1 | −79.22 (17) |
| C7—C8—C9—N3 | −175.44 (12) | C8—C9—N3—S1 | 98.63 (14) |
| C8—C9—C10—C11 | −1.6 (2) | O2B—C3—O1—C2 | 18 (2) |
| N3—C9—C10—C11 | 176.25 (14) | O2A—C3—O1—C2 | −16.5 (14) |
| C9—C10—C11—C12 | −0.4 (3) | C4—C3—O1—C2 | −178.05 (17) |
| C10—C11—C12—C7 | 1.5 (2) | C1—C2—O1—C3 | 121.8 (2) |
| C6—C7—C12—C11 | 177.37 (16) | C19—C18—O6—C21 | 0.2 (3) |
| C8—C7—C12—C11 | −0.5 (2) | C17—C18—O6—C21 | −178.6 (2) |
| C20—C15—C16—C17 | 1.0 (3) | C13—N3—S1—O5 | −63.19 (14) |
| S1—C15—C16—C17 | 177.49 (17) | C9—N3—S1—O5 | 113.25 (12) |
| C15—C16—C17—C18 | −1.4 (3) | C13—N3—S1—O4 | 169.72 (12) |
| C16—C17—C18—O6 | 179.3 (2) | C9—N3—S1—O4 | −13.83 (13) |
| C16—C17—C18—C19 | 0.5 (3) | C13—N3—S1—C15 | 54.49 (13) |
| O6—C18—C19—C20 | −177.76 (18) | C9—N3—S1—C15 | −129.06 (11) |
| C17—C18—C19—C20 | 0.9 (3) | C20—C15—S1—O5 | −6.70 (18) |
| C18—C19—C20—C15 | −1.4 (3) | C16—C15—S1—O5 | 176.77 (16) |
| C16—C15—C20—C19 | 0.4 (3) | C20—C15—S1—O4 | 124.38 (15) |
| S1—C15—C20—C19 | −176.12 (15) | C16—C15—S1—O4 | −52.16 (17) |
| C7—C6—N1—N2 | −1.29 (17) | C20—C15—S1—N3 | −124.30 (15) |
| Cl1—C6—N1—N2 | 178.64 (10) | C16—C15—S1—N3 | 59.16 (17) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2*A*···O4$^{i}$ | 0.97 | 2.58 | 3.438 (3) | 148 |
| C21—H21*A*···O2*B*$^{ii}$ | 0.96 | 2.44 | 3.273 (7) | 144 |
| C21—H21*A*···O2*A*$^{ii}$ | 0.96 | 2.60 | 3.43 (2) | 145 |

| | | | | |
|---|---|---|---|---|
| C2—H2*B*···O6$^{iii}$ | 0.97 | 2.71 | 3.510 (3) | 140 |
| C14—H14*C*···N2$^{iv}$ | 0.96 | 2.55 | 3.501 (2) | 173 |
| C14—H14*B*···O5$^{v}$ | 0.96 | 2.45 | 3.348 (2) | 155 |

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