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# Crystal structure of (Z)-N'-[1-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)propyl]-benzenesulfonohydrazide

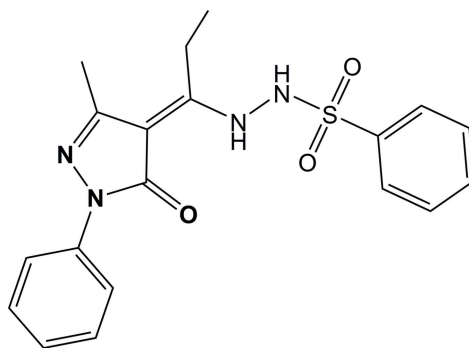
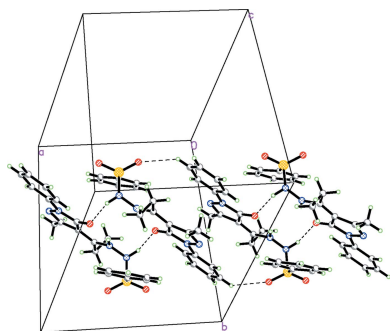
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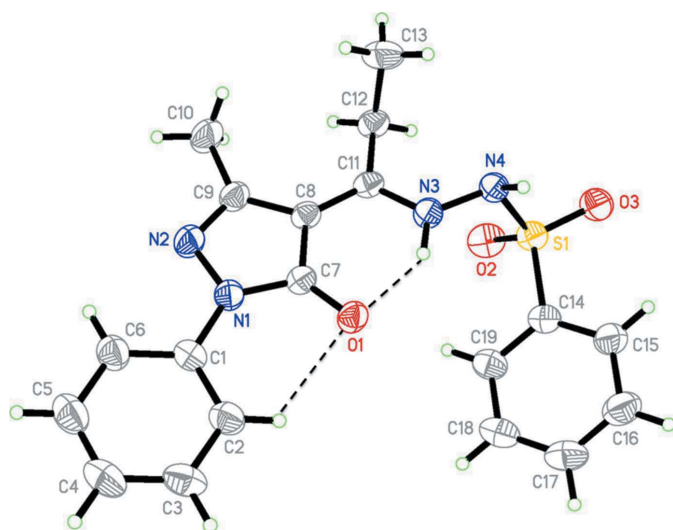
The title compound,  $C_{19}H_{20}N_4O_3S$ , was synthesized by refluxing equimolar amounts of 1-phenyl-3-methyl-4-propionylpyrazol-5-one and benzenesulfonyl hydrazide in ethanol. The compound crystallizes in the keto form and the carbonyl O atom forms an intramolecular N—H···O hydrogen bond with the neighbouring NH group. There is also C—H···O short contact involving the neighbouring phenyl ring. Probably as a result of this, the phenyl ring is inclined to the pyrazolone ring by only  $7.58(12)^\circ$ . The dihedral angle between the phenyl ring and the benzenesulfonyl ring is  $22.78(11)^\circ$ . In the crystal, molecules are linked by pairs of N—H···O hydrogen bonds, forming inversion dimers with an  $R_2^2(14)$  ring motif. The dimers are linked *via* pairs of C—H···O hydrogen bonds, forming chains propagating along [100].

## 1. Chemical context

Many pyrazolones and their derivatives possess biological and pharmaceutical activities, such as anticancer, antitumor and antifungal activities as well as the inhibition of lipid peroxidation (Wang *et al.*, 1991; Yu *et al.*, 1993; Padhyé & Kauffman, 1985; Yang *et al.*, 1992). Among them, the 4-acyl pyrazolone derivatives have aroused great scientific interest because of their relatively simple synthesis, wide availability and structural versatility (Raman *et al.*, 2001; Yoshikuni, 1999; Uzoukwu *et al.*, 1996; Yang *et al.*, 2000).



