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# Ethyl 6-methylsulfanyl-2-phenyl-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate monohydrate

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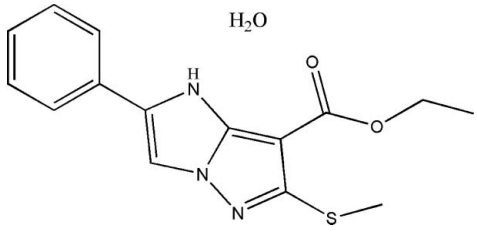
Key indicators: single-crystal X-ray study; $T$ = 273 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.044; $wR$ factor = 0.094; data-to-parameter ratio = 16.1.

The title compound, $C_{15}H_{15}N_3O_2S\cdot H_2O$, has been obtained in a search for new imidazo[1,2-*b*]pyrazole derivatives with better biological activity. The 1*H*-imidazo[1,2-*b*]pyrazole plane forms a dihedral angle of 16.90 (3)° with the benzene ring. $\pi$–$\pi$ interactions are indicated by the short distance of 3.643 (2) Å between the centroids of the benzene and imidazole rings. The crystal structure also involves intermolecular O—H···N hydrogen bonds.

## Related literature

For the biological activity of imidazo[1,2-*b*]pyrazole derivatives, see: Vanotti *et al.* (1994); Kinnamon *et al.* (2000); Li *et al.* (2005). For bond-length data, see: Allen *et al.*, 1987.




## Experimental

### Crystal data

$C_{15}H_{15}N_3O_2S\cdot H_2O$
$M_r$ = 319.38
Orthorhombic, $Pna2_1$
$a$ = 19.017 (2) Å
$b$ = 5.4854 (7) Å
$c$ = 15.2314 (18) Å
$V$ = 1588.9 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.22 mm$^{-1}$
$T$ = 273 K
0.20 × 0.10 × 0.10 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.957, $T_{max}$ = 0.978
8763 measured reflections
3326 independent reflections
1877 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.051

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.094
$S$ = 0.97
3326 reflections
207 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.15 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.14 e Å$^{-3}$
Absolute structure: Flack (1983), 1442 Friedel pairs
Flack parameter: −0.01 (9)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H3$A$···N3$^{i}$ | 0.99 (6) | 1.86 (6) | 2.809 (4) | 160 (5) |

Symmetry code: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2495).

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# supporting information

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# Ethyl 6-methylsulfanyl-2-phenyl-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate monohydrate

**Teng-fei Shao, Gui-long Zhao and Jian-wu Wang**

## S1. Comment

Imidazo[1,2-*b*]pyrazole derivatives have been reported to show various biological activities [Vanotti *et al.*, 1994; Kinnamon *et al.*, 2000], in continuation of our research interest in this field [Li *et al.*, 2005], the new title compound has been synthesized in a search for new compounds with better biological activity, and its crystal structure was determined by X-ray diffraction method.

The title compound crystallizes as a monohydrate (Fig. 1), all bond lengths are normal and in a good agreement with those reported previously (Allen *et al.*, 1987). Atoms S1/O1/O2/C12/C13/C14 lie in 1*H*-imidazo[1,2-*b*]pyrazole (C7—C11/N1/N2/N3) plane with maximum least squares plane deviation for C14 0.070 (3) Å. The 1*H*-imidazo[1,2-*b*]pyrazole plane forms dihedral angles of 16.90 (3)° with the benzene ring (C1—C6). $\pi$-$\pi$ stacking interactions (Table 1) are present in the structure. The crystal structure involves intermolecular are O–H···N hydrogen bonds.

## S2. Experimental

A suspended solution in 30 ml of acetonitrile containing 5 mmol (1.01 g) of ethyl 5-amino-3-methylthio-1*H*-pyrazole-4-carboxylate, 5 mmol (1.00) of $\alpha$-bromoacetophenone and 10 mmol (1.38 g) of sodium carbonate was refluxed for about 10 h until the starting materials were consumed completely, as indicated by TLC. On cooling, the solid was removed through filtration, and the filtrate was evaporated to afford a residue, which was dissolved in 30 ml of absolute ethanol, followed by the addition of several drops of concentrated hydrochloric acid. The resulting solution was then refluxed for about 3 h, and cooled to room temperature. The solution was then evaporated in vacuo to afford the crude product, which was purified by column chromatography using ethyl acetate/petroleum ether (1:5) to give 0.87 g of pure title compound. Crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution of the title compound in dichloromethane/ethyl acetate/petroleum ether (1/2/1) at room temperature.

