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5-(4-*tert*-Butylbenzylsulfanyl)-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde

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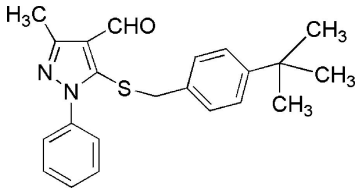
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.048; wR factor = 0.146; data-to-parameter ratio = 13.2.

The title compound, $C_{22}H_{24}N_2OS$, has been synthesized as a potent fungicidal agent and its crystal structure determined. In the crystal structure, weak intermolecular C—H···O interactions are observed. The dihedral angles between the planes of the pyrazole and phenyl rings, and between the benzene and pyrazole rings are 54.2 (2) and 25.0 (3)°, respectively. The methyl groups of the *tert*-butyl group are disordered over two positions; the site occupancies are *ca* 0.65 and 0.35.

Related literature

For related literature, see: Becher *et al.* (1986); Bekhit & Abdel-Aziem (2004); Comber *et al.* (1991); Dannhardt & Kiefer (2001); Gamage *et al.* (2002); Goekan-Kelekci *et al.* (2007); Hashizume *et al.* (2004); Park *et al.* (2005).



Experimental

Crystal data

$C_{22}H_{24}N_2OS$
M_r = 364.49
Orthorhombic, *Pbca*
a = 11.129 (3) Å
b = 16.181 (4) Å
c = 22.429 (6) Å
V = 4039.0 (18) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 294 (2) K
0.24 × 0.20 × 0.16 mm

Data collection

Bruker SMART 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.945, T_{max} = 0.973
19461 measured reflections
3568 independent reflections
1788 reflections with $I > 2\sigma(I)$
R_{int} = 0.087

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.146
S = 1.01
3568 reflections
271 parameters
57 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12A···O2^{i}	0.97	2.54	3.486 (3)	165

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EM2002).

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5-(4-*tert*-Butylbenzylsulfanyl)-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde

Chen-Yi Wang

S1. Comment

The pyrazole ring is an important structural motif found in many biologically and pharmaceutically active compounds. In the past few years, pyrazoles and their derivatives have attracted much attention because they show several biological activities, such as antimicrobial, anti-inflammatory, antiviral, anticancer, insecticidal, herbicidal and plant growth regulatory (Bekhit *et al.*, 2004; Goekan-Kelekci *et al.*, 2007; Gamage *et al.*, 2002; Hashizume *et al.*, 2004). Many pyrazoles are currently being tested and clinically evaluated as potential new drugs (Dannhardt *et al.*, 2001; Park *et al.*, 2005). For example, the natural pyrazole C-glycoside, pyrazofurin, an antibiotic, was reported to possess a broad spectrum of antimicrobial and antiviral activities in addition to being active against several tumor cell lines (Comber *et al.*, 1991). In the search for more biologically active pyrazole derivatives, the title compound, **I**, was synthesized and we report here its crystal structure (Fig.1). The title compound contains three planar groups: (*a*) the phenyl ring composed of atoms C6—C11, (*b*) the pyrazole ring composed of atoms N, N2, C2, C3 and C4, (*c*) the C_6H_4 ring composed of atoms C13—C18, The dihedral angles between the planes of (*a*) and (*b*), and between (*b*) and (*c*) are 54.2 (2) ° and 25.0 (3) ° respectively. The crystal structure is stabilized by weak intermolecular C—H···O hydrogen bonds (Table 1 & Fig.2).

S2. Experimental

To a cooled solution of sodium hydride (0.023 mol) in anhydrous THF (15 ml), was added dropwise (4-*tert*-butylphenyl)-methanethiol (0.022 mol). The reaction mixture was stirred at room temperature for 1 h, and then a solution of 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (Becher *et al.*,1986; 0.020 mol) in anhydrous THF (25 ml) was added dropwise. The mixture was stirred at room temperature for another 2 h, and then poured into water (50 ml) to yield a colourless precipitate (Scheme 1). The resulting precipitate was recrystallized from petroleum ether/ethyl acetate (5:1 *v*/*v*) to give colourless crystals (yield 60%).

