Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-[(3-Methyl-5-phenoxy-1-phenylpyrazol-4-yl)carbonyl]-*N*′-(5-propyl-1,3,4-thiadiazol-2-yl)thiourea

Yan-Rong Sun,[a] Gang Liu,[a] Chen-Jiang Liu[a,b]* and Yan-Ping Li[a]

[a]Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education, School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, People's Republic of China, and [b]School of Sciences, Xi'an Jiaotong University, Xian 710049, People's Republic of China
Correspondence e-mail: pxylcj@126.com

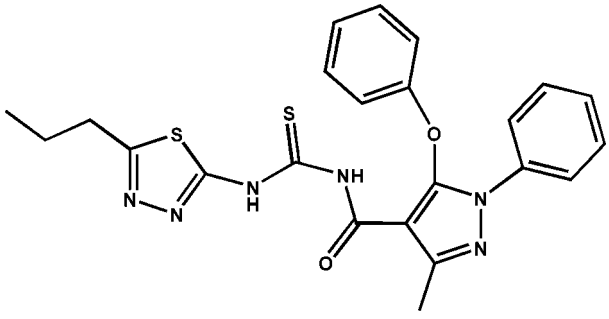
Received 14 November 2007; accepted 24 December 2007

Key indicators: single-crystal X-ray study; T = 153 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.043; wR factor = 0.165; data-to-parameter ratio = 16.3.

In the crystal structure of the title compound, $C_{23}H_{22}N_6O_2S_2$, there are two intramolecular N—H···O hydrogen bonds. The propyl chain is disordered over two sites, with occupancy factors of 0.639 (5) and 0.361 (5).

Related literature

For pharmacological and biological properties, see: Ranise *et al.* (2003); Akbas *et al.* (2005); Daidone *et al.* (2004); Park *et al.* (2005); Thomasco *et al.* (2003); Foroumadi *et al.* (2002); Supuran & Scozzafava (2000).



Experimental

Crystal data

$C_{23}H_{22}N_6O_2S_2$
M_r = 478.58
Triclinic, $P\overline{1}$
a = 8.4489 (3) Å
b = 9.9099 (4) Å
c = 14.3492 (5) Å
α = 86.089 (1)°
β = 74.048 (1)°
γ = 81.591 (1)°
V = 1142.25 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 153 (2) K
0.32 × 0.15 × 0.13 mm

Data collection

Rigaku R-AXIS SPIDER diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.919, T_{max} = 0.966
11326 measured reflections
5171 independent reflections
3376 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.165
S = 1.05
5171 reflections
317 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3*A*···O1	0.88	2.18	2.917 (2)	141
N4—H4*A*···O2	0.88	1.89	2.623 (2)	139

Data collection: *RAPID-AUTO* (Rigaku 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors gratefully acknowledge support from the National Natural Science Foundation of China (grant No. 20662009), the Program for Century Excellent Talents in Universities (grant No. NCET-04-0987) and the Specialized Research Fund for the Doctoral Program of Higher Education (grant No. 20050755003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2066).

References

Akbas, E., Berber, I., Sener, A. & Hasanov, B. (2005). *Farmaco*, **60**, 23–26.
Daidone, G., Maggio, B., Raffa, D., Plescia, S., Schillaci, D. & Raimondi, M. V. (2004). *Farmaco*, **59**, 413–417.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Foroumadi, A., Asadipour, A., Mirzaei, M., Karimi, J. & Emami, S. (2002). *Farmaco*, **57**, 765–769.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Park, H.-J., Lee, K., Park, S.-J., Ahn, B., Lee, J.-C., Cho, H. Y. & Lee, K.-I. (2005). *Bioorg. Med. Chem. Lett.* **15**, 3307–3312.
Ranise, A., Spallarossa, A., Bruno, O., Schenone, S., Fossa, P., Menozzi, G., Bondavalli, F., Mosti, L., Capuano, A., Mazzeo, F., Falcone, G. & Filippelli, W. (2003). *Farmaco*, **58**, 765–780.
Rigaku (2004). *RAPID-AUTO*. Version 3.0. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Supuran, C. T. & Scozzafava, A. (2000). *Eur. J. Med. Chem.* **35**, 867–874.
Thomasco, L. M., Gadwood, R. C., Weaver, E. A., Ochoada, J. M., Ford, C. W., Zurenko, G. E., Hamel, J. C., Stapert, D., Moerman, J. K., Schaadt, R. D. & Yagi, B. H. (2003). *Bioorg. Med. Chem. Lett.* **13**, 4193–4196.