## S3. Refinement

All H atoms were found on difference maps. The water H atoms were refined freely, giving 0.85 (6) and 0.99 (6)Å, and included in the final cycles of refinement using a riding model, with $U_{iso}$(H) = 1.2$U_{eq}$(C, N) and 1.5$U_{eq}$(C) for the methyl H atoms.

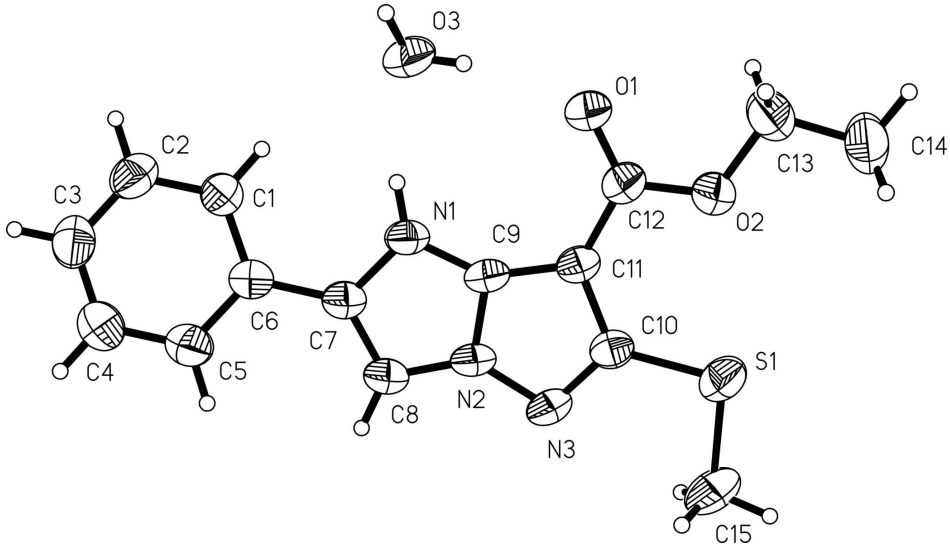


**Figure 1**

View of the title compound, with displacement ellipsoids drawn at the 40% probability level.

**Ethyl 6-methylsulfanyl-2-phenyl-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate monohydrate**

*Crystal data*

$C_{15}H_{15}N_3O_2S\cdot H_2O$
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$b = 5.4854\ (7)$ Å
$c = 15.2314\ (18)$ Å
$V = 1588.9\ (3)$ Å$^3$
$Z = 4$
$F(000) = 672$
$D_x = 1.335$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1077 reflections
$\theta = 2.5–18.0°$
$\mu = 0.22$ mm$^{-1}$
$T = 273$ K
Block, colorless
0.20 × 0.10 × 0.10 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.957$, $T_{max} = 0.978$
8763 measured reflections
3326 independent reflections
1877 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$
$h = -24\rightarrow17$
$k = -7\rightarrow6$
$l = -19\rightarrow19$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.094$
$S = 0.97$
3326 reflections
207 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.15$ e Å$^{-3}$

$\Delta\rho_{min} = -0.14$ e Å$^{-3}$

Absolute structure: Flack (1983), 1442 Friedel pairs
Absolute structure parameter: −0.01 (9)