S3. Refinement

In the *t*-butyl group the methyl groups were disordered over two sets positions with occupy factors 0.655 (12)/0.345 (12). The displacement parameters of atoms C20, C21, C22, C20′, C21′ and C22′ were restrained to behave approximately isotropically. The C—C distances of the disordered *t*-butyl group were restrained to be 1.54 (1) Å. H atoms were placed in calculated positions, with C—H = 0.93 (aryl), 0.96 (methyl) or 0.97 (methylene) Å, using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(CH_3).

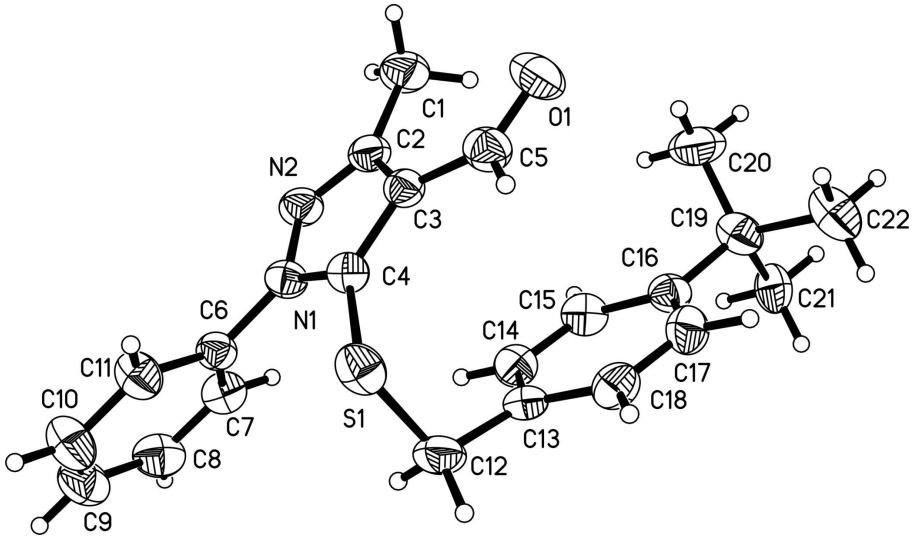

Figure 1

View of the title compound, **I**, with displacement ellipsoids drawn at the 30% probability level and minor disorder component omitted for clarity.

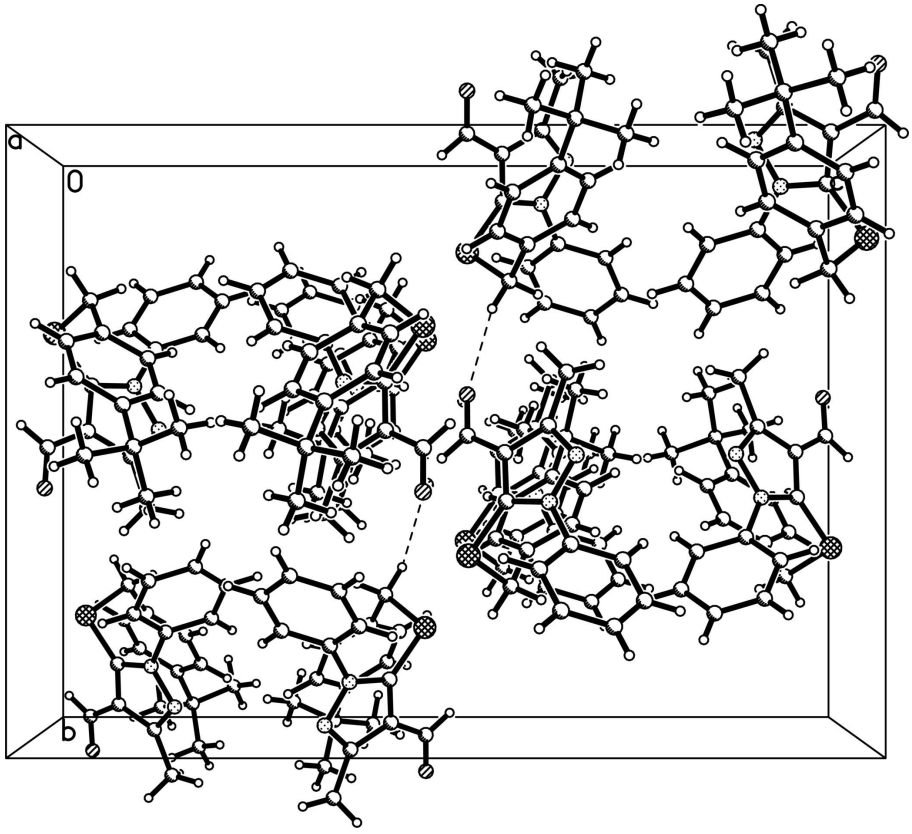

Figure 2

Packing diagram of **I**. Dashed lines indicate C—H···O hydrogen-bond interactions.