 doi:10.1107/S1600536807068353

supporting information

Acta Cryst. (2008). E**64**, o413 [doi:10.1107/S1600536807068353]

N-[(3-Methyl-5-phenoxy-1-phenylpyrazol-4-yl)carbonyl]-*N*′-(5-propyl-1,3,4-thiadiazol-2-yl)thiourea

Yan-Rong Sun, Gang Liu, Chen-Jiang Liu and Yan-Ping Li

S1. Comment

In previous papers, aroylthioureas were reported to be endowed with various and interesting pharmacological properties (Ranize *et al.*, 2003). Compounds including pyrazole ring are known to possess several biological properties, such as antisepsis, antileukosis, antitumor (Akbas *et al.*, 2005; Daidone *et al.*, 2004; Park *et al.*, 2005). The 1,3,4-thiadiazoles also have widespread biological activity, such as antibacterial, antitubercular, antineoplastic activities (Thomasco *et al.*, 2003; Foroumadi *et al.*, 2002; Supuran & Scozzafava, 2000). Due to identical molecular including many heterocyclic nucleus can attain to effective superimposetion of biological activity, we designed and synthesized *N*-(2-propyl-1,3,4-thiodiazol-5-yl)-*N*′-(1-phenyl-3-methyl-5- phenoxylpyrazol-4-yl)-carbonylthiourea.

The molecule of the title complex (Fig. 1) has two intramolecular hydrogen bonds, which were formed between N3—H3A and O1 and between N4—H4A and O2, which lead to the formation of two six–membered closed loop. Creation of these (pseudo) rings is crucial for the molecular conformations, because it prevents free rotation within the central carbonylthiourea moiety and locks its atoms in a nearly planar arrangement.

S2. Experimental

A mixture of 1-phenyl-3-methyl-5-phenoxylpyrazole-4-isothiocyanate (1 mmol) and 5-propyl-2-amino-1,3,4-thiodiazole (1 mmol) in absolute acetonitrile was refluxed for 10 h at about 354–364 K, then the product was decanted from the hot solution in a funnel, and dried at room temperature for a yield 25.1% (0.12 g), m.p. 461–463 K. Block-like single-crystal of compound (I) was grown from solution of ethanol by slow evaporation.

S3. Refinement

All H atoms were found in difference electron maps and were subsequently refined in the riding-model approximation with C—H = 0.95–0.99 Å, and with U_{iso}(H) = 1.2U_{eq}(C) or U_{iso}(H) = 1.5U_{eq}(C); N—H = 0.88 Å, and with U_{iso}(H) = 1.2U_{eq}(N).

It is disordered in the propyl moiety of molecule. The propyl chain was splited into two chains and the restraints applied to the two chains and the two chains can share the same C21 atom. The ratio of occupancy factors is 0.639 (5)/0.361.

