## organic compounds

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## True symmetry or pseudosymmetry: 5-amino-1-(4-methylphenylsulfonyl)-4-pyrazolin-3-one and a comparison with its 1-phenylsulfonyl analogue

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The title compound,  $C_{10}H_{11}N_3O_3S$ , (I), crystallizes as the NH tautomer. The two rings subtend an interplanar angle of 72.54 (4)°. An intramolecular hydrogen bond is formed from the NH<sub>2</sub> group to a sulfonyl O atom. The molecular packing involves layers of molecules parallel to the *bc* plane at  $x \simeq 0, 1$  *etc.*, with two classical linear hydrogen bonds (amino–sulfonyl and pyrazoline–carbonyl N–H···O) and a further interaction (amino–sulfonyl N–H···O) completing a three-centre system with the intramolecular contact. The analogous phenyl derivative, (II) [Elgemeie, Hanfy, Hopf & Jones (1998). Acta Cryst. C**54**, 136–138], crystallizes with essentially the same unit cell and packing pattern, but with two independent molecules that differ significantly in the orientation of the phenyl groups. The space group is  $P2_1/c$  for (I) but  $P2_1$  for (II), which is thus a pseudosymmetric counterpart of (I).

### Comment

Recent reports from our laboratory have demonstrated the effectiveness of a variety of N-sulfonylated heterocycles and other antimetabolites as antiplastic agents in a number of experimental murine tumour systems (Elgemeie & Sood, 2006; Elgemeie et al., 2009). These compounds have been shown to cause inhibition of thymidine and uridine incorporation into DNA and RNA, and appear to constitute a new class of antimetabolites (Elgemeie et al., 2007). It was of interest to study their stereostructures and evaluate the effects of various structural modifications on their biological activity. Recently, some of our synthesized N-sulfonylated pyrazoles proved to be inhibitors of the enzyme cathepsin B (Myers et al., 2007). Members of this class, along with functional group analogues, were synthesized in an effort to define the structural requirements for activity. We report here the synthesis and structure of the title compound, (I), an N-sulfonated pyrazole obtained by intramolecular cyclization of N'-(2-cyanoacetyl)-4-methylbenzenesulfonohydrazide. Some time ago, we reported the structure of the corresponding 1-phenyl derivative, (II) (Elgemeie *et al.*, 1998).



Compound (I) can potentially exist in a different tautomeric (hydroxy) form. However, spectroscopic studies indicated the presence of the NH tautomer in solution (e.g. the <sup>13</sup>C NMR signal at 172.65 p.p.m. indicates a carbonyl C atom rather than a C-OH group). X-ray analysis (Fig. 1) establishes the exclusive presence of the ketonic form in the solid state; all H atoms could be located unambiguously, and bond lengths are also consistent with the NH form. Molecular dimensions (Table 1) may be regarded as normal. Atoms N2 and N3 are pyramidally coordinated; they lie 0.31 (1) and 0.21 (1) Å, respectively, out of the plane of their three substituents. The pyrazoline ring is reasonably planar (r.m.s. deviation = 0.04 Å), although its largest absolute torsion angle is N1-N2-C3-C4,  $-10.30 (11)^{\circ}$ . The two rings subtend an interplanar angle of 72.54 (4)°, and their orientation is further described by the torsion angles C12-C11-S1-O2 = $-0.31 (11)^{\circ}$  and N2-N1-S1-O3 =  $-179.59 (7)^{\circ}$ . In other words, C12-C11 is synperiplanar to S1-O2, and N1-N2 is antiperiplanar to S1-O3. An intramolecular N3-H03A···O3 hydrogen bond is observed, albeit with a narrow angle of 116.6 (14)° at the H atom; at N3, atoms H03A and H03B lie out of the plane (of the pyrazoline ring plus N3) by 0.28 (2) and 0.25 (2) Å, respectively, both in the opposite direction to atom O3.

