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3,4,6-Trimethyl-1-phenyl-5-(thiophen-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine

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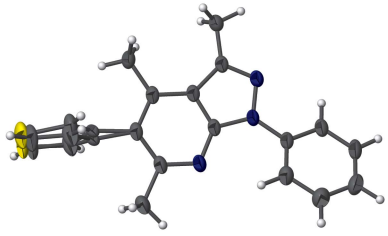
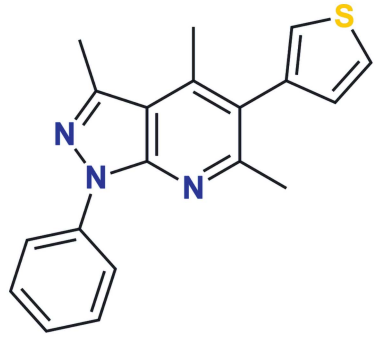
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{19}H_{17}N_3S$, the pyrazolo[3,4-*b*]pyridine unit is slightly bowed across the C—C bond common to the two rings. In the crystal, ribbons extending along the *a*-axis direction are formed by C—H···π(ring) interactions. The ribbons are packed into corrugated layers inclined to the *ac* plane by approximately 22°. The thiophenyl group is rotationally disordered over two sites 180° apart in a 0.606 (2)/0.394 (2) ratio.

3D view



Chemical scheme



Structure description

Bi-heterocyclic systems have received considerable attention due to their biologically interesting properties that are often exploited in drug manufacture. The pyrazolo[3,4-*b*]-pyridines are bi-heterocyclic systems that are included in many drugs targeting bacterial diseases and malaria. They are also active anti-proliferative and anti-coagulant agents (Goda *et al.*, 2004; Kundariya *et al.*, 2011). This work is part of our continuing efforts to develop new pyrazolo[3,4-*b*]pyridine derivatives (Jouha *et al.*, 2017).

In the title compound (Fig. 1), the pyrazolo[3,4-*b*]pyridine unit is slightly bowed about the C1···C5 axis with an angle of 2.2 (1)° between the two constituent rings. The thiophenyl ring (major orientation) is almost orthogonal to the mean plane of the pyridine ring with an angle of 89.8 (2)° between them. In contrast, the C14–C19 phenyl ring is almost coplanar with the pyrazole ring with an interplanar angle of 22.3 (1)°. This conformation is aided by the formation of an intramolecular C15—H15···N1 hydrogen bond (Table 1).

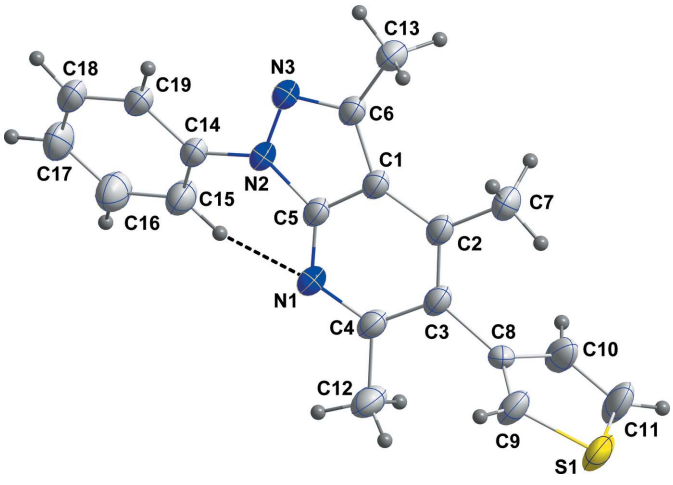


Figure 1
The title molecule with the labelling scheme and 50% probability ellipsoids. The intramolecular C—H···N hydrogen bond is shown as a dashed line.