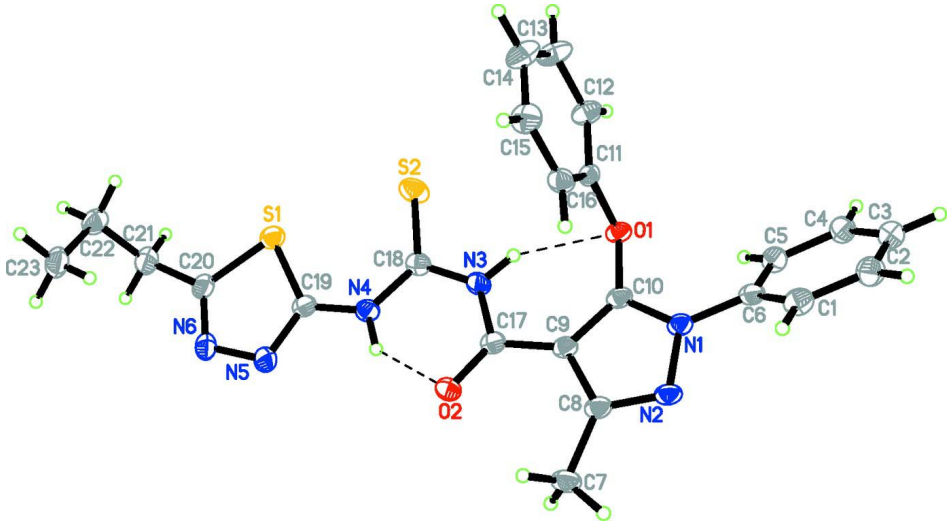


Figure 1

The molecule structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The H atoms are shown as spheres of arbitrary radus. The intramolecular H bond are marked as dashed lines. Only major fragment of propyl chain are drawn.

_N_-[(3-Methyl-5-phenoxy-1-phenylpyrazol-4-yl)carbonyl]-_N′_-(5-propyl-1,3,4- thiadiazol-2-yl)thiourea

Crystal data

$C_{23}H_{22}N_6O_2S_2$
$M_r = 478.58$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.4489$ (3) Å
$b = 9.9099$ (4) Å
$c = 14.3492$ (5) Å
$\alpha = 86.089$ (1)°
$\beta = 74.048$ (1)°
$\gamma = 81.591$ (1)°
$V = 1142.25$ (7) Å^3
$Z = 2$
$F(000) = 500$
$D_x = 1.391$ Mg m^{-3}
Melting point = 461–463 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7971 reflections
$\theta = 3.1$–27.5°
$\mu = 0.27$ mm^{-1}
$T = 153$ K
Block, yellow
0.32 × 0.15 × 0.13 mm

Data collection

Rigaku R-AXIS Spider diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: empirical (using intensity measurements) (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.919$, $T_{max} = 0.966$
11326 measured reflections
5171 independent reflections
3376 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.165$
$S = 1.05$
5171 reflections
317 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
$w = 1/[\sigma^2(F_o^2) + (0.1061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ 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 $F^2 > 2\sigma(F^2)$ 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)
S1	0.56160 (7)	0.15893 (6)	0.37164 (4)	0.04016 (19)	
S2	0.56697 (9)	0.18955 (7)	0.58112 (5)	0.0511 (2)	
O1	0.72651 (18)	0.43251 (15)	0.78717 (10)	0.0330 (3)	
O2	0.7995 (2)	0.57769 (18)	0.48360 (11)	0.0438 (4)	
N1	0.8356 (2)	0.63699 (19)	0.78887 (13)	0.0328 (4)	
N2	0.8911 (2)	0.74382 (19)	0.72761 (13)	0.0360 (4)	
N3	0.6887 (2)	0.4151 (2)	0.59251 (13)	0.0346 (4)	
H3A	0.6652	0.3916	0.6546	0.042*	
N4	0.6649 (2)	0.3756 (2)	0.44130 (13)	0.0357 (4)	
H4A	0.7085	0.4522	0.4261	0.043*	
N5	0.6442 (3)	0.3835 (2)	0.28420 (14)	0.0439 (5)	
N6	0.6035 (3)	0.3101 (2)	0.21699 (14)	0.0480 (5)	
C1	0.9603 (3)	0.6775 (3)	0.91597 (18)	0.0408 (5)	
H1A	1.0540	0.7037	0.8681	0.049*	
C2	0.9530 (3)	0.6782 (3)	1.01344 (19)	0.0467 (6)	
H2B	1.0420	0.7061	1.0326	0.056*	
C3	0.8177 (3)	0.6388 (3)	1.08327 (18)	0.0452 (6)	
H3B	0.8146	0.6389	1.1500	0.054*	
C4	0.6870 (3)	0.5994 (3)	1.05608 (17)	0.0418 (6)	
H4B	0.5946	0.5714	1.1041	0.050*	
C5	0.6905 (3)	0.6005 (2)	0.95854 (16)	0.0364 (5)	
H5B	0.5996	0.5761	0.9395	0.044*	
C6	0.8294 (3)	0.6380 (2)	0.88941 (16)	0.0336 (5)	
C7	0.9194 (3)	0.8149 (3)	0.55833 (18)	0.0433 (6)	
H7A	0.9635	0.8908	0.5786	0.065*	