The molecular packing of (I) involves thick layers of molecules parallel to the *bc* plane at  $x \simeq 0, 1$  *etc.* (Fig. 2); the tolyl groups project into the space between the layers (Fig. 3). In the order shown in Table 2, hydrogen bond 1 forms eightmembered rings of the common graph set  $R_2^2(8)$  (Bernstein *et al.*, 1995) over an inversion centre, hydrogen bonds 2 and 3



#### Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the intramolecular  $N-H\cdots O$  hydrogen bond.





A packing diagram for (I), viewed parallel to the a axis. For clarity, the tolyl rings are reduced to the *ipso*-C atom, and all H atoms not involved in hydrogen bonding have also been omitted. Hydrogen bonds are indicated by thick (two-centre) or thin dashed lines (three-centre) and are numbered according to their order in Table 2.

form a three-centre system (2 is the intramolecular hydrogen bond mentioned above), and hydrogen bond 4 connects the  $R_2^2(8)$  rings in the direction of the diagonals [011] and [011]. We note that the H03B···O2<sup>ii</sup> [symmetry code: (ii)  $x, -y + \frac{1}{2}$ ,  $z + \frac{1}{2}$ ] contact of 2.76 (2) Å would complete a bifurcated hydrogen-bond system with hydrogen bond 3, but we regard it as too long.

Several years ago, we published the structure of the phenyl analogue, (II), of (I) (Elgemeie *et al.*, 1998). The unit cells are strikingly similar, except that the *a* axis of (II) is around 1.2 Å shorter [for (II): a = 10.7794 (19), b = 7.8301 (8) and c = 11.8317 (12) Å, and  $\beta = 97.505$  (8)°, at 173 K]. The space group of (II) was originally thought to be  $P2_1/c$ , but a more detailed analysis showed that the true space group was  $P2_1$ . The packing diagram of (II) is shown in Fig. 4. The two



Figure 3

A packing diagram for (I), viewed parallel to the b axis. Dashed lines indicate hydrogen bonds.





A packing diagram for (II) (Elgemeie *et al.*, 1998), viewed parallel to the *a* axis. The first independent molecule is drawn with full bonds and the second with open bonds. For clarity, phenyl rings are reduced to the *ipso*-C atom, and all H atoms not involved in hydrogen bonding have also been omitted. Hydrogen bonds are indicated by thick (two-centre) or thin dashed lines (three-centre) and are numbered analogously to those of (I) in Table 2, with an additional 'a' for those with the donor in molecule 1 and 'b' for those with the donor in molecule 2. The origin has been shifted along the *b* axis to be consistent with Fig. 2, but not along the *c* axis, where it would be shifted by  $\frac{1}{4}$  with respect to (I).





A least-squares fit of the two molecules of (II). The r.m.s. deviation for all atoms except the non-*ipso* atoms of the phenyl ring is 0.06 Å. Molecule 1 (unprimed atoms) was inverted and is shown with dashed bonds.

independent molecules in the asymmetric unit, which are related to each other by a local inversion centre, differ significantly in the orientation of the phenyl rings (Fig. 5), with torsion angles N1-S1-C11-C12 = 109.5 (3) and -73.0 (3)°. The two independent molecules of (II) form an exactly equivalent set of hydrogen bonds to each other and to (I), so that the packing pattern is topologically the same in both structures. Compound (II) is thus a pseudosymmetric counterpart of (I). The absence of the methyl group leads to the shorter *a* axis in (II).

### Experimental

Compound (I) was obtained by refluxing an ethanolic solution (30 ml) of N'-(2-cyanoacetyl)-4-methylbenzenesulfonohydrazide (2.53 g, 0.01 mol) containing a few drops of piperidine for 1 h. After cooling, the precipitate, (I), was filtered off and recrystallized from ethanol

Table 1	
Selected geometric parameters (Å, °).	