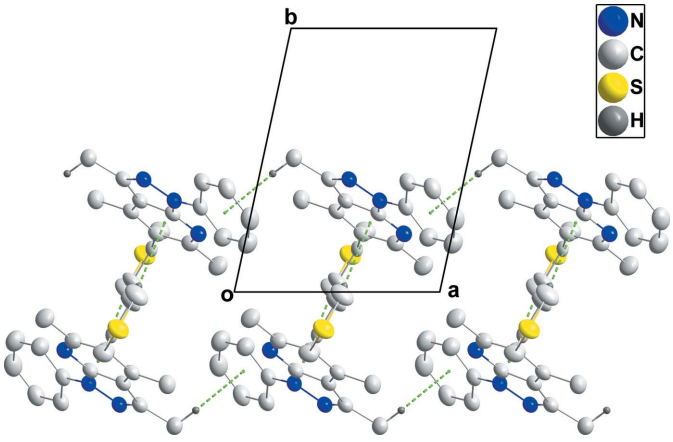


Figure 2
Detail of the C—H···π(ring) interactions (dashed lines) viewed along the *c*-axis direction.

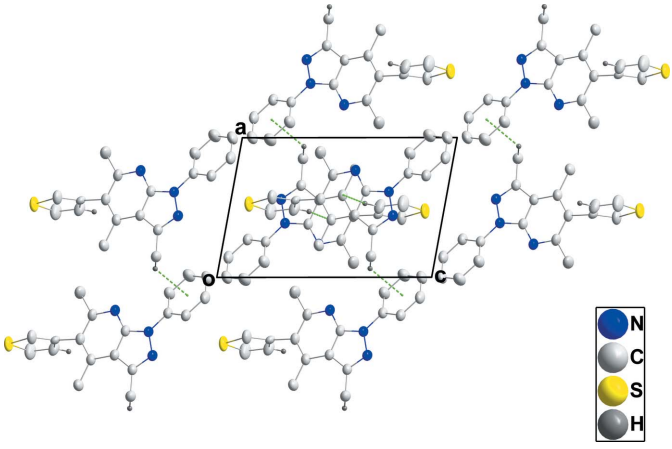


Figure 3
Packing viewed along the *b*-axis direction with intermolecular interactions depicted as in Fig. 2.

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

*Cg*4 and *Cg*5 are the centroids of the N1/C1–C5 and C14–C19 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···*Cg*4^{i}	0.95	2.63	3.491 (3)	151
C13—H13*A*···*Cg*5^{ii}	0.97 (2)	2.70 (2)	3.4771 (18)	138.1 (16)
C15—H15···N1	0.98 (2)	2.44 (2)	3.040 (2)	119.2 (15)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{17}N_3S$
M_r	319.41
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, *b*, *c* (Å)	7.6672 (3), 9.9098 (4), 11.4101 (4)
α, β, γ (°)	82.548 (1), 78.176 (2), 76.607 (2)
V (Å^3)	822.39 (6)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.75
Crystal size (mm)	0.43 × 0.17 × 0.16
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.63, 0.77
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6351, 3048, 2722
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.043, 0.117, 1.04
No. of reflections	3048
No. of parameters	262
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.26

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

In the crystal, inversion-related pairs of C10—H10···*Cg*4 interactions (Table 1) form dimers, which are joined into ribbons extending along the *a*-axis direction by C13—H13*A*···*Cg*5 interactions (Table 1 and Fig. 2). The ribbons are packed to form corrugated layers (Fig. 3) inclined to the *ac* plane by approximately 22°.

Synthesis and crystallization

A flask containing a stirring bar was charged with 5-bromo-3,4,6-trimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (100 mg, 0.31 mmol), 3-thiopheneboronic acid (52 mg, 0.35 mmol) and sodium bicarbonate (1.5 equiv, 0.47 mmol) in a mixture of toluene/ethanol (2/1 *v*/*v*). $Pd(PPh_3)_4$ (0.05 equiv, 0.018 mmol)

was added and the mixture was refluxed for 12 h. After cooling, solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel (90:10 petroleum ether/ethyl acetate). The title compound was recrystallized from ethanol, at room temperature, giving colourless crystals (yield: 74%; m.p. 434–436 K).