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.09788 (5) | −0.14517 (15) | 0.84062 (6) | 0.0691 (3) |
| O1 | 0.15780 (12) | 0.2624 (4) | 0.58697 (15) | 0.0736 (7) |
| O2 | 0.09476 (11) | −0.0245 (4) | 0.65679 (14) | 0.0650 (6) |
| O3 | 0.2436 (2) | 0.6611 (6) | 0.55376 (16) | 0.0945 (10) |
| H3A | 0.275 (3) | 0.647 (9) | 0.502 (4) | 0.16 (2)* |
| H3C | 0.223 (3) | 0.523 (10) | 0.551 (3) | 0.15 (2)* |
| N1 | 0.25532 (13) | 0.5824 (4) | 0.73178 (16) | 0.0526 (7) |
| H1A | 0.2568 | 0.6315 | 0.6782 | 0.063* |
| N2 | 0.22812 (12) | 0.3832 (5) | 0.84912 (16) | 0.0525 (6) |
| N3 | 0.19001 (14) | 0.2003 (5) | 0.88960 (15) | 0.0577 (7) |
| C1 | 0.34450 (18) | 1.0192 (6) | 0.7130 (2) | 0.0603 (9) |
| H1B | 0.3120 | 0.9869 | 0.6689 | 0.072* |
| C2 | 0.3920 (2) | 1.2072 (6) | 0.7024 (2) | 0.0719 (11) |
| H2A | 0.3909 | 1.3011 | 0.6516 | 0.086* |
| C3 | 0.4406 (2) | 1.2562 (7) | 0.7662 (3) | 0.0738 (10) |
| H3B | 0.4727 | 1.3824 | 0.7588 | 0.089* |
| C4 | 0.4416 (2) | 1.1188 (7) | 0.8405 (3) | 0.0839 (10) |
| H4A | 0.4748 | 1.1508 | 0.8838 | 0.101* |
| C5 | 0.39376 (19) | 0.9320 (6) | 0.8522 (3) | 0.0759 (10) |
| H5A | 0.3947 | 0.8413 | 0.9038 | 0.091* |
| C6 | 0.34440 (16) | 0.8779 (6) | 0.7882 (2) | 0.0512 (8) |
| C7 | 0.29409 (17) | 0.6804 (5) | 0.8010 (2) | 0.0527 (8) |
| C8 | 0.27674 (16) | 0.5545 (6) | 0.8748 (2) | 0.0544 (9) |
| H8A | 0.2942 | 0.5792 | 0.9312 | 0.065* |
| C9 | 0.21516 (17) | 0.3985 (6) | 0.76236 (19) | 0.0490 (8) |
| C10 | 0.15369 (15) | 0.1013 (5) | 0.8233 (2) | 0.0511 (8) |
| C11 | 0.16699 (17) | 0.2151 (5) | 0.7410 (2) | 0.0502 (8) |
| C12 | 0.14107 (16) | 0.1594 (6) | 0.6547 (2) | 0.0542 (8) |
| C13 | 0.0647 (2) | −0.1008 (7) | 0.5744 (2) | 0.0850 (12) |
| H13A | 0.1009 | −0.1654 | 0.5360 | 0.102* |
| H13B | 0.0422 | 0.0358 | 0.5452 | 0.102* |
| C14 | 0.0120 (2) | −0.2929 (7) | 0.5953 (3) | 0.0986 (13) |

| | | | | |
|---|---|---|---|---|
| H14A | −0.0095 | −0.3494 | 0.5421 | 0.148* |
| H14B | −0.0235 | −0.2265 | 0.6333 | 0.148* |
| H14C | 0.0349 | −0.4267 | 0.6242 | 0.148* |
| C15 | 0.1101 (2) | −0.1931 (7) | 0.9562 (3) | 0.0873 (13) |
| H15A | 0.0816 | −0.3276 | 0.9751 | 0.131* |
| H15B | 0.0966 | −0.0488 | 0.9876 | 0.131* |
| H15C | 0.1587 | −0.2285 | 0.9677 | 0.131* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0711 (6) | 0.0678 (5) | 0.0682 (6) | −0.0051 (5) | 0.0093 (5) | 0.0161 (5) |
| O1 | 0.0939 (19) | 0.0829 (16) | 0.0440 (12) | −0.0255 (15) | −0.0010 (14) | 0.0096 (12) |
| O2 | 0.0703 (14) | 0.0722 (15) | 0.0526 (14) | −0.0146 (14) | −0.0035 (12) | 0.0025 (12) |
| O3 | 0.131 (3) | 0.107 (3) | 0.0453 (15) | −0.041 (2) | 0.0042 (15) | 0.0143 (15) |
| N1 | 0.0628 (17) | 0.0571 (16) | 0.0377 (15) | 0.0017 (14) | −0.0024 (13) | 0.0054 (14) |
| N2 | 0.0642 (17) | 0.0573 (16) | 0.0359 (15) | 0.0048 (13) | −0.0019 (14) | 0.0087 (13) |
| N3 | 0.0700 (19) | 0.0583 (16) | 0.0448 (16) | −0.0010 (15) | 0.0068 (15) | 0.0150 (14) |
| C1 | 0.057 (2) | 0.067 (2) | 0.056 (2) | −0.0041 (19) | −0.0011 (16) | 0.0014 (18) |
| C2 | 0.082 (3) | 0.074 (3) | 0.060 (2) | −0.006 (2) | 0.013 (2) | 0.007 (2) |
| C3 | 0.070 (2) | 0.076 (2) | 0.076 (3) | −0.015 (2) | 0.010 (2) | −0.010 (2) |
| C4 | 0.089 (3) | 0.088 (3) | 0.075 (3) | −0.019 (2) | −0.015 (3) | −0.003 (3) |
| C5 | 0.088 (3) | 0.077 (2) | 0.062 (2) | −0.011 (2) | −0.018 (2) | 0.006 (2) |
| C6 | 0.054 (2) | 0.0534 (18) | 0.046 (2) | 0.0094 (16) | 0.0014 (15) | −0.0006 (15) |
| C7 | 0.060 (2) | 0.0549 (19) | 0.0435 (19) | 0.0042 (17) | −0.0012 (17) | 0.0009 (17) |
| C8 | 0.062 (2) | 0.060 (2) | 0.0403 (18) | 0.0040 (18) | −0.0048 (15) | 0.0020 (16) |
| C9 | 0.0551 (19) | 0.056 (2) | 0.0365 (18) | 0.0079 (17) | 0.0028 (15) | 0.0095 (16) |
| C10 | 0.0534 (19) | 0.0508 (18) | 0.049 (2) | 0.0074 (15) | 0.0022 (15) | 0.0050 (16) |
| C11 | 0.057 (2) | 0.054 (2) | 0.0405 (17) | 0.0023 (17) | 0.0057 (16) | 0.0049 (16) |
| C12 | 0.055 (2) | 0.055 (2) | 0.053 (2) | 0.0005 (17) | 0.0055 (17) | 0.0062 (18) |
| C13 | 0.087 (3) | 0.101 (3) | 0.066 (3) | −0.026 (2) | −0.005 (2) | −0.011 (2) |
| C14 | 0.108 (3) | 0.094 (3) | 0.095 (3) | −0.043 (3) | 0.001 (3) | −0.013 (2) |
| C15 | 0.107 (3) | 0.089 (3) | 0.067 (3) | −0.005 (2) | 0.026 (2) | 0.027 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C10 | 1.739 (3) | C3—H3B | 0.9300 |
| S1—C15 | 1.795 (4) | C4—C5 | 1.382 (4) |
| O1—C12 | 1.219 (4) | C4—H4A | 0.9300 |
| O2—C12 | 1.339 (3) | C5—C6 | 1.385 (4) |
| O2—C13 | 1.442 (4) | C5—H5A | 0.9300 |
| O3—H3A | 0.99 (6) | C6—C7 | 1.459 (4) |
| O3—H3C | 0.85 (6) | C7—C8 | 1.359 (4) |
| N1—C9 | 1.348 (3) | C8—H8A | 0.9300 |
| N1—C7 | 1.395 (4) | C9—C11 | 1.399 (4) |
| N1—H1A | 0.8600 | C10—C11 | 1.423 (4) |
| N2—C9 | 1.347 (4) | C11—C12 | 1.436 (4) |
| N2—C8 | 1.375 (4) | C13—C14 | 1.489 (5) |