In recent years, we have devoted our efforts to the design and synthesis of 4-acyl pyrazolone derivatives and their transition metal complexes (Zhang *et al.*, 2004; Xu *et al.*, 2013; Yi *et al.*, 2014; Li *et al.*, 2013). Such 4-acyl pyrazolone derivatives can form different types of complexes due to the multiple coordination sites and the tautomeric enol-to-keto effect. Furthermore, some of complexes have been shown to have strong antibacterial activity. For example, the copper complex  $[CuL(EtOH)]$  [where *L* is the *N*-(1-phenyl-3-methyl-4-

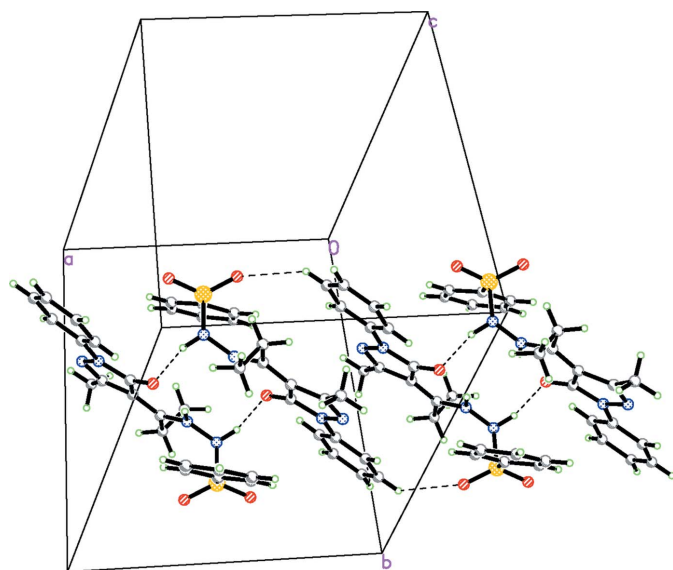


**Figure 1**  
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

propenylidene-5-pyrazolone)salicylidene hydrazide anion] may be a promising drug for cancer chemotherapy (Wang *et al.*, 2007). This has encouraged us to investigate more 4-acyl pyrazolone derivatives and herein we report on the synthesis and crystal structure of the title compound.

## 2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The bond lengths and angles are close to the expected values. For example, the C7—O1 bond length of 1.259 (2) Å is in good agreement with that for a C=O double bond. The C9—N2 bond length of 1.298 (3) Å is consistent with that for a



**Figure 2**  
A view of the crystal packing of the title compound, with the hydrogen bonds shown as dashed lines (see Table 1 for details).

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H3A···O1	0.92	1.88	2.667 (2)	142
C2—H2···O1	0.93	2.35	2.958 (3)	123
N4—H4A···O1 <sup>i</sup>	0.93	1.90	2.800 (2)	162
C5—H5···O2 <sup>ii</sup>	0.93	2.56	3.299 (3)	137

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

normal C=N double bond, which indicates that the compound exists in the keto form. In addition, the C11—N3 bond length of 1.335 (2) Å, is very close to that for a C—N single bond. The C8—C11 bond [1.387 (3) Å] approaches the normal C=C bond length. These results indicate that the compound does not adopt the structure of a Schiff base.

The carbonyl O atom, O1, forms an intramolecular N—H···O hydrogen bond with the neighbouring NH group (N3—H3A), and there is a short intramolecular C—H···O contact involving the neighbouring phenyl ring (C1—C6) (Table 1 and Fig. 1). This phenyl ring is inclined to the pyrazolone ring (N1/N2/C7—C9) by 7.58 (12)°, which is close to the value of 6.2 (2)° reported for a related compound, 4-isopropylidene-3-methyl-1-(3-nitrophenyl)-1*H*-pyrazol-5(4*H*)-one, which also exists in the keto form (Wardell *et al.*, 2007). The dihedral angle between the phenyl ring and the benzenesulfonyl ring (C14—C19) is 22.78 (11)°. Hence, the whole molecule is non-planar, with the torsion angle about the hydrazide bond, C11—N3—N4—S1, being  $-105.91$  (18)°.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>19</sub> H <sub>20</sub> N <sub>4</sub> O <sub>3</sub> S
<i>M<sub>r</sub></i>	384.45
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.601 (2), 16.954 (3), 11.246 (2)
β (°)	107.19 (3)
<i>V</i> (Å <sup>3</sup> )	1931.0 (7)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.19
Crystal size (mm)	0.22 × 0.21 × 0.20
Data collection	
Diffractometer	Rigaku R-Axis SPIDER
Absorption correction	Multi-scan ( <i>ABSCOR</i> ; Higashi, 1995)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.959, 0.962
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	14175, 3339, 2574
<i>R<sub>int</sub></i>	0.024
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.595
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.040, 0.131, 1.08
No. of reflections	3339
No. of parameters	247
No. of restraints	6
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.19, -0.26