Refinement

Crystal and refinement details are presented in Table 2. The thiophenyl group is rotationally disordered over two sites 180° apart in a 0.606 (2)/0.394 (2) ratio. The two components of the disorder were refined as idealized rigid groups.

Funding information

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full crystallographic data

IUCrData (2018). **3**, x181593 [https://doi.org/10.1107/S2414314618015936]

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Crystal data

$C_{19}H_{17}N_3S$
M_r = 319.41
Triclinic, $P\overline{1}$
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c = 11.4101 (4) Å
α = 82.548 (1)°
β = 78.176 (2)°
γ = 76.607 (2)°
V = 822.39 (6) Å^3
Z = 2
$F(000)$ = 336
D_x = 1.290 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 5350 reflections
θ = 4.0–72.2°
μ = 1.75 mm^{-1}
T = 150 K
Column, colourless
0.43 × 0.17 × 0.16 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.63, T_{max} = 0.77
6351 measured reflections
3048 independent reflections
2722 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 72.2°, θ_{min} = 4.0°
h = −8→9
k = −11→11
l = −14→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.117
S = 1.03
3048 reflections
262 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2279P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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. The thiophenyl group is rotationally disordered over two sites 180° apart. The two components of the disorder were refined as idealized rigid groups with riding hydrogens.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.76462 (17)	0.22090 (13)	0.55436 (11)	0.0343 (3)	
N2	0.61196 (17)	0.34682 (13)	0.72855 (11)	0.0318 (3)	
N3	0.44124 (17)	0.42717 (13)	0.76695 (11)	0.0329 (3)	
C1	0.4452 (2)	0.34579 (14)	0.58985 (12)	0.0304 (3)	
C2	0.4127 (2)	0.30555 (15)	0.48398 (13)	0.0321 (3)	
C3	0.5603 (2)	0.22109 (15)	0.41634 (13)	0.0330 (3)	
C4	0.7329 (2)	0.18473 (15)	0.45272 (13)	0.0345 (3)	
C5	0.6183 (2)	0.29736 (15)	0.62018 (13)	0.0308 (3)	
C6	0.3413 (2)	0.42794 (15)	0.68545 (13)	0.0319 (3)	
C7	0.2296 (2)	0.3506 (2)	0.44751 (15)	0.0402 (4)	
H7A	0.234 (3)	0.329 (2)	0.368 (2)	0.063 (6)*	
H7B	0.138 (3)	0.312 (2)	0.505 (2)	0.063 (6)*	
H7C	0.185 (3)	0.450 (3)	0.445 (2)	0.066 (7)*	
C8	0.5523 (7)	0.1636 (3)	0.30143 (14)	0.0277 (8)	0.606 (2)
C9	0.5743 (8)	0.2332 (3)	0.18973 (18)	0.0423 (8)	0.606 (2)
H9	0.610994	0.319952	0.171281	0.051*	0.606 (2)
S1	0.52573 (14)	0.14045 (9)	0.08737 (6)	0.0471 (3)	0.606 (2)
C10	0.4936 (5)	0.0382 (3)	0.30243 (10)	0.0463 (10)	0.606 (2)
H10	0.471090	−0.021735	0.373322	0.056*	0.606 (2)
C11	0.4724 (5)	0.0112 (2)	0.19456 (14)	0.0581 (5)	0.606 (2)
H11	0.433455	−0.068226	0.179727	0.070*	0.606 (2)
C8A	0.5135 (13)	0.1704 (6)	0.3104 (3)	0.0277 (8)	0.394 (2)
C9A	0.4500 (8)	0.0520 (4)	0.31229 (13)	0.0423 (8)	0.394 (2)
H9A	0.410352	−0.003177	0.382854	0.051*	0.394 (2)
S1A	0.4527 (3)	0.01780 (16)	0.16774 (12)	0.0581 (5)	0.394 (2)
C10A	0.5659 (13)	0.2295 (6)	0.1924 (4)	0.0463 (10)	0.394 (2)
H10A	0.613757	0.311623	0.175878	0.056*	0.394 (2)
C11A	0.5421 (9)	0.1596 (4)	0.1058 (2)	0.0471 (3)	0.394 (2)
H11A	0.570836	0.185035	0.022056	0.056*	0.394 (2)
C12	0.8937 (3)	0.0994 (2)	0.37643 (16)	0.0462 (4)	
H12A	0.879 (4)	0.005 (3)	0.387 (2)	0.071 (7)*	
H12B	0.907 (3)	0.133 (3)	0.292 (2)	0.068 (7)*	
H12C	1.006 (3)	0.094 (2)	0.407 (2)	0.060 (6)*	
C13	0.1498 (2)	0.50792 (18)	0.69981 (15)	0.0380 (4)	