H7B	0.8206	0.8502	0.5366	0.065*	
H7C	1.0040	0.7683	0.5050	0.065*	
C8	0.8741 (3)	0.7167 (2)	0.64179 (16)	0.0354 (5)	
C9	0.8061 (3)	0.5921 (2)	0.64604 (15)	0.0325 (5)	
C10	0.7862 (3)	0.5469 (2)	0.74127 (16)	0.0320 (5)	
C11	0.8364 (3)	0.3093 (2)	0.77255 (14)	0.0283 (4)	
C12	0.7675 (3)	0.1955 (3)	0.81626 (19)	0.0417 (6)	
H12A	0.6567	0.2036	0.8563	0.050*	
C13	0.8630 (3)	0.0697 (3)	0.8006 (2)	0.0516 (7)	
H13A	0.8178	−0.0100	0.8302	0.062*	
C14	1.0242 (3)	0.0589 (3)	0.7422 (2)	0.0530 (7)	
H14A	1.0888	−0.0282	0.7308	0.064*	
C15	1.0906 (3)	0.1736 (3)	0.70074 (19)	0.0473 (6)	
H15A	1.2016	0.1657	0.6609	0.057*	
C16	0.9973 (3)	0.3014 (3)	0.71634 (16)	0.0370 (5)	
H16A	1.0438	0.3814	0.6887	0.044*	
C17	0.7669 (3)	0.5307 (2)	0.56726 (16)	0.0329 (5)	
C18	0.6421 (3)	0.3310 (2)	0.53439 (16)	0.0335 (5)	
C19	0.6281 (3)	0.3158 (2)	0.36680 (16)	0.0351 (5)	
C20	0.5602 (3)	0.1932 (3)	0.25151 (17)	0.0428 (6)	
C21	0.5096 (4)	0.0933 (3)	0.1944 (2)	0.0555 (7)	
H21A	0.4153	0.0522	0.2383	0.067*	
H21B	0.4675	0.1455	0.1428	0.067*	
C22	0.6339 (5)	−0.0172 (4)	0.1491 (3)	0.0465 (11)	0.639 (5)
H22A	0.5827	−0.0767	0.1163	0.056*	0.639 (5)
H22B	0.6754	−0.0730	0.1995	0.056*	0.639 (5)
C23	0.7787 (7)	0.0383 (5)	0.0753 (3)	0.0568 (13)	0.639 (5)
H23A	0.8616	−0.0378	0.0465	0.085*	0.639 (5)
H23B	0.8293	0.0972	0.1077	0.085*	0.639 (5)
H23C	0.7381	0.0912	0.0243	0.085*	0.639 (5)
C22′	0.6510 (12)	0.0828 (9)	0.0931 (5)	0.053 (2)	0.361 (5)
H22C	0.6563	0.1730	0.0591	0.064*	0.361 (5)
H22D	0.7611	0.0490	0.1038	0.064*	0.361 (5)
C23′	0.6019 (12)	−0.0149 (10)	0.0362 (6)	0.064 (3)	0.361 (5)
H23D	0.6845	−0.0268	−0.0267	0.096*	0.361 (5)
H23E	0.4931	0.0205	0.0260	0.096*	0.361 (5)
H23F	0.5954	−0.1029	0.0715	0.096*	0.361 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0411 (3)	0.0325 (3)	0.0431 (3)	−0.0066 (2)	−0.0042 (3)	−0.0007 (2)
S2	0.0611 (4)	0.0503 (4)	0.0486 (4)	−0.0317 (3)	−0.0178 (3)	0.0171 (3)
O1	0.0335 (8)	0.0240 (8)	0.0338 (8)	−0.0074 (6)	0.0049 (6)	0.0028 (6)
O2	0.0581 (11)	0.0374 (10)	0.0327 (8)	−0.0179 (8)	−0.0026 (8)	0.0059 (7)
N1	0.0345 (9)	0.0273 (10)	0.0335 (9)	−0.0100 (8)	−0.0016 (8)	0.0017 (8)
N2	0.0399 (10)	0.0260 (10)	0.0380 (10)	−0.0109 (8)	−0.0015 (8)	0.0055 (8)
N3	0.0350 (10)	0.0361 (11)	0.0306 (9)	−0.0125 (8)	−0.0027 (8)	0.0046 (8)