Computer programs: *RAPID-AUTO* (Rigaku, 2004), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

### 3. Supramolecular features

In the crystal, atom N4 acts as a donor and forms an N—H...O hydrogen bond with atom O1<sup>i</sup> (Table 1). Molecules are linked by pairs of these hydrogen bonds, forming inversion dimers with an  $R_2^2(14)$  ring motif. Neighbouring dimers are linked by pairs of C—H...O hydrogen bonds, forming chains propagating along [100] (Table 1 and Fig. 2).

### 4. Synthesis and crystallization

1-Phenyl-3-methyl-4-propionyl-pyrazolone-5 (20 mmol, 4.6 g) was dissolved in 25 mL of hot anhydrous ethanol, and an ethanol solution of benzenesulfonyl hydrazide (20 mmol, 3.4 g) was slowly added with constant stirring. After adding a few drops of glacial acetic acid as catalyst, the mixture was refluxed for 4 h. After cooling, the precipitate that had formed was collected by filtration. A light-yellow product was obtained (yield 87%; m.p.: 483–484 K). Yellow block-like crystals, suitable for X-ray diffraction analysis, were obtained from a methanol solution upon slow evaporation at room temperature.

### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH H atoms were located in a difference Fourier map and refined as riding atoms. C-bound H atoms were positioned geometrically and refined as riding: C—H = 0.93–0.97 Å with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{N,C})$  for other H atoms.

### Acknowledgements

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## supporting information

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## Crystal structure of (Z)-N'-[1-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)propyl]benzenesulfonohydrazide

Chuan-Chuan He and Guan-Cheng Xu

### Computing details

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO* (Rigaku, 2004); data reduction: *RAPID-AUTO* (Rigaku, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

### (Z)-N'-[1-(3-Methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)propyl]benzenesulfonohydrazide

#### Crystal data

C<sub>19</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub>S

*M<sub>r</sub>* = 384.45

Monoclinic, *P*2<sub>1</sub>/*n*

Hall symbol: -*P* 2<sub>1</sub>*n*

*a* = 10.601 (2) Å

*b* = 16.954 (3) Å

*c* = 11.246 (2) Å

$\beta$  = 107.19 (3)°

*V* = 1931.0 (7) Å<sup>3</sup>

*Z* = 4

*F*(000) = 808

*D<sub>x</sub>* = 1.322 Mg m<sup>-3</sup>

Melting point: 483 K

Mo *K*α radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 11125 reflections

$\theta$  = 3.1–27.5°

$\mu$  = 0.19 mm<sup>-1</sup>

*T* = 295 K

Block, yellow

0.22 × 0.21 × 0.20 mm

#### Data collection

Rigaku R-AXIS SPIDER

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  oscillation scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

*T<sub>min</sub>* = 0.959, *T<sub>max</sub>* = 0.962

14175 measured reflections

3339 independent reflections

2574 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.024

$\theta_{\max}$  = 25.0°,  $\theta_{\min}$  = 3.1°

*h* = -12→12

*k* = -20→20

*l* = -13→12

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

*wR*(*F*<sup>2</sup>) = 0.131

*S* = 1.08

3339 reflections

247 parameters

6 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

$w = 1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.2317P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.002$$

$$\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008),  $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.016 (2)