H13A	0.063 (3)	0.449 (2)	0.7058 (19)	0.055 (6)*
H13B	0.132 (3)	0.577 (2)	0.6308 (19)	0.050 (5)*
H13C	0.121 (3)	0.562 (2)	0.770 (2)	0.058 (6)*
C14	0.7449 (2)	0.32305 (16)	0.80297 (13)	0.0337 (3)
C15	0.8874 (2)	0.20766 (19)	0.79334 (15)	0.0433 (4)
H15	0.899 (3)	0.142 (2)	0.7341 (19)	0.049 (5)*
C16	1.0143 (3)	0.1856 (2)	0.86897 (18)	0.0530 (5)
H16	1.113 (3)	0.099 (2)	0.866 (2)	0.062 (6)*
C17	0.9990 (3)	0.2778 (2)	0.95380 (16)	0.0515 (4)
H17	1.087 (3)	0.263 (2)	1.007 (2)	0.057 (6)*
C18	0.8557 (2)	0.3923 (2)	0.96290 (14)	0.0445 (4)
H18	0.836 (3)	0.456 (2)	1.023 (2)	0.056 (6)*
C19	0.7284 (2)	0.41651 (17)	0.88843 (13)	0.0371 (3)
H19	0.625 (3)	0.4989 (19)	0.8953 (16)	0.038 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0383 (7)	0.0391 (7)	0.0284 (6)	−0.0103 (5)	−0.0050 (5)	−0.0118 (5)
N2	0.0338 (6)	0.0375 (6)	0.0280 (6)	−0.0104 (5)	−0.0055 (5)	−0.0123 (5)
N3	0.0356 (7)	0.0367 (6)	0.0296 (6)	−0.0114 (5)	−0.0046 (5)	−0.0107 (5)
C1	0.0359 (7)	0.0334 (7)	0.0258 (7)	−0.0136 (6)	−0.0044 (6)	−0.0067 (5)
C2	0.0401 (8)	0.0342 (7)	0.0268 (7)	−0.0157 (6)	−0.0060 (6)	−0.0061 (5)
C3	0.0428 (8)	0.0348 (7)	0.0260 (7)	−0.0149 (6)	−0.0059 (6)	−0.0074 (5)
C4	0.0425 (8)	0.0369 (8)	0.0265 (7)	−0.0112 (6)	−0.0040 (6)	−0.0098 (6)
C5	0.0374 (7)	0.0338 (7)	0.0256 (7)	−0.0143 (6)	−0.0043 (6)	−0.0081 (5)
C6	0.0369 (8)	0.0352 (7)	0.0276 (7)	−0.0140 (6)	−0.0045 (6)	−0.0080 (5)