N4	0.0368 (10)	0.0328 (11)	0.0341 (9)	−0.0113 (8)	−0.0009 (8)	0.0025 (8)
N5	0.0511 (12)	0.0401 (12)	0.0344 (10)	−0.0093 (10)	0.0008 (9)	−0.0035 (9)
N6	0.0606 (14)	0.0455 (14)	0.0335 (10)	−0.0092 (11)	−0.0020 (10)	−0.0095 (9)
C1	0.0337 (12)	0.0384 (14)	0.0479 (13)	−0.0099 (10)	−0.0050 (11)	0.0007 (11)
C2	0.0472 (14)	0.0464 (16)	0.0520 (15)	−0.0117 (12)	−0.0202 (12)	−0.0003 (12)
C3	0.0545 (15)	0.0401 (15)	0.0429 (13)	−0.0073 (12)	−0.0157 (12)	−0.0015 (11)
C4	0.0441 (13)	0.0412 (14)	0.0363 (12)	−0.0096 (11)	−0.0024 (11)	−0.0015 (10)
C5	0.0322 (11)	0.0381 (13)	0.0357 (11)	−0.0091 (10)	−0.0016 (9)	−0.0014 (10)
C6	0.0359 (11)	0.0248 (11)	0.0356 (11)	−0.0041 (9)	−0.0029 (9)	0.0021 (9)
C7	0.0466 (13)	0.0353 (14)	0.0425 (13)	−0.0110 (11)	−0.0026 (11)	0.0099 (10)
C8	0.0352 (11)	0.0273 (12)	0.0376 (11)	−0.0055 (9)	0.0004 (10)	0.0014 (9)
C9	0.0313 (11)	0.0259 (11)	0.0332 (11)	−0.0043 (9)	0.0029 (9)	0.0013 (9)
C10	0.0296 (10)	0.0242 (11)	0.0367 (11)	−0.0054 (8)	0.0007 (9)	0.0005 (9)
C11	0.0316 (10)	0.0262 (11)	0.0272 (9)	−0.0060 (8)	−0.0065 (8)	−0.0029 (8)
C12	0.0357 (12)	0.0302 (13)	0.0578 (15)	−0.0106 (10)	−0.0077 (11)	0.0013 (11)
C13	0.0462 (14)	0.0266 (13)	0.084 (2)	−0.0097 (11)	−0.0190 (14)	0.0010 (13)
C14	0.0469 (15)	0.0330 (14)	0.080 (2)	0.0041 (12)	−0.0211 (14)	−0.0101 (13)
C15	0.0344 (12)	0.0494 (16)	0.0518 (14)	0.0023 (11)	−0.0049 (11)	−0.0035 (12)
C16	0.0361 (12)	0.0368 (13)	0.0359 (11)	−0.0075 (10)	−0.0057 (10)	0.0041 (10)
C17	0.0287 (10)	0.0288 (11)	0.0342 (11)	−0.0025 (9)	0.0028 (9)	−0.0005 (9)
C18	0.0266 (10)	0.0362 (13)	0.0346 (11)	−0.0069 (9)	−0.0024 (9)	0.0031 (9)
C19	0.0318 (11)	0.0286 (12)	0.0372 (11)	−0.0041 (9)	0.0035 (9)	−0.0013 (9)
C20	0.0478 (14)	0.0350 (14)	0.0384 (12)	−0.0033 (11)	0.0005 (11)	−0.0074 (10)
C21	0.0705 (19)	0.0468 (17)	0.0462 (15)	−0.0094 (14)	−0.0078 (14)	−0.0112 (13)
C22	0.051 (2)	0.038 (2)	0.054 (2)	−0.0081 (18)	−0.019 (2)	−0.0067 (19)
C23	0.063 (3)	0.052 (3)	0.046 (2)	−0.013 (2)	0.006 (2)	−0.015 (2)
C22′	0.064 (6)	0.050 (5)	0.042 (4)	−0.015 (4)	−0.004 (4)	−0.013 (4)
C23′	0.093 (6)	0.064 (6)	0.042 (4)	−0.034 (5)	−0.017 (4)	−0.006 (4)

