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Crystal structure of 1,5-diethyl-3′,5′-diphenyl-1,5-dihydro-3′*H*-spiro[pyrazolo[3,4-*d*]pyrimidine-4,2′-[1,3,4]thiadiazole]

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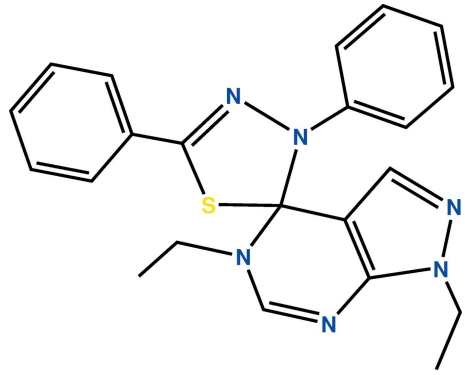
In the title compound, $C_{22}H_{22}N_6S$, the pyrazolo[3,4-*d*]pyrimi-]pyrimidine rings system is almost planar, with the r.m.s. deviation for the fitted atoms being 0.011 Å. The two phenyl groups linked to the thiadiazole ring are nearly perpendicular to the fused-ring system as indicated by the dihedral angles of 86.93 (10) and 83.35 (11)°. However, the phenyl rings are almost coplanar with the thiadiazole ring (r.m.s. deviation = 0.015 Å), forming dihedral angles of 10.44 (11) and 10.06 (12)°. In the crystal, molecules are connected into a supramolecular layer in the *ac* plane *via* C—H···π interactions.

Keywords: crystal structure; pyrazolo[3,4-*d*]pyrimidine; thiadiazole.

CCDC reference: 1425539

1. Related literature

For biological properties of pyrazolo[3,4-*d*]pyrimidine derivatives, see: Chern *et al.* (2004); Schenone *et al.* (2009); Dinér *et al.* (2012); Taliani *et al.* (2010); Trivedi *et al.* (2012). For related structures, see: El Fal *et al.* (2014, 2015); Ahoya *et al.* (2011); Anothane *et al.* (2012).



2. Experimental

2.1. Crystal data

$C_{22}H_{22}N_6S$
M_r = 402.51
Orthorhombic, *Pbca*
a = 14.501 (5) Å
b = 22.898 (5) Å
c = 12.468 (4) Å
V = 4140 (2) Å^3
Z = 8
Mo *K*α radiation
μ = 0.18 mm^{-1}
T = 296 K
0.37 × 0.34 × 0.29 mm

2.2. Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.589, T_{max} = 0.746
25025 measured reflections
4224 independent reflections
2566 reflections with $I > 2\sigma(I)$
R_{int} = 0.079

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.138
S = 1.00
4224 reflections
262 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

*Cg*1 and *Cg*2 are the centroids of the C17–C22 and C11–C16 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···*Cg*1^{i}	0.93	2.75	3.615 (3)	155
C20—H20···*Cg*2^{ii}	0.93	2.77	3.564 (4)	144

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT-Plus* (Bruker, 2009); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2013*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5387).

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Acta Cryst. (2015). E**71**, o769–o770 [doi:10.1107/S2056989015017405]

Crystal structure of 1,5-diethyl-3′,5′-diphenyl-1,5-dihydro-3′*H*-spiro[pyrazolo-[3,4-*d*]pyrimidine-4,2′-[1,3,4]thiadiazole]

Mohammed El Fal, Youssef Ramli, El Mokhtar Essassi, Mohamed Saadi and Lahcen El Ammari

S1. Comment

The pyrazolo[3,4-*d*]pyrimidine nucleus is considered as a very interesting and versatile scaffold for the synthesis of potential drug candidates acting on a wide range of biological targets (Schenone *et al.*, 2009). Among their many applications, they have been used as kinase inhibitors (Dinér *et al.*, 2012), antiviral agents (Chern *et al.*, 2004), adenosine antagonists (Taliani *et al.*, 2010 and as antitubercular agents (Trivedi *et al.*, 2012). In the search for new compounds with therapeutic interest, we have prepared spiro[pyrazolo[3,4-*d*]pyrimidine-1,2′-[1,3,4]thiadiazole] derivatives *via* 1,3-dipolar cycloaddition using diphenyl hydrazonoyl chloride as the precursor for diphenyl nitrilimine, and 1,5-diethyl-1*H*-pyrazolo [3,4-*d*]pyrimidin-4(5*H*)-thione as the dipolarophile (El Fal *et al.*, 2014; El Fal *et al.*, 2015; Ahoya *et al.*, 2011, Anothane *et al.*, 2012).