*Special details*

**Experimental.** Jacobson, R. (1998) Private communication

**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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.51056 (18)	0.94366 (12)	0.32605 (18)	0.0557 (5)
N1	0.60151 (15)	0.92936 (10)	0.44496 (15)	0.0567 (4)
O1	0.78565 (13)	1.00662 (8)	0.44919 (12)	0.0578 (4)
S1	1.10584 (5)	1.10154 (3)	0.79571 (4)	0.0588 (2)
C2	0.5311 (2)	1.00300 (15)	0.2494 (2)	0.0724 (6)
H2	0.6053	1.0352	0.2752	0.087*
N2	0.56682 (17)	0.87417 (11)	0.52278 (17)	0.0663 (5)
O2	1.00939 (16)	1.10824 (10)	0.85989 (14)	0.0776 (5)
C3	0.4398 (3)	1.01385 (17)	0.1336 (2)	0.0815 (7)
H3	0.4538	1.0532	0.0813	0.098*
N3	0.97144 (15)	0.98778 (9)	0.66664 (14)	0.0547 (4)
H3A	0.9375	1.0074	0.5869	0.066*
O3	1.24221 (15)	1.11194 (9)	0.85898 (14)	0.0796 (5)
C4	0.3288 (2)	0.96752 (17)	0.0949 (2)	0.0838 (8)
H4	0.2683	0.9752	0.0170	0.101*
N4	1.09686 (15)	1.00946 (9)	0.74215 (14)	0.0535 (4)
H4A	1.1524	1.0060	0.6915	0.064*
C5	0.3086 (2)	0.91035 (17)	0.1718 (2)	0.0815 (7)
H5	0.2329	0.8794	0.1464	0.098*
C6	0.3989 (2)	0.89727 (13)	0.2873 (2)	0.0676 (6)
H6	0.3843	0.8574	0.3385	0.081*
C7	0.72508 (18)	0.95903 (11)	0.49872 (17)	0.0501 (4)
C8	0.76992 (18)	0.92317 (11)	0.61970 (17)	0.0503 (4)
C9	0.66454 (19)	0.87097 (12)	0.62447 (19)	0.0589 (5)
C10	0.6554 (2)	0.81416 (16)	0.7229 (2)	0.0835 (7)
H10A	0.5741	0.7853	0.6947	0.125*
H10B	0.6578	0.8425	0.7974	0.125*
H10C	0.7284	0.7781	0.7399	0.125*
C11	0.89157 (18)	0.93953 (11)	0.70462 (16)	0.0493 (4)
C12	0.9392 (2)	0.90616 (12)	0.83395 (18)	0.0600 (5)
H12A	0.8637	0.8913	0.8610	0.072*