Geometric parameters (Å, º)

S1—C19	1.719 (2)	C7—H7C	0.9800
S1—C20	1.737 (2)	C8—C9	1.427 (3)
S2—C18	1.648 (2)	C9—C10	1.381 (3)
O1—C10	1.362 (3)	C9—C17	1.455 (3)
O1—C11	1.411 (3)	C11—C16	1.371 (3)
O2—C17	1.230 (3)	C11—C12	1.378 (3)
N1—C10	1.337 (3)	C12—C13	1.378 (4)
N1—N2	1.380 (2)	C12—H12A	0.9500
N1—C6	1.430 (3)	C13—C14	1.382 (4)
N2—C8	1.328 (3)	C13—H13A	0.9500
N3—C17	1.383 (3)	C14—C15	1.368 (4)
N3—C18	1.384 (3)	C14—H14A	0.9500
N3—H3A	0.8800	C15—C16	1.387 (3)
N4—C18	1.349 (3)	C15—H15A	0.9500
N4—C19	1.384 (3)	C16—H16A	0.9500
N4—H4A	0.8800	C20—C21	1.503 (4)
N5—C19	1.305 (3)	C21—C22	1.453 (5)

N5—N6	1.389 (3)	C21—C22′	1.607 (8)
N6—C20	1.292 (3)	C21—H21A	0.9900
C1—C6	1.379 (3)	C21—H21B	0.9900
C1—C2	1.383 (3)	C22—C23	1.525 (6)
C1—H1A	0.9500	C22—H22A	0.9900
C2—C3	1.382 (4)	C22—H22B	0.9900
C2—H2B	0.9500	C23—H23A	0.9800
C3—C4	1.381 (3)	C23—H23B	0.9800
C3—H3B	0.9500	C23—H23C	0.9800
C4—C5	1.391 (3)	C22′—C23′	1.479 (10)
C4—H4B	0.9500	C22′—H22C	0.9900
C5—C6	1.392 (3)	C22′—H22D	0.9900
C5—H5B	0.9500	C23′—H23D	0.9800
C7—C8	1.492 (3)	C23′—H23E	0.9800
C7—H7A	0.9800	C23′—H23F	0.9800
C7—H7B	0.9800		