C7	0.0410 (9)	0.0523 (10)	0.0328 (8)	−0.0129 (7)	−0.0103 (7)	−0.0122 (7)
C8	0.022 (2)	0.0366 (8)	0.0257 (7)	−0.0083 (10)	0.0019 (10)	−0.0121 (6)
C9	0.0608 (18)	0.0439 (18)	0.0282 (16)	−0.0170 (13)	−0.0100 (12)	−0.0112 (14)
S1	0.0692 (5)	0.0549 (5)	0.0266 (4)	−0.0235 (3)	−0.0131 (3)	−0.0123 (3)
C10	0.064 (2)	0.051 (2)	0.0330 (18)	−0.0355 (16)	0.0003 (13)	−0.0078 (14)
C11	0.0854 (8)	0.0653 (7)	0.0400 (8)	−0.0407 (6)	−0.0121 (6)	−0.0181 (5)
C8A	0.022 (2)	0.0366 (8)	0.0257 (7)	−0.0083 (10)	0.0019 (10)	−0.0121 (6)
C9A	0.0608 (18)	0.0439 (18)	0.0282 (16)	−0.0170 (13)	−0.0100 (12)	−0.0112 (14)
S1A	0.0854 (8)	0.0653 (7)	0.0400 (8)	−0.0407 (6)	−0.0121 (6)	−0.0181 (5)
C10A	0.064 (2)	0.051 (2)	0.0330 (18)	−0.0355 (16)	0.0003 (13)	−0.0078 (14)
C11A	0.0692 (5)	0.0549 (5)	0.0266 (4)	−0.0235 (3)	−0.0131 (3)	−0.0123 (3)
C12	0.0486 (10)	0.0536 (11)	0.0366 (9)	−0.0026 (8)	−0.0070 (7)	−0.0201 (8)
C13	0.0373 (8)	0.0458 (9)	0.0324 (8)	−0.0081 (7)	−0.0055 (6)	−0.0115 (7)
C14	0.0355 (8)	0.0441 (8)	0.0263 (7)	−0.0159 (6)	−0.0048 (6)	−0.0081 (6)
C15	0.0456 (9)	0.0492 (9)	0.0391 (9)	−0.0077 (7)	−0.0131 (7)	−0.0143 (7)
C16	0.0488 (10)	0.0629 (12)	0.0500 (10)	−0.0037 (8)	−0.0190 (8)	−0.0129 (8)
C17	0.0500 (10)	0.0740 (12)	0.0384 (9)	−0.0185 (9)	−0.0182 (8)	−0.0073 (8)
C18	0.0490 (10)	0.0636 (11)	0.0296 (8)	−0.0248 (8)	−0.0067 (7)	−0.0132 (7)
C19	0.0405 (8)	0.0475 (9)	0.0282 (7)	−0.0167 (7)	−0.0040 (6)	−0.0109 (6)