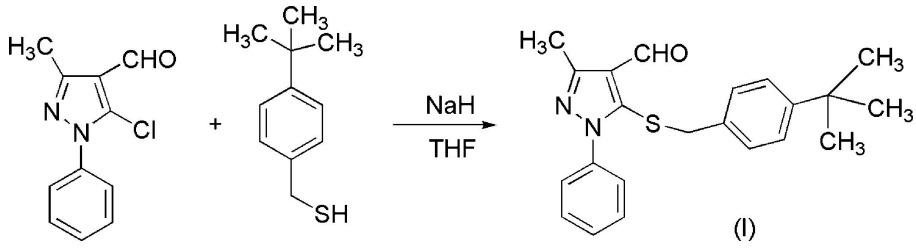

Figure 3

The formation of the title compound.

5-(4-*tert*-Butylbenzylsulfanyl)-3-methyl-1-phenyl-1*H*-pyrazole-4- carbaldehyde

Crystal data

$C_{22}H_{24}N_2OS$
$M_r = 364.49$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 11.129$ (3) Å
$b = 16.181$ (4) Å
$c = 22.429$ (6) Å
$V = 4039.0$ (18) Å^3
$Z = 8$
$F(000) = 1552$
$D_x = 1.199$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2619 reflections
$\theta = 2.4$–23.4°
$\mu = 0.17$ mm^{-1}
$T = 294$ K
Orthorhombic, colourless
0.24 × 0.20 × 0.16 mm

Data collection

Bruker SMART 1000 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.945$, $T_{max} = 0.973$
19461 measured reflections
3568 independent reflections
1788 reflections with $I > 2\sigma(I)$
$R_{int} = 0.087$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.8°$
$h = -12 \rightarrow 13$
$k = -16 \rightarrow 19$
$l = -26 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.146$
$S = 1.01$
3568 reflections
271 parameters
57 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
$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 1.5678P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0053 (5)