C19—S1—C20	85.87 (11)	C15—C14—C13	120.0 (2)
C10—O1—C11	116.95 (16)	C15—C14—H14A	120.0
C10—N1—N2	110.63 (17)	C13—C14—H14A	120.0
C10—N1—C6	129.28 (19)	C14—C15—C16	120.6 (2)
N2—N1—C6	120.00 (17)	C14—C15—H15A	119.7
C8—N2—N1	105.57 (18)	C16—C15—H15A	119.7
C17—N3—C18	129.42 (18)	C11—C16—C15	118.4 (2)
C17—N3—H3A	115.3	C11—C16—H16A	120.8
C18—N3—H3A	115.3	C15—C16—H16A	120.8
C18—N4—C19	128.0 (2)	O2—C17—N3	121.6 (2)
C18—N4—H4A	116.0	O2—C17—C9	122.9 (2)
C19—N4—H4A	116.0	N3—C17—C9	115.49 (19)
C19—N5—N6	111.0 (2)	N4—C18—N3	114.41 (19)
C20—N6—N5	112.6 (2)	N4—C18—S2	125.85 (18)
C6—C1—C2	118.9 (2)	N3—C18—S2	119.73 (16)
C6—C1—H1A	120.5	N5—C19—N4	117.9 (2)
C2—C1—H1A	120.5	N5—C19—S1	115.74 (18)
C3—C2—C1	120.8 (2)	N4—C19—S1	126.40 (17)
C3—C2—H2B	119.6	N6—C20—C21	123.7 (2)
C1—C2—H2B	119.6	N6—C20—S1	114.75 (18)
C4—C3—C2	120.0 (2)	C21—C20—S1	121.5 (2)
C4—C3—H3B	120.0	C22—C21—C20	118.1 (3)
C2—C3—H3B	120.0	C22—C21—C22′	47.1 (4)
C3—C4—C5	120.1 (2)	C20—C21—C22′	104.9 (3)
C3—C4—H4B	119.9	C22—C21—H21A	107.8
C5—C4—H4B	119.9	C20—C21—H21A	107.8
C4—C5—C6	118.9 (2)	C22′—C21—H21A	146.2
C4—C5—H5B	120.6	C22—C21—H21B	107.8
C6—C5—H5B	120.6	C20—C21—H21B	107.8
C1—C6—C5	121.3 (2)	C22′—C21—H21B	69.9
C1—C6—N1	119.4 (2)	H21A—C21—H21B	107.1

C5—C6—N1	119.32 (19)	C21—C22—C23	110.9 (4)
C8—C7—H7A	109.5	C21—C22—H22A	109.5
C8—C7—H7B	109.5	C23—C22—H22A	109.5
H7A—C7—H7B	109.5	C21—C22—H22B	109.5
C8—C7—H7C	109.5	C23—C22—H22B	109.5
H7A—C7—H7C	109.5	H22A—C22—H22B	108.0
H7B—C7—H7C	109.5	C22—C23—H23A	109.5
N2—C8—C9	111.13 (19)	C22—C23—H23B	109.5
N2—C8—C7	119.6 (2)	H23A—C23—H23B	109.5
C9—C8—C7	129.2 (2)	C22—C23—H23C	109.5
C10—C9—C8	103.68 (19)	H23A—C23—H23C	109.5
C10—C9—C17	129.3 (2)	H23B—C23—H23C	109.5
C8—C9—C17	127.0 (2)	C23′—C22′—C21	105.3 (6)
N1—C10—O1	121.07 (19)	C23′—C22′—H22C	110.7
N1—C10—C9	108.98 (19)	C21—C22′—H22C	110.7
O1—C10—C9	130.0 (2)	C23′—C22′—H22D	110.7
C16—C11—C12	122.1 (2)	C21—C22′—H22D	110.7
C16—C11—O1	123.2 (2)	H22C—C22′—H22D	108.8
C12—C11—O1	114.70 (18)	C22′—C23′—H23D	109.5
C11—C12—C13	118.6 (2)	C22′—C23′—H23E	109.5
C11—C12—H12A	120.7	H23D—C23′—H23E	109.5
C13—C12—H12A	120.7	C22′—C23′—H23F	109.5
C12—C13—C14	120.3 (2)	H23D—C23′—H23F	109.5
C12—C13—H13A	119.8	H23E—C23′—H23F	109.5
C14—C13—H13A	119.8		