O1-C3	1.2483 (13)	N3-C5	1.3478 (13)
N1-C5	1.4184 (13)	C3-C4	1.4284 (14)
N1-N2	1.4188 (12)	C4-C5	1.3702 (14)
N2-C3	1.3891 (14)		
O3-S1-N1-N2	-179.59 (7)	C3-C4-C5-N1	-2.41(12)
C5-N1-N2-C3	8.76 (11)	N2-N1-C5-C4	-3.86(11)
N1-N2-C3-C4	-10.30(11)	O2-S1-C11-C12	-0.31(11)
N2-C3-C4-C5	7.95 (12)		

(yield 87%; m.p. 500 K). IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3550, 3500, 3420 (NH<sub>2</sub>, NH), 1630 (C=O, *s*); <sup>1</sup>H NMR (DMSO):  $\delta$  2.34 (*s*, 3H, CH<sub>3</sub>), 4.48 (*s*, 1H, CH), 6.88 (*s*, br, 2H, NH<sub>2</sub>), 7.41–7.92 (*m*, 4H, C<sub>6</sub>H<sub>4</sub>); MS, *m*/*z* = 253. Elemental analysis calculated for C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>S: C 47.42, H 4.37, N 16.59, O 18.95, S 12.66%; found: C 47.66, H 4.47, N 16.62, O 19.18, S 12.71%.

Crystal data

 $\begin{array}{l} C_{10}H_{11}N_{3}O_{3}S\\ M_{r}=253.28\\ Monoclinic, P2_{1}/c\\ a=11.9857~(2)~\text{\AA}\\ b=7.9094~(2)~\text{\AA}\\ c=11.6777~(2)~\text{\AA}\\ \beta=93.778~(2)^{\circ} \end{array}$ 

#### Data collection

Oxford Xcalibur Eos diffractometer Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2011)  $T_{min} = 0.962, T_{max} = 1.000$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$   $wR(F^2) = 0.083$  S = 1.053349 reflections 167 parameters 55463 measured reflections 3349 independent reflections 3081 reflections with  $I > 2\sigma(I)$  $R_{int} = 0.029$ 

V = 1104.63 (4) Å<sup>3</sup>

Mo Ka radiation

 $0.35 \times 0.30 \times 0.10 \ \mathrm{mm}$ 

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

T = 100 K

Z = 4

H atoms treated by a mixture of
independent and constrained
refinement
$\Delta \rho_{\rm max} = 0.44 \text{ e} \text{ Å}^{-3}$
$\Delta \rho_{\rm min} = -0.44 \ {\rm e} \ {\rm \AA}^{-3}$

The N-bound H atoms were refined freely. The methyl group was refined as an idealized rigid group [C-H = 0.98 Å and H-C-H =

# Table 2 Hydrogen-bond geometry (Å, °).

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
$N2-H02\cdotsO1^{i}$	0.891 (17)	1.926 (18)	2.8153 (12)	175.4 (16)
N3-H03A···O3	0.859 (18)	2.333 (17)	2.8241 (13)	116.6 (14)
$N3-H03A\cdots O2^{ii}$	0.859 (18)	2.512 (17)	2.9359 (12)	111.3 (13)
$N3 - H03B \cdots O1^{iii}$	0.859 (18)	1.986 (18)	2.8322 (12)	168.0 (16)

Symmetry codes: (i) -x + 2, -y + 1, -z; (ii) x,  $-y + \frac{1}{2}$ ,  $z + \frac{1}{2}$ ; (iii) x,  $-y + \frac{3}{2}$ ,  $z + \frac{1}{2}$ .

109.5°;  $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})]$  allowed to rotate but not tip; slow convergence of this group may indicate some degree of rotational disorder. Other H atoms were included using a riding model starting from calculated positions [C-H = 0.95 Å and  $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ ].

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3297). Services for accessing these data are described at the back of the journal.