| | | | |
|---|---|---|---|
| N2—N3 | 1.383 (3) | C13—H13A | 0.9700 |
| N3—C10 | 1.339 (4) | C13—H13B | 0.9700 |
| C1—C2 | 1.380 (4) | C14—H14A | 0.9600 |
| C1—C6 | 1.383 (4) | C14—H14B | 0.9600 |
| C1—H1B | 0.9300 | C14—H14C | 0.9600 |
| C2—C3 | 1.368 (5) | C15—H15A | 0.9600 |
| C2—H2A | 0.9300 | C15—H15B | 0.9600 |
| C3—C4 | 1.360 (5) | C15—H15C | 0.9600 |
| | | | |
| Cg1···Cg2$^{i}$ | 3.643 (2) | | |
| | | | |
| C10—S1—C15 | 100.60 (17) | C7—C8—H8A | 127.0 |
| C12—O2—C13 | 117.3 (3) | N2—C8—H8A | 127.0 |
| H3A—O3—H3C | 99 (4) | N2—C9—N1 | 106.4 (3) |
| C9—N1—C7 | 109.0 (3) | N2—C9—C11 | 107.7 (3) |
| C9—N1—H1A | 125.5 | N1—C9—C11 | 146.0 (3) |
| C7—N1—H1A | 125.5 | N3—C10—C11 | 113.3 (3) |
| C9—N2—C8 | 111.1 (3) | N3—C10—S1 | 121.0 (2) |
| C9—N2—N3 | 112.8 (3) | C11—C10—S1 | 125.7 (2) |
| C8—N2—N3 | 136.2 (3) | C9—C11—C10 | 103.1 (3) |
| C10—N3—N2 | 103.2 (2) | C9—C11—C12 | 126.2 (3) |
| C2—C1—C6 | 121.1 (3) | C10—C11—C12 | 130.6 (3) |
| C2—C1—H1B | 119.4 | O1—C12—O2 | 122.7 (3) |
| C6—C1—H1B | 119.4 | O1—C12—C11 | 125.9 (3) |
| C3—C2—C1 | 120.4 (3) | O2—C12—C11 | 111.4 (3) |
| C3—C2—H2A | 119.8 | O2—C13—C14 | 106.6 (3) |
| C1—C2—H2A | 119.8 | O2—C13—H13A | 110.4 |
| C4—C3—C2 | 119.5 (4) | C14—C13—H13A | 110.4 |
| C4—C3—H3B | 120.3 | O2—C13—H13B | 110.4 |
| C2—C3—H3B | 120.3 | C14—C13—H13B | 110.4 |
| C3—C4—C5 | 120.6 (4) | H13A—C13—H13B | 108.6 |
| C3—C4—H4A | 119.7 | C13—C14—H14A | 109.5 |
| C5—C4—H4A | 119.7 | C13—C14—H14B | 109.5 |
| C4—C5—C6 | 120.9 (4) | H14A—C14—H14B | 109.5 |
| C4—C5—H5A | 119.5 | C13—C14—H14C | 109.5 |
| C6—C5—H5A | 119.5 | H14A—C14—H14C | 109.5 |
| C1—C6—C5 | 117.5 (3) | H14B—C14—H14C | 109.5 |
| C1—C6—C7 | 121.9 (3) | S1—C15—H15A | 109.5 |
| C5—C6—C7 | 120.6 (3) | S1—C15—H15B | 109.5 |
| C8—C7—N1 | 107.5 (3) | H15A—C15—H15B | 109.5 |
| C8—C7—C6 | 130.3 (3) | S1—C15—H15C | 109.5 |
| N1—C7—C6 | 122.1 (3) | H15A—C15—H15C | 109.5 |
| C7—C8—N2 | 106.0 (3) | H15B—C15—H15C | 109.5 |
| | | | |
| C9—N2—N3—C10 | 0.9 (3) | N3—N2—C9—C11 | −1.2 (3) |
| C8—N2—N3—C10 | −178.6 (3) | C7—N1—C9—N2 | 0.5 (3) |
| C6—C1—C2—C3 | 0.6 (5) | C7—N1—C9—C11 | −177.5 (4) |
| C1—C2—C3—C4 | −0.3 (5) | N2—N3—C10—C11 | −0.2 (3) |