H12B	0.9879	0.9464	0.8903	0.072*
C13	1.0270 (3)	0.83473 (15)	0.8404 (2)	0.0869 (8)
H13A	0.9812	0.7962	0.7806	0.130*
H13B	1.0492	0.8124	0.9224	0.130*
H13C	1.1064	0.8504	0.8222	0.130*
C14	1.06098 (19)	1.16434 (11)	0.66519 (18)	0.0568 (5)
C15	1.1583 (2)	1.20180 (14)	0.6279 (2)	0.0734 (6)
H15	1.2470	1.1931	0.6698	0.088*
C16	1.1223 (3)	1.25235 (15)	0.5273 (2)	0.0871 (7)
H16	1.1871	1.2779	0.5012	0.104*
C17	0.9924 (3)	1.26498 (15)	0.4660 (2)	0.0838 (7)
H17	0.9691	1.3005	0.4001	0.101*
C18	0.8952 (3)	1.22547 (15)	0.5008 (2)	0.0790 (6)
H18	0.8068	1.2326	0.4564	0.095*
C19	0.9296 (2)	1.17543 (13)	0.60173 (19)	0.0655 (6)
H19	0.8646	1.1493	0.6268	0.079*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0531 (11)	0.0625 (12)	0.0501 (11)	0.0071 (8)	0.0130 (8)	-0.0009 (9)
N1	0.0555 (9)	0.0618 (10)	0.0502 (9)	-0.0073 (7)	0.0115 (7)	0.0068 (8)
O1	0.0642 (8)	0.0615 (8)	0.0462 (7)	-0.0117 (6)	0.0141 (6)	0.0059 (6)
S1	0.0705 (4)	0.0586 (4)	0.0406 (3)	-0.0030 (2)	0.0062 (2)	-0.0046 (2)
C2	0.0652 (13)	0.0841 (16)	0.0624 (14)	0.0019 (11)	0.0100 (10)	0.0130 (12)
N2	0.0668 (11)	0.0688 (12)	0.0632 (11)	-0.0128 (8)	0.0187 (9)	0.0121 (9)
O2	0.1026 (11)	0.0837 (11)	0.0520 (9)	0.0062 (8)	0.0312 (8)	-0.0069 (8)
C3	0.0821 (17)	0.0970 (19)	0.0604 (14)	0.0190 (13)	0.0132 (12)	0.0191 (13)
N3	0.0611 (10)	0.0595 (10)	0.0388 (8)	-0.0095 (7)	0.0075 (7)	0.0013 (7)
O3	0.0780 (8)	0.0758 (10)	0.0623 (9)	-0.0147 (7)	-0.0146 (7)	-0.0001 (7)
C4	0.0763 (16)	0.100 (2)	0.0614 (15)	0.0200 (14)	-0.0012 (12)	-0.0071 (14)
N4	0.0558 (9)	0.0574 (10)	0.0437 (9)	-0.0033 (7)	0.0091 (7)	-0.0008 (7)
C5	0.0689 (15)	0.0896 (18)	0.0735 (16)	0.0018 (12)	0.0019 (12)	-0.0150 (14)
C6	0.0627 (13)	0.0680 (14)	0.0670 (14)	-0.0012 (10)	0.0112 (10)	-0.0069 (11)
C7	0.0576 (11)	0.0464 (10)	0.0469 (11)	-0.0025 (8)	0.0162 (8)	-0.0002 (8)
C8	0.0609 (11)	0.0474 (10)	0.0427 (10)	-0.0016 (8)	0.0156 (8)	0.0021 (8)
C9	0.0655 (12)	0.0557 (12)	0.0559 (12)	-0.0068 (9)	0.0185 (10)	0.0068 (9)
C10	0.0920 (17)	0.0807 (16)	0.0752 (16)	-0.0210 (12)	0.0207 (13)	0.0245 (13)
C11	0.0635 (11)	0.0435 (10)	0.0409 (10)	0.0012 (8)	0.0154 (8)	0.0002 (8)
C12	0.0749 (13)	0.0577 (12)	0.0436 (11)	-0.0016 (9)	0.0116 (9)	0.0051 (9)
C13	0.1057 (19)	0.0747 (17)	0.0699 (16)	0.0203 (13)	0.0099 (13)	0.0182 (12)
C14	0.0694 (13)	0.0503 (11)	0.0460 (11)	0.0037 (9)	0.0099 (9)	-0.0067 (8)
C15	0.0750 (14)	0.0680 (14)	0.0705 (14)	-0.0041 (11)	0.0113 (11)	0.0089 (12)
C16	0.1027 (19)	0.0792 (17)	0.0794 (17)	-0.0031 (14)	0.0272 (15)	0.0186 (14)
C17	0.1109 (19)	0.0750 (16)	0.0588 (14)	0.0157 (12)	0.0145 (13)	0.0111 (12)
C18	0.0837 (15)	0.0764 (16)	0.0664 (14)	0.0237 (11)	0.0060 (11)	0.0025 (12)
C19	0.0697 (13)	0.0644 (13)	0.0600 (13)	0.0122 (10)	0.0155 (10)	-0.0039 (10)