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# supplementary materials

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## True symmetry or pseudosymmetry: 5-amino-1-(4-methylphenylsulfonyl)-4pyrazolin-3-one and a comparison with its 1-phenylsulfonyl analogue

### Galal H. Elgemeie, Shahinaz H. Sayed and Peter G. Jones

### 5-Amino-1-(4-methylphenylsulfonyl)-4-pyrazolin-3-one

Crystal data

 $C_{10}H_{11}N_3O_3S$   $M_r = 253.28$ Monoclinic,  $P2_1/c$  a = 11.9857 (2) Å b = 7.9094 (2) Å c = 11.6777 (2) Å  $\beta = 93.778$  (2)° V = 1104.63 (4) Å<sup>3</sup> Z = 4

### Data collection

Oxford Xcalibur Eos
diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1419 pixels mm <sup>-1</sup>
$\omega$ scans
Absorption correction: multi-scan
(CrysAlis PRO; Oxford Diffraction, 2011)
$T_{\min} = 0.962, \ T_{\max} = 1.000$

### Refinement

Refinement on  $F^2$ Least-squares matrix: full  $R[F^2 > 2\sigma(F^2)] = 0.031$  $wR(F^2) = 0.083$ S = 1.053349 reflections 167 parameters 0 restraints Primary atom site location: structure-invariant direct methods F(000) = 528  $D_x = 1.523 \text{ Mg m}^{-3}$ Mo K\alpha radiation, \lambda = 0.71073 \mathbf{A} Cell parameters from 20410 reflections  $\theta = 2.4-30.8^{\circ}$   $\mu = 0.29 \text{ mm}^{-1}$  T = 100 KTablet, colourless  $0.35 \times 0.30 \times 0.10 \text{ mm}$ 

55463 measured reflections 3349 independent reflections 3081 reflections with  $I > 2\sigma(I)$  $R_{int} = 0.029$  $\theta_{max} = 30.9^{\circ}, \theta_{min} = 3.1^{\circ}$  $h = -17 \rightarrow 17$  $k = -11 \rightarrow 11$  $l = -16 \rightarrow 16$ 

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  $w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.8152P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{max} = 0.008$  $\Delta\rho_{max} = 0.44$  e Å<sup>-3</sup>  $\Delta\rho_{min} = -0.44$  e Å<sup>-3</sup>

### 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.

 $U_{\rm iso}$ \*/ $U_{\rm eq}$ х v Ζ **S**1 0.82267 (2) 0.20196 (3) 0.22306 (2) 0.00923(7)01 0.92704 (7) 0.70212 (10) 0.02289(7)0.01415 (16) O2 0.86903(7)0.08937(10)0.14307(7)0.01331 (16) 03 0.82447 (7) 0.15888 (11) 0.34220(7) 0.01446 (16) N1 0.89922(7)0.38073 (11) 0.21784(7)0.00910 (16) N2 0.90457 (8) 0.44047 (12) 0.10377 (8) 0.01045 (17) H02 0.9571 (15) 0.390(2)0.0653 (14) 0.021 (4)\* N3 0.86198 (8) 0.50217 (13) 0.39905 (8) 0.01302 (18) 0.020 (4)\* H03A 0.8868(14)0.410(2)0.4299(14)H03B 0.8723 (14) 0.591(2)0.4407 (14) 0.019 (4)\* C3 0.90350 (8) 0.61599 (14) 0.10757 (9) 0.01048 (19) C4 0.87726(9)0.66602 (14) 0.22022(9)0.01122 (19) H4 0.8622 0.7779 0.2446 0.013\* C5 0.87772 (8) 0.52327 (13) 0.28673 (9) 0.00963 (18) C11 0.68587 (9) 0.25427 (14) 0.17167 (9) 0.01096 (19) C12 0.64353 (10) 0.18606 (16) 0.06803(10)0.0170(2)0.6889 0.020\* H12 0.1166 0.0237 C13 0.53346 (10) 0.22144(17)0.03042 (11) 0.0198(2)H13 0.5036 0.1741 -0.03980.024\* C14 0.46595 (9) 0.32476 (16) 0.09343(10)0.0162(2)C15 0.51177 (10) 0.39525 (17) 0.19568 (11) 0.0191(2)0.023\* H15 0.4674 0.4684 0.2385 C16 0.62106 (10) 0.36036 (16) 0.23585 (10) 0.0167 (2) H16 0.020\* 0.6512 0.4080 0.3059 C17 0.05166 (12) 0.0237(3)0.34648 (10) 0.35846 (19) H17A 0.2962 0.2995 0.1011 0.036\* H17B 0.3337 0.3176 -0.02730.036\* H17C 0.3318 0.4803 0.0540 0.036\*