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)
S1	0.56005 (9)	0.18185 (6)	0.52594 (4)	0.0692 (3)	
O1	0.7233 (2)	−0.07664 (16)	0.52505 (12)	0.0888 (9)	
N1	0.4568 (2)	0.09456 (16)	0.61696 (12)	0.0539 (7)	
N2	0.4616 (3)	0.02084 (17)	0.64732 (13)	0.0622 (8)	
C1	0.5704 (4)	−0.1109 (2)	0.63859 (17)	0.0809 (12)	
H1A	0.5296	−0.1218	0.6755	0.121*	
H1B	0.6556	−0.1146	0.6447	0.121*	
H1C	0.5461	−0.1507	0.6093	0.121*	
C2	0.5388 (3)	−0.0253 (2)	0.61720 (16)	0.0589 (9)	
C3	0.5853 (3)	0.0175 (2)	0.56780 (14)	0.0520 (8)	
C4	0.5313 (3)	0.09467 (19)	0.56915 (13)	0.0503 (8)	
C5	0.6746 (3)	−0.0098 (2)	0.52514 (16)	0.0676 (10)	
H5	0.6964	0.0273	0.4953	0.081*	
C6	0.3817 (3)	0.1594 (2)	0.63937 (14)	0.0535 (9)	
C7	0.3931 (3)	0.1839 (2)	0.69794 (15)	0.0651 (10)	
H7	0.4507	0.1598	0.7224	0.078*	
C8	0.3183 (4)	0.2443 (3)	0.71983 (18)	0.0787 (12)	
H8	0.3249	0.2607	0.7594	0.094*	
C9	0.2340 (4)	0.2806 (3)	0.6837 (2)	0.0861 (13)	
H9	0.1839	0.3216	0.6987	0.103*	
C10	0.2239 (4)	0.2559 (3)	0.6255 (2)	0.0875 (13)	
H10	0.1668	0.2806	0.6010	0.105*	
C11	0.2967 (3)	0.1955 (2)	0.60299 (16)	0.0704 (10)	
H11	0.2890	0.1789	0.5635	0.084*	
C12	0.6681 (3)	0.2339 (2)	0.57569 (17)	0.0752 (11)	
H12A	0.7027	0.2808	0.5550	0.090*	
H12B	0.6257	0.2546	0.6104	0.090*	
C13	0.7670 (3)	0.17787 (19)	0.59573 (16)	0.0594 (9)	
C14	0.7591 (3)	0.1360 (2)	0.64906 (15)	0.0621 (10)	
H14	0.6952	0.1469	0.6746	0.075*	
C15	0.8436 (3)	0.0784 (2)	0.66528 (15)	0.0655 (10)	
H15	0.8356	0.0516	0.7018	0.079*	
C16	0.9402 (3)	0.0589 (2)	0.62918 (15)	0.0588 (9)	
C17	0.9495 (3)	0.1031 (2)	0.57631 (17)	0.0720 (11)	
H17	1.0145	0.0932	0.5512	0.086*	
C18	0.8651 (4)	0.1614 (2)	0.55988 (17)	0.0709 (11)	
H18	0.8745	0.1900	0.5242	0.085*	
C19	1.0287 (3)	−0.0081 (2)	0.64643 (16)	0.0720 (11)	
C20	0.9655 (8)	−0.0873 (4)	0.6579 (6)	0.115 (3)	0.655 (12)
H20A	1.0227	−0.1284	0.6699	0.172*	0.655 (12)