| | | | |
|---|---|---|---|
| C2—C3—C4—C5 | −0.5 (6) | N2—N3—C10—S1 | 178.80 (19) |
| C3—C4—C5—C6 | 1.0 (6) | C15—S1—C10—N3 | −0.8 (3) |
| C2—C1—C6—C5 | −0.1 (5) | C15—S1—C10—C11 | 178.0 (3) |
| C2—C1—C6—C7 | 179.2 (3) | N2—C9—C11—C10 | 1.0 (3) |
| C4—C5—C6—C1 | −0.7 (5) | N1—C9—C11—C10 | 179.0 (4) |
| C4—C5—C6—C7 | 179.9 (3) | N2—C9—C11—C12 | −177.1 (3) |
| C9—N1—C7—C8 | −0.4 (3) | N1—C9—C11—C12 | 0.9 (7) |
| C9—N1—C7—C6 | 178.0 (2) | N3—C10—C11—C9 | −0.5 (3) |
| C1—C6—C7—C8 | −165.9 (3) | S1—C10—C11—C9 | −179.5 (2) |
| C5—C6—C7—C8 | 13.5 (5) | N3—C10—C11—C12 | 177.5 (3) |
| C1—C6—C7—N1 | 16.2 (4) | S1—C10—C11—C12 | −1.4 (5) |
| C5—C6—C7—N1 | −164.4 (3) | C13—O2—C12—O1 | 0.4 (4) |
| N1—C7—C8—N2 | 0.1 (3) | C13—O2—C12—C11 | −179.7 (3) |
| C6—C7—C8—N2 | −178.1 (3) | C9—C11—C12—O1 | 0.8 (5) |
| C9—N2—C8—C7 | 0.2 (3) | C10—C11—C12—O1 | −176.9 (3) |
| N3—N2—C8—C7 | 179.7 (3) | C9—C11—C12—O2 | −179.1 (3) |
| C8—N2—C9—N1 | −0.5 (3) | C10—C11—C12—O2 | 3.2 (4) |
| N3—N2—C9—N1 | 179.9 (2) | C12—O2—C13—C14 | −176.1 (3) |
| C8—N2—C9—C11 | 178.4 (2) | | |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3*A*···N3$^{ii}$ | 0.99 (6) | 1.86 (6) | 2.809 (4) | 160 (5) |

Symmetry code: (ii) −$x$+1/2, $y$+1/2, $z$−1/2.