C10—N1—N2—C8	0.1 (2)	C11—C12—C13—C14	−0.1 (4)
C6—N1—N2—C8	−176.87 (19)	C12—C13—C14—C15	1.1 (4)
C19—N5—N6—C20	−0.2 (3)	C13—C14—C15—C16	−0.4 (4)
C6—C1—C2—C3	0.6 (4)	C12—C11—C16—C15	2.3 (3)
C1—C2—C3—C4	−0.6 (4)	O1—C11—C16—C15	−175.1 (2)
C2—C3—C4—C5	−0.6 (4)	C14—C15—C16—C11	−1.3 (4)
C3—C4—C5—C6	1.9 (4)	C18—N3—C17—O2	3.3 (4)
C2—C1—C6—C5	0.6 (4)	C18—N3—C17—C9	−177.0 (2)
C2—C1—C6—N1	179.9 (2)	C10—C9—C17—O2	−175.8 (2)
C4—C5—C6—C1	−1.9 (4)	C8—C9—C17—O2	5.0 (4)
C4—C5—C6—N1	178.8 (2)	C10—C9—C17—N3	4.6 (3)
C10—N1—C6—C1	140.6 (2)	C8—C9—C17—N3	−174.7 (2)
N2—N1—C6—C1	−43.1 (3)	C19—N4—C18—N3	−178.9 (2)
C10—N1—C6—C5	−40.1 (3)	C19—N4—C18—S2	1.5 (3)
N2—N1—C6—C5	136.3 (2)	C17—N3—C18—N4	−5.9 (3)
N1—N2—C8—C9	0.4 (2)	C17—N3—C18—S2	173.78 (18)
N1—N2—C8—C7	178.47 (19)	N6—N5—C19—N4	179.78 (19)
N2—C8—C9—C10	−0.7 (2)	N6—N5—C19—S1	−0.4 (3)
C7—C8—C9—C10	−178.6 (2)	C18—N4—C19—N5	173.0 (2)
N2—C8—C9—C17	178.7 (2)	C18—N4—C19—S1	−6.8 (3)
C7—C8—C9—C17	0.9 (4)	C20—S1—C19—N5	0.63 (19)
N2—N1—C10—O1	179.90 (18)	C20—S1—C19—N4	−179.6 (2)

C6—N1—C10—O1	−3.5 (3)	N5—N6—C20—C21	179.9 (2)
N2—N1—C10—C9	−0.6 (2)	N5—N6—C20—S1	0.7 (3)
C6—N1—C10—C9	176.1 (2)	C19—S1—C20—N6	−0.7 (2)
C11—O1—C10—N1	−101.1 (2)	C19—S1—C20—C21	−179.9 (2)
C11—O1—C10—C9	79.5 (3)	N6—C20—C21—C22	97.3 (4)
C8—C9—C10—N1	0.7 (2)	S1—C20—C21—C22	−83.6 (3)
C17—C9—C10—N1	−178.7 (2)	N6—C20—C21—C22′	48.3 (5)
C8—C9—C10—O1	−179.8 (2)	S1—C20—C21—C22′	−132.6 (4)
C17—C9—C10—O1	0.8 (4)	C20—C21—C22—C23	−61.3 (4)
C10—O1—C11—C16	0.9 (3)	C22′—C21—C22—C23	23.1 (5)
C10—O1—C11—C12	−176.69 (18)	C22—C21—C22′—C23′	65.6 (6)
C16—C11—C12—C13	−1.7 (4)	C20—C21—C22′—C23′	−179.7 (6)
O1—C11—C12—C13	175.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O1	0.88	2.18	2.917 (2)	141
N4—H4*A*···O2	0.88	1.89	2.623 (2)	139