H20B	0.9256	−0.1051	0.6222	0.172*	0.655 (12)
H20C	0.9073	−0.0796	0.6890	0.172*	0.655 (12)
C21	1.1021 (7)	0.0212 (5)	0.7014 (3)	0.073 (2)	0.655 (12)
H21A	1.0489	0.0298	0.7345	0.110*	0.655 (12)
H21B	1.1424	0.0720	0.6921	0.110*	0.655 (12)
H21C	1.1605	−0.0201	0.7117	0.110*	0.655 (12)
C22	1.1279 (8)	−0.0210 (6)	0.5970 (3)	0.094 (3)	0.655 (12)
H22A	1.1839	−0.0624	0.6100	0.141*	0.655 (12)
H22B	1.1697	0.0300	0.5904	0.141*	0.655 (12)
H22C	1.0905	−0.0386	0.5606	0.141*	0.655 (12)
C20′	0.9620 (13)	−0.0696 (9)	0.6921 (7)	0.087 (5)	0.345 (12)
H20D	0.8867	−0.0868	0.6753	0.130*	0.345 (12)
H20E	0.9480	−0.0415	0.7291	0.130*	0.345 (12)
H20F	1.0116	−0.1172	0.6990	0.130*	0.345 (12)
C21′	1.1392 (14)	0.0222 (13)	0.6765 (9)	0.132 (9)	0.345 (12)
H21D	1.1231	0.0745	0.6952	0.197*	0.345 (12)
H21E	1.2022	0.0288	0.6477	0.197*	0.345 (12)
H21F	1.1638	−0.0170	0.7063	0.197*	0.345 (12)
C22′	1.0496 (18)	−0.0659 (9)	0.5928 (5)	0.101 (6)	0.345 (12)
H22D	1.1070	−0.1076	0.6035	0.151*	0.345 (12)
H22E	1.0797	−0.0344	0.5598	0.151*	0.345 (12)
H22F	0.9751	−0.0916	0.5818	0.151*	0.345 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0791 (7)	0.0673 (6)	0.0612 (6)	0.0141 (5)	0.0036 (5)	0.0218 (5)
O1	0.100 (2)	0.0657 (18)	0.101 (2)	0.0241 (16)	−0.0006 (17)	−0.0163 (16)
N1	0.0617 (18)	0.0461 (16)	0.0538 (16)	0.0022 (14)	−0.0019 (15)	0.0038 (13)
N2	0.069 (2)	0.0478 (17)	0.0697 (19)	−0.0030 (15)	−0.0048 (16)	0.0110 (15)
C1	0.091 (3)	0.050 (2)	0.102 (3)	0.000 (2)	−0.007 (3)	0.014 (2)
C2	0.061 (2)	0.046 (2)	0.070 (2)	−0.0044 (19)	−0.008 (2)	0.0021 (18)
C3	0.053 (2)	0.049 (2)	0.054 (2)	0.0004 (17)	−0.0086 (18)	−0.0034 (16)
C4	0.056 (2)	0.051 (2)	0.0435 (18)	0.0005 (16)	−0.0050 (17)	0.0027 (15)
C5	0.072 (3)	0.063 (2)	0.067 (2)	0.004 (2)	−0.009 (2)	−0.008 (2)
C6	0.057 (2)	0.048 (2)	0.055 (2)	0.0002 (17)	0.0020 (18)	0.0028 (16)
C7	0.074 (2)	0.066 (2)	0.055 (2)	−0.004 (2)	−0.0009 (19)	0.0041 (19)
C8	0.103 (3)	0.072 (3)	0.061 (2)	−0.005 (3)	0.014 (3)	−0.009 (2)
C9	0.097 (3)	0.073 (3)	0.088 (3)	0.015 (2)	0.022 (3)	−0.007 (2)
C10	0.089 (3)	0.090 (3)	0.083 (3)	0.030 (3)	0.000 (2)	−0.009 (3)
C11	0.079 (3)	0.072 (3)	0.061 (2)	0.014 (2)	−0.006 (2)	−0.003 (2)
C12	0.089 (3)	0.043 (2)	0.094 (3)	−0.002 (2)	0.009 (2)	0.008 (2)
C13	0.065 (2)	0.0383 (19)	0.075 (2)	−0.0072 (18)	0.003 (2)	0.0000 (18)
C14	0.068 (2)	0.067 (2)	0.051 (2)	−0.003 (2)	0.0059 (19)	−0.0109 (19)
C15	0.081 (3)	0.066 (2)	0.050 (2)	−0.001 (2)	−0.002 (2)	0.0011 (18)
C16	0.065 (2)	0.056 (2)	0.055 (2)	−0.0014 (19)	−0.003 (2)	−0.0115 (17)
C17	0.065 (3)	0.076 (3)	0.075 (3)	0.000 (2)	0.018 (2)	0.001 (2)
C18	0.074 (3)	0.066 (3)	0.073 (3)	−0.011 (2)	0.015 (2)	0.014 (2)

C19	0.082 (3)	0.067 (3)	0.068 (3)	0.013 (2)	−0.005 (2)	−0.011 (2)
C20	0.110 (6)	0.058 (4)	0.175 (8)	−0.011 (4)	−0.029 (6)	−0.012 (5)
C21	0.053 (4)	0.095 (5)	0.072 (4)	0.011 (3)	−0.006 (4)	0.001 (4)
C22	0.101 (6)	0.100 (6)	0.082 (4)	0.033 (5)	−0.001 (4)	−0.015 (4)
C20′	0.101 (9)	0.059 (7)	0.100 (9)	0.018 (6)	−0.013 (7)	−0.001 (6)
C21′	0.113 (11)	0.123 (11)	0.158 (13)	−0.008 (9)	0.001 (9)	−0.008 (9)
C22′	0.120 (10)	0.085 (8)	0.098 (8)	0.017 (7)	0.014 (7)	−0.001 (7)

Geometric parameters (Å, º)