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

Atomic displacement parameters  $(Å^2)$ 

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.01033 (12)	0.00810 (12)	0.00918 (12)	-0.00069 (8)	-0.00006 (8)	0.00048 (8)
01	0.0163 (4)	0.0134 (4)	0.0132 (4)	0.0029 (3)	0.0043 (3)	0.0053 (3)
O2	0.0140 (4)	0.0107 (4)	0.0152 (4)	0.0018 (3)	0.0001 (3)	-0.0032 (3)
O3	0.0184 (4)	0.0140 (4)	0.0108 (3)	-0.0033 (3)	-0.0003 (3)	0.0039 (3)
N1	0.0113 (4)	0.0090 (4)	0.0071 (4)	-0.0012 (3)	0.0013 (3)	0.0004 (3)

# supplementary materials

N2	0.0140 (4)	0.0103 (4)	0.0073 (4)	0.0001 (3)	0.0028 (3)	0.0019 (3)
N3	0.0189 (5)	0.0118 (4)	0.0084 (4)	-0.0025 (3)	0.0011 (3)	-0.0014 (3)
C3	0.0089 (4)	0.0109 (4)	0.0117 (4)	0.0012 (3)	0.0007 (3)	0.0015 (4)
C4	0.0123 (4)	0.0096 (4)	0.0119 (4)	0.0000 (3)	0.0022 (4)	0.0002 (4)
C5	0.0086 (4)	0.0102 (4)	0.0101 (4)	-0.0009 (3)	0.0003 (3)	-0.0014 (3)
C11	0.0098 (4)	0.0117 (4)	0.0113 (4)	-0.0009 (4)	0.0009 (3)	0.0000 (4)
C12	0.0136 (5)	0.0218 (6)	0.0155 (5)	0.0030 (4)	-0.0008 (4)	-0.0068 (4)
C13	0.0146 (5)	0.0271 (6)	0.0172 (5)	0.0020 (4)	-0.0036 (4)	-0.0074 (5)
C14	0.0113 (5)	0.0183 (5)	0.0188 (5)	0.0002 (4)	0.0003 (4)	0.0006 (4)
C15	0.0141 (5)	0.0235 (6)	0.0199 (5)	0.0039 (4)	0.0027 (4)	-0.0057 (5)
C16	0.0144 (5)	0.0213 (6)	0.0144 (5)	0.0012 (4)	0.0006 (4)	-0.0061 (4)
C17	0.0119 (5)	0.0298 (7)	0.0288 (6)	0.0034 (5)	-0.0024 (4)	-0.0018 (5)

Geometric parameters (Å, °)

S1—O2	1.4293 (8)	C14—C15	1.3970 (17)
S1—O3	1.4313 (8)	C14—C17	1.5057 (16)
S1—N1	1.6889 (9)	C15—C16	1.3897 (16)
S1—C11	1.7578 (11)	N2—H02	0.891 (17)
O1—C3	1.2483 (13)	N3—H03A	0.859 (18)
N1—C5	1.4184 (13)	N3—H03B	0.859 (18)
N1—N2	1.4188 (12)	C4—H4	0.9500
N2—C3	1.3891 (14)	C12—H12	0.9500
N3—C5	1.3478 (13)	C13—H13	0.9500
C3—C4	1.4284 (14)	C15—H15	0.9500
C4—C5	1.3702 (14)	C16—H16	0.9500
C11—C12	1.3901 (15)	C17—H17A	0.9800
C11—C16	1.3950 (15)	C17—H17B	0.9800
C12—C13	1.3911 (16)	C17—H17C	0.9800
C13—C14	1.3938 (17)		
02 - 81 - 03	120 36 (5)	C15—C14—C17	121 21 (11)
02 - S1 - 03 02 - S1 - N1	120.30(5) 105.22(5)	C16-C15-C14	121.21 (11)
02 S1 N1 03 = S1 = N1	105.22(5) 105.12(5)	$C_{15}$ $-C_{16}$ $-C_{11}$	118.95 (10)
03 - 51 - 011	103.12(5) 108.52(5)	$C_{3}$ N2 H02	118.2 (11)
03 - 81 - C11	100.92(5)	N1—N2—H02	113.6 (11)
N1-S1-C11	106.70 (5)	C5—N3—H03A	116.5 (11)
C5-N1-N2	106.79 (8)	C5-N3-H03B	115.2 (11)
C5-N1-S1	121.71 (7)	H03A—N3—H03B	115.2 (15)
N2—N1—S1	111.77 (7)	C5—C4—H4	126.2
C3—N2—N1	107.56 (8)	C3—C4—H4	126.2
01—C3—N2	121.13 (10)	C11—C12—H12	120.6
O1—C3—C4	130.79 (10)	C13—C12—H12	120.6
N2—C3—C4	108.02 (9)	C12—C13—H13	119.2
C5—C4—C3	107.51 (9)	C14—C13—H13	119.2
N3—C5—C4	131.15 (10)	C16—C15—H15	119.4
N3—C5—N1	119.73 (9)	C14—C15—H15	119.4
C4—C5—N1	109.12 (9)	C15—C16—H16	120.5
C12—C11—C16	121.13 (10)	C11—C16—H16	120.5
C12—C11—S1	118.99 (8)	C14—C17—H17A	109.5