Geometric parameters (Å, º)

N1—C4	1.3403 (18)	C11—H11	0.9500
N1—C5	1.3438 (19)	C8A—C9A	1.3662
N2—C5	1.3760 (17)	C8A—C10A	1.4147
N2—N3	1.3827 (17)	C9A—S1A	1.7217
N2—C14	1.4170 (18)	C9A—H9A	0.9500
N3—C6	1.3189 (18)	S1A—C11A	1.7128
C1—C5	1.401 (2)	C10A—C11A	1.3415
C1—C2	1.4050 (19)	C10A—H10A	0.9500
C1—C6	1.4356 (19)	C11A—H11A	0.9500
C2—C3	1.396 (2)	C12—H12A	0.95 (3)
C2—C7	1.499 (2)	C12—H12B	0.97 (3)
C3—C4	1.421 (2)	C12—H12C	0.98 (2)
C3—C8A	1.504 (2)	C13—H13A	0.97 (2)
C3—C8	1.5133 (16)	C13—H13B	0.98 (2)
C4—C12	1.504 (2)	C13—H13C	0.98 (2)
C6—C13	1.486 (2)	C14—C15	1.385 (2)
C7—H7A	0.95 (2)	C14—C19	1.398 (2)
C7—H7B	0.97 (3)	C15—C16	1.392 (2)
C7—H7C	0.96 (3)	C15—H15	0.98 (2)
C8—C9	1.3662	C16—C17	1.386 (3)
C8—C10	1.4147	C16—H16	1.00 (2)
C9—S1	1.7216	C17—C18	1.382 (3)
C9—H9	0.9500	C17—H17	0.97 (2)
S1—C11	1.7128	C18—C19	1.382 (2)
C10—C11	1.3415	C18—H18	0.96 (2)
C10—H10	0.9500	C19—H19	0.994 (18)
C4—N1—C5	114.22 (13)	C9A—C8A—C10A	112.6
C5—N2—N3	110.22 (11)	C9A—C8A—C3	125.5 (3)
C5—N2—C14	130.64 (13)	C10A—C8A—C3	120.8 (3)
N3—N2—C14	119.08 (11)	C8A—C9A—S1A	109.9
C6—N3—N2	107.32 (11)	C8A—C9A—H9A	125.1
C5—C1—C2	118.55 (13)	S1A—C9A—H9A	125.1
C5—C1—C6	105.07 (12)	C11A—S1A—C9A	92.9
C2—C1—C6	136.37 (14)	C11A—C10A—C8A	114.2
C3—C2—C1	115.97 (13)	C11A—C10A—H10A	122.9
C3—C2—C7	122.59 (13)	C8A—C10A—H10A	122.9
C1—C2—C7	121.44 (13)	C10A—C11A—S1A	110.4
C2—C3—C4	120.47 (13)	C10A—C11A—H11A	124.8
C2—C3—C8A	113.7 (4)	S1A—C11A—H11A	124.8
C4—C3—C8A	125.8 (4)	C4—C12—H12A	108.1 (15)
C2—C3—C8	124.2 (2)	C4—C12—H12B	112.5 (14)
C4—C3—C8	115.3 (2)	H12A—C12—H12B	111 (2)
N1—C4—C3	123.97 (13)	C4—C12—H12C	110.9 (13)
N1—C4—C12	115.76 (14)	H12A—C12—H12C	103 (2)
C3—C4—C12	120.27 (13)	H12B—C12—H12C	111.0 (19)

N1—C5—N2	126.35 (13)	C6—C13—H13A	112.5 (12)
N1—C5—C1	126.65 (13)	C6—C13—H13B	110.9 (12)
N2—C5—C1	106.97 (12)	H13A—C13—H13B	107.0 (17)
N3—C6—C1	110.41 (13)	C6—C13—H13C	110.2 (13)
N3—C6—C13	120.49 (13)	H13A—C13—H13C	110.6 (18)
C1—C6—C13	129.09 (13)	H13B—C13—H13C	105.5 (17)
C2—C7—H7A	111.4 (14)	C15—C14—C19	120.19 (14)
C2—C7—H7B	111.1 (14)	C15—C14—N2	120.79 (13)
H7A—C7—H7B	112 (2)	C19—C14—N2	119.01 (14)
C2—C7—H7C	112.7 (15)	C14—C15—C16	119.59 (15)
H7A—C7—H7C	104 (2)	C14—C15—H15	120.4 (12)
H7B—C7—H7C	105 (2)	C16—C15—H15	120.0 (12)
C9—C8—C10	112.6	C17—C16—C15	120.55 (18)
C9—C8—C3	124.92 (17)	C17—C16—H16	119.6 (13)
C10—C8—C3	121.82 (18)	C15—C16—H16	119.7 (13)
C8—C9—S1	109.9	C18—C17—C16	119.31 (16)
C8—C9—H9	125.1	C18—C17—H17	119.8 (12)
S1—C9—H9	125.1	C16—C17—H17	120.9 (12)
C11—S1—C9	92.9	C19—C18—C17	121.11 (15)
C11—C10—C8	114.2	C19—C18—H18	116.5 (13)
C11—C10—H10	122.9	C17—C18—H18	122.3 (13)
C8—C10—H10	122.9	C18—C19—C14	119.25 (16)
C10—C11—S1	110.4	C18—C19—H19	120.9 (11)
C10—C11—H11	124.8	C14—C19—H19	119.9 (11)
S1—C11—H11	124.8		