S1—C4	1.741 (3)	C14—H14	0.9300
S1—C12	1.844 (4)	C15—C16	1.382 (5)
O1—C5	1.210 (4)	C15—H15	0.9300
N1—C4	1.355 (4)	C16—C17	1.389 (5)
N1—N2	1.375 (3)	C16—C19	1.515 (5)
N1—C6	1.432 (4)	C17—C18	1.381 (5)
N2—C2	1.324 (4)	C17—H17	0.9300
C1—C2	1.507 (4)	C18—H18	0.9300
C1—H1A	0.9600	C19—C20	1.485 (6)
C1—H1B	0.9600	C19—C21′	1.487 (9)
C1—H1C	0.9600	C19—C22′	1.541 (8)
C2—C3	1.406 (4)	C19—C21	1.554 (6)
C3—C4	1.386 (4)	C19—C22	1.578 (6)
C3—C5	1.448 (4)	C19—C20′	1.609 (8)
C5—H5	0.9300	C20—H20A	0.9600
C6—C7	1.378 (4)	C20—H20B	0.9600
C6—C11	1.380 (4)	C20—H20C	0.9600
C7—C8	1.375 (5)	C21—H21A	0.9600
C7—H7	0.9300	C21—H21B	0.9600
C8—C9	1.371 (5)	C21—H21C	0.9600
C8—H8	0.9300	C22—H22A	0.9600
C9—C10	1.371 (5)	C22—H22B	0.9600
C9—H9	0.9300	C22—H22C	0.9600
C10—C11	1.366 (5)	C20′—H20D	0.9600
C10—H10	0.9300	C20′—H20E	0.9600
C11—H11	0.9300	C20′—H20F	0.9600
C12—C13	1.495 (5)	C21′—H21D	0.9600
C12—H12A	0.9700	C21′—H21E	0.9600
C12—H12B	0.9700	C21′—H21F	0.9600
C13—C14	1.378 (4)	C22′—H22D	0.9600
C13—C18	1.382 (5)	C22′—H22E	0.9600
C14—C15	1.372 (5)	C22′—H22F	0.9600
C4—S1—C12	98.81 (15)	C15—C14—H14	119.3
C4—N1—N2	111.6 (3)	C13—C14—H14	119.3
C4—N1—C6	129.3 (3)	C14—C15—C16	122.2 (3)
N2—N1—C6	119.0 (3)	C14—C15—H15	118.9
C2—N2—N1	105.2 (3)	C16—C15—H15	118.9

C2—C1—H1A	109.5	C15—C16—C17	116.1 (3)
C2—C1—H1B	109.5	C15—C16—C19	121.3 (3)
H1A—C1—H1B	109.5	C17—C16—C19	122.6 (3)
C2—C1—H1C	109.5	C18—C17—C16	121.9 (3)
H1A—C1—H1C	109.5	C18—C17—H17	119.0
H1B—C1—H1C	109.5	C16—C17—H17	119.0
N2—C2—C3	111.3 (3)	C17—C18—C13	120.9 (3)
N2—C2—C1	120.5 (3)	C17—C18—H18	119.6
C3—C2—C1	128.2 (3)	C13—C18—H18	119.6
C4—C3—C2	105.5 (3)	C20—C19—C16	110.7 (5)
C4—C3—C5	125.9 (3)	C21′—C19—C16	114.7 (9)
C2—C3—C5	128.6 (3)	C16—C19—C22′	109.5 (6)
N1—C4—C3	106.4 (3)	C20—C19—C21	112.0 (5)
N1—C4—S1	123.6 (2)	C16—C19—C21	109.0 (4)
C3—C4—S1	129.6 (3)	C20—C19—C22	109.8 (5)
O1—C5—C3	125.5 (4)	C16—C19—C22	111.8 (4)
O1—C5—H5	117.3	C21—C19—C22	103.3 (4)
C3—C5—H5	117.3	C16—C19—C20′	107.8 (6)
C7—C6—C11	120.3 (3)	C19—C20—H20A	109.5
C7—C6—N1	119.5 (3)	C19—C20—H20B	109.5
C11—C6—N1	120.2 (3)	C19—C20—H20C	109.5
C8—C7—C6	119.3 (4)	C19—C21—H21A	109.5
C8—C7—H7	120.3	C19—C21—H21B	109.5
C6—C7—H7	120.3	C19—C21—H21C	109.5
C9—C8—C7	120.5 (4)	C19—C22—H22A	109.5
C9—C8—H8	119.7	C19—C22—H22B	109.5
C7—C8—H8	119.7	C19—C22—H22C	109.5
C8—C9—C10	119.7 (4)	C19—C20′—H20D	109.5
C8—C9—H9	120.2	C19—C20′—H20E	109.5
C10—C9—H9	120.2	H20D—C20′—H20E	109.5
C11—C10—C9	120.7 (4)	C19—C20′—H20F	109.5
C11—C10—H10	119.6	H20D—C20′—H20F	109.5
C9—C10—H10	119.6	H20E—C20′—H20F	109.5
C10—C11—C6	119.5 (3)	C19—C21′—H21D	109.5
C10—C11—H11	120.3	C19—C21′—H21E	109.5
C6—C11—H11	120.3	H21D—C21′—H21E	109.5
C13—C12—S1	112.7 (2)	C19—C21′—H21F	109.5
C13—C12—H12A	109.1	H21D—C21′—H21F	109.5
S1—C12—H12A	109.1	H21E—C21′—H21F	109.5
C13—C12—H12B	109.1	C19—C22′—H22D	109.5
S1—C12—H12B	109.1	C19—C22′—H22E	109.5
H12A—C12—H12B	107.8	H22D—C22′—H22E	109.5
C14—C13—C18	117.4 (3)	C19—C22′—H22F	109.5
C14—C13—C12	120.8 (3)	H22D—C22′—H22F	109.5
C18—C13—C12	121.6 (3)	H22E—C22′—H22F	109.5
C15—C14—C13	121.4 (3)		