C16—C11—S1	119.87 (8)	C14—C17—H17B	109.5
C11—C12—C13	118.75 (11)	H17A—C17—H17B	109.5
C12—C13—C14	121.52 (11)	С14—С17—Н17С	109.5
C13—C14—C15	118.42 (11)	H17A—C17—H17C	109.5
C13—C14—C17	120.37 (11)	H17B—C17—H17C	109.5
O2—S1—N1—C5	-179.86 (8)	S1—N1—C5—C4	-133.79 (8)
O3—S1—N1—C5	-51.83 (9)	O2—S1—C11—C12	-0.31 (11)
C11—S1—N1—C5	64.97 (9)	O3—S1—C11—C12	-133.86 (10)
O2—S1—N1—N2	52.38 (8)	N1-S1-C11-C12	112.62 (10)
O3—S1—N1—N2	-179.59 (7)	O2—S1—C11—C16	178.57 (9)
C11—S1—N1—N2	-62.80 (8)	O3—S1—C11—C16	45.01 (11)
C5—N1—N2—C3	8.76 (11)	N1-S1-C11-C16	-68.50 (10)
S1—N1—N2—C3	144.13 (7)	C16—C11—C12—C13	-1.86 (18)
N1—N2—C3—O1	167.27 (9)	S1—C11—C12—C13	177.00 (10)
N1—N2—C3—C4	-10.30 (11)	C11—C12—C13—C14	0.8 (2)
O1—C3—C4—C5	-169.30 (11)	C12—C13—C14—C15	0.9 (2)
N2—C3—C4—C5	7.95 (12)	C12-C13-C14-C17	-178.94 (12)
C3—C4—C5—N3	177.50 (11)	C13—C14—C15—C16	-1.67 (19)
C3—C4—C5—N1	-2.41 (12)	C17—C14—C15—C16	178.19 (12)
N2—N1—C5—N3	176.21 (9)	C14—C15—C16—C11	0.67 (19)
S1—N1—C5—N3	46.28 (13)	C12-C11-C16-C15	1.14 (18)
N2—N1—C5—C4	-3.86 (11)	S1-C11-C16-C15	-177.71 (10)

### Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	D—H	Н…А	D···A	<i>D</i> —H··· <i>A</i>
N2—H02···O1 <sup>i</sup>	0.891 (17)	1.926 (18)	2.8153 (12)	175.4 (16)
N3—H03A····O3	0.859 (18)	2.333 (17)	2.8241 (13)	116.6 (14)
N3—H03A···O2 <sup>ii</sup>	0.859 (18)	2.512 (17)	2.9359 (12)	111.3 (13)
N3—H03 <i>B</i> …O1 <sup>iii</sup>	0.859 (18)	1.986 (18)	2.8322 (12)	168.0 (16)

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