*Geometric parameters (Å, °)*

C1—C6	1.380 (3)	C8—C11	1.387 (3)
C1—C2	1.383 (3)	C8—C9	1.439 (3)
C1—N1	1.419 (2)	C9—C10	1.492 (3)
N1—C7	1.366 (2)	C10—H10A	0.9600
N1—N2	1.402 (2)	C10—H10B	0.9600
O1—C7	1.259 (2)	C10—H10C	0.9600
S1—O2	1.4197 (17)	C11—C12	1.502 (3)
S1—O3	1.4211 (16)	C12—C13	1.517 (3)
S1—N4	1.6658 (17)	C12—H12A	0.9700
S1—C14	1.761 (2)	C12—H12B	0.9700
C2—C3	1.386 (3)	C13—H13A	0.9600
C2—H2	0.9300	C13—H13B	0.9600
N2—C9	1.298 (3)	C13—H13C	0.9600
C3—C4	1.374 (4)	C14—C19	1.378 (3)
C3—H3	0.9300	C14—C15	1.379 (3)
N3—C11	1.335 (2)	C15—C16	1.380 (3)
N3—N4	1.399 (2)	C15—H15	0.9300
N3—H3A	0.9241	C16—C17	1.362 (3)
C4—C5	1.357 (4)	C16—H16	0.9300
C4—H4	0.9300	C17—C18	1.380 (4)
N4—H4A	0.9335	C17—H17	0.9300
C5—C6	1.385 (3)	C18—C19	1.377 (3)
C5—H5	0.9300	C18—H18	0.9300
C6—H6	0.9300	C19—H19	0.9300
C7—C8	1.437 (3)		
C6—C1—C2	119.73 (19)	N2—C9—C10	118.08 (18)
C6—C1—N1	118.73 (19)	C8—C9—C10	130.27 (18)
C2—C1—N1	121.54 (18)	C9—C10—H10A	109.5
C7—N1—N2	111.31 (15)	C9—C10—H10B	109.5
C7—N1—C1	130.51 (17)	H10A—C10—H10B	109.5
N2—N1—C1	118.13 (15)	C9—C10—H10C	109.5
O2—S1—O3	120.96 (10)	H10A—C10—H10C	109.5
O2—S1—N4	106.62 (9)	H10B—C10—H10C	109.5
O3—S1—N4	103.79 (9)	N3—C11—C8	116.80 (16)
O2—S1—C14	108.53 (10)	N3—C11—C12	118.51 (16)
O3—S1—C14	109.05 (10)	C8—C11—C12	124.69 (17)
N4—S1—C14	107.02 (8)	C11—C12—C13	111.87 (18)
C1—C2—C3	119.1 (2)	C11—C12—H12A	109.2
C1—C2—H2	120.4	C13—C12—H12A	109.2
C3—C2—H2	120.4	C11—C12—H12B	109.2
C9—N2—N1	106.83 (16)	C13—C12—H12B	109.2
C4—C3—C2	121.1 (3)	H12A—C12—H12B	107.9
C4—C3—H3	119.4	C12—C13—H13A	109.5
C2—C3—H3	119.4	C12—C13—H13B	109.5
C11—N3—N4	123.07 (15)	H13A—C13—H13B	109.5

C11—N3—H3A	115.4	C12—C13—H13C	109.5
N4—N3—H3A	121.5	H13A—C13—H13C	109.5
C5—C4—C3	119.2 (2)	H13B—C13—H13C	109.5
C5—C4—H4	120.4	C19—C14—C15	120.9 (2)
C3—C4—H4	120.4	C19—C14—S1	119.79 (17)
N3—N4—S1	114.10 (12)	C15—C14—S1	119.35 (16)
N3—N4—H4A	105.7	C14—C15—C16	119.0 (2)
S1—N4—H4A	107.5	C14—C15—H15	120.5
C4—C5—C6	121.1 (2)	C16—C15—H15	120.5
C4—C5—H5	119.5	C17—C16—C15	120.4 (2)
C6—C5—H5	119.5	C17—C16—H16	119.8
C1—C6—C5	119.7 (2)	C15—C16—H16	119.8
C1—C6—H6	120.2	C16—C17—C18	120.5 (2)
C5—C6—H6	120.2	C16—C17—H17	119.7
O1—C7—N1	126.01 (17)	C18—C17—H17	119.7
O1—C7—C8	128.38 (17)	C19—C18—C17	119.7 (2)
N1—C7—C8	105.59 (16)	C19—C18—H18	120.2
C11—C8—C7	123.18 (17)	C17—C18—H18	120.2
C11—C8—C9	132.19 (17)	C18—C19—C14	119.5 (2)
C7—C8—C9	104.62 (16)	C18—C19—H19	120.3
N2—C9—C8	111.59 (18)	C14—C19—H19	120.3

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3A...O1	0.92	1.88	2.667 (2)	142
C2—H2...O1	0.93	2.35	2.958 (3)	123
N4—H4A...O1 <sup>i</sup>	0.93	1.90	2.800 (2)	162
C5—H5...O2 <sup>ii</sup>	0.93	2.56	3.299 (3)	137

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