C4—N1—N2—C2	−0.9 (3)	C9—C10—C11—C6	−0.4 (6)

C6—N1—N2—C2	−178.7 (3)	C7—C6—C11—C10	0.1 (5)
N1—N2—C2—C3	0.5 (4)	N1—C6—C11—C10	178.4 (3)
N1—N2—C2—C1	178.1 (3)	C4—S1—C12—C13	50.4 (3)
N2—C2—C3—C4	0.1 (4)	S1—C12—C13—C14	−94.5 (4)
C1—C2—C3—C4	−177.3 (3)	S1—C12—C13—C18	80.7 (4)
N2—C2—C3—C5	177.6 (3)	C18—C13—C14—C15	−1.8 (5)
C1—C2—C3—C5	0.2 (6)	C12—C13—C14—C15	173.6 (3)
N2—N1—C4—C3	1.0 (3)	C13—C14—C15—C16	−0.4 (5)
C6—N1—C4—C3	178.5 (3)	C14—C15—C16—C17	2.2 (5)
N2—N1—C4—S1	−172.5 (2)	C14—C15—C16—C19	−176.7 (3)
C6—N1—C4—S1	5.0 (5)	C15—C16—C17—C18	−1.9 (5)
C2—C3—C4—N1	−0.6 (3)	C19—C16—C17—C18	177.0 (3)
C5—C3—C4—N1	−178.2 (3)	C16—C17—C18—C13	−0.3 (6)
C2—C3—C4—S1	172.3 (3)	C14—C13—C18—C17	2.1 (5)
C5—C3—C4—S1	−5.3 (5)	C12—C13—C18—C17	−173.3 (3)
C12—S1—C4—N1	78.5 (3)	C15—C16—C19—C20	55.1 (7)
C12—S1—C4—C3	−93.3 (3)	C17—C16—C19—C20	−123.7 (6)
C4—C3—C5—O1	178.3 (3)	C15—C16—C19—C21′	−96.3 (11)
C2—C3—C5—O1	1.2 (6)	C17—C16—C19—C21′	84.9 (11)
C4—N1—C6—C7	−125.0 (4)	C15—C16—C19—C22′	132.1 (9)
N2—N1—C6—C7	52.4 (4)	C17—C16—C19—C22′	−46.8 (9)
C4—N1—C6—C11	56.7 (5)	C15—C16—C19—C21	−68.6 (5)
N2—N1—C6—C11	−126.0 (3)	C17—C16—C19—C21	112.6 (5)
C11—C6—C7—C8	0.4 (5)	C15—C16—C19—C22	177.9 (5)
N1—C6—C7—C8	−177.9 (3)	C17—C16—C19—C22	−1.0 (6)
C6—C7—C8—C9	−0.6 (6)	C15—C16—C19—C20′	23.1 (8)
C7—C8—C9—C10	0.4 (6)	C17—C16—C19—C20′	−155.8 (7)
C8—C9—C10—C11	0.1 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*A*···O2^{i}	0.97	2.54	3.486 (3)	165

Symmetry code: (i) *x*+3/2, −*y*+1/2, −*z*.