C5—N2—N3—C6	0.41 (16)	C2—C1—C6—C13	−2.9 (3)
C14—N2—N3—C6	−177.05 (12)	C2—C3—C8—C9	84.6 (2)
C5—C1—C2—C3	−1.1 (2)	C4—C3—C8—C9	−94.6 (2)
C6—C1—C2—C3	−179.68 (16)	C2—C3—C8—C10	−85.7 (4)
C5—C1—C2—C7	178.51 (14)	C4—C3—C8—C10	95.0 (4)
C6—C1—C2—C7	−0.1 (3)	C10—C8—C9—S1	−1.1
C1—C2—C3—C4	−2.4 (2)	C3—C8—C9—S1	−172.2 (4)
C7—C2—C3—C4	178.02 (15)	C8—C9—S1—C11	1.0
C1—C2—C3—C8A	174.6 (2)	C9—C8—C10—C11	0.5
C7—C2—C3—C8A	−4.9 (3)	C3—C8—C10—C11	171.9 (4)
C1—C2—C3—C8	178.37 (17)	C8—C10—C11—S1	0.3
C7—C2—C3—C8	−1.2 (3)	C9—S1—C11—C10	−0.7
C5—N1—C4—C3	−0.8 (2)	C2—C3—C8A—C9A	−88.1 (6)
C5—N1—C4—C12	179.82 (14)	C4—C3—C8A—C9A	88.7 (6)
C2—C3—C4—N1	3.6 (2)	C2—C3—C8A—C10A	104.4 (4)
C8A—C3—C4—N1	−173.1 (2)	C4—C3—C8A—C10A	−78.8 (4)
C8—C3—C4—N1	−177.12 (17)	C10A—C8A—C9A—S1A	−1.1
C2—C3—C4—C12	−177.07 (15)	C3—C8A—C9A—S1A	−169.5 (7)
C8A—C3—C4—C12	6.3 (3)	C8A—C9A—S1A—C11A	1.0
C8—C3—C4—C12	2.2 (2)	C9A—C8A—C10A—C11A	0.5
C4—N1—C5—N2	179.18 (14)	C3—C8A—C10A—C11A	169.5 (7)
C4—N1—C5—C1	−3.1 (2)	C8A—C10A—C11A—S1A	0.3

N3—N2—C5—N1	177.01 (14)	C9A—S1A—C11A—C10A	−0.7
C14—N2—C5—N1	−5.9 (2)	C5—N2—C14—C15	−20.9 (2)
N3—N2—C5—C1	−1.05 (16)	N3—N2—C14—C15	155.93 (15)
C14—N2—C5—C1	176.02 (14)	C5—N2—C14—C19	160.39 (15)
C2—C1—C5—N1	4.2 (2)	N3—N2—C14—C19	−22.8 (2)
C6—C1—C5—N1	−176.83 (14)	C19—C14—C15—C16	−0.2 (3)
C2—C1—C5—N2	−177.77 (12)	N2—C14—C15—C16	−178.91 (16)
C6—C1—C5—N2	1.23 (16)	C14—C15—C16—C17	0.2 (3)
N2—N3—C6—C1	0.40 (16)	C15—C16—C17—C18	0.1 (3)
N2—N3—C6—C13	−179.02 (13)	C16—C17—C18—C19	−0.4 (3)
C5—C1—C6—N3	−1.03 (16)	C17—C18—C19—C14	0.3 (3)
C2—C1—C6—N3	177.70 (16)	C15—C14—C19—C18	0.0 (2)
C5—C1—C6—C13	178.33 (15)	N2—C14—C19—C18	178.71 (14)

Hydrogen-bond geometry (Å, º)

Cg4 and Cg5 are the centroids of the N1/C1–C5 and C14–C19 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···*Cg*4^{i}	0.95	2.63	3.491 (3)	151
C13—H13*A*···*Cg*5^{ii}	0.97 (2)	2.70 (2)	3.4771 (18)	138.1 (16)
C15—H15···N1	0.98 (2)	2.44 (2)	3.040 (2)	119.2 (15)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) *x*−1, *y*, *z*.