The molecule of the title compound is built up from two fused five- and six-membered heterocycles linked to two ethyls and to two phenyl rings *via* the thiadiazole ring as shown in Fig. 1. The pyrazolo[3,4-*d*]pyrimidine system is virtually planar with the largest deviation from the mean plane being 0.016 (2) Å at N3 and makes dihedral angles of 86.93 (10) and 83.35 (11)° with the mean plane through the first (C11 to C16) and the second (C17 to C22) phenyl rings, respectively. Furthermore, the two phenyl rings are virtually coplanar with the largest deviation from the mean plane of -0.069 (2) Å, and makes a dihedral angle of 9.88 (9)° with the thiadiazole ring. No classic hydrogen bonds are observed in the structure.

S2. Experimental

To a solution of 1,5-diethyl-1*H*-pyrazolo [3,4-*d*] pyrimidin-4(5*H*)–thione (2.08 g, 10 mmol) and diphenyl hydrazonoyl chloride (3.00 g, 13 mmol) in THF (30 ml) was added triethylamine (2 ml). The mixture was refluxed for 24 h. The precipitate was collected by filtration and was separated by silica gel chromatography (hexane/ethyl acetate: 8/2). The solid obtained was recrystallized from ethanol to afford the title compound as yellow crystals (yield: 60%; m.p. = 468 K).

S3. Refinement

The H atoms were located in a difference map and treated as riding with C—H = 0.93 Å (aromatic), C—H = 0.97 Å (methylene) and C—H = 0.96 Å (methyl). All hydrogen with U_{iso}(H) = 1.2 U_{eq}(aromatic and methylene) and U_{iso}(H) = 1.5 U_{eq}(methyl). The reflection (0 2 0) was affected by beamstop and was removed from the refinement.

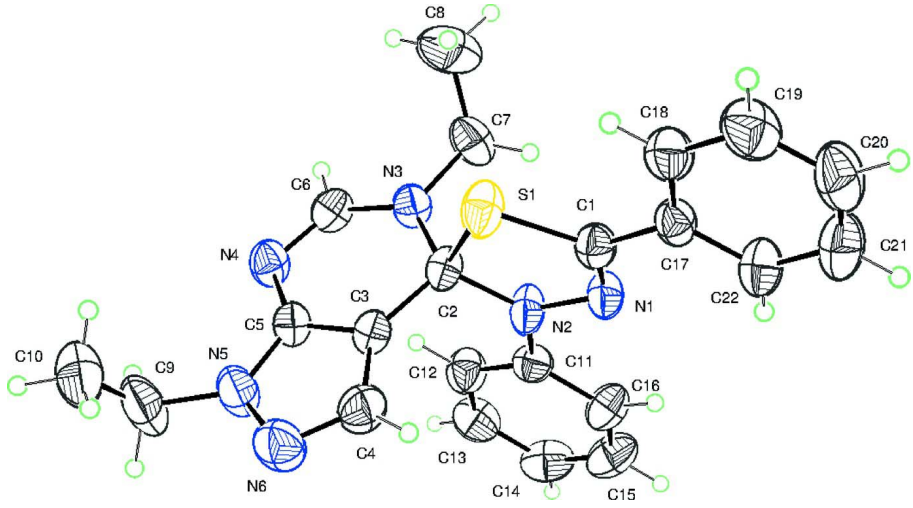

Figure 1

Molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles.

1,5-Diethyl-3′,5′-diphenyl-1,5-dihydro-3′*H*-spiro[pyrazolo[3,4-*d*]pyrimidine-4,2′-[1,3,4]thiadiazole]

Crystal data

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Orthorhombic, *Pbca*
$a = 14.501$ (5) Å
$b = 22.898$ (5) Å
$c = 12.468$ (4) Å
$V = 4140$ (2) Å^3
$Z = 8$
$F(000) = 1696$
$D_x = 1.292$ Mg m^{-3}
Melting point: 468 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4224 reflections
$\theta = 2.3$–$26.4°$
$\mu = 0.18$ mm^{-1}
$T = 296$ K
Block, yellow
0.37 × 0.34 × 0.29 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.589$, $T_{max} = 0.746$
25025 measured reflections
4224 independent reflections
2566 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.3°$
$h = -18 \rightarrow 17$
$k = -24 \rightarrow 28$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.138$
$S = 1.00$
4224 reflections
262 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 0.732P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.48041 (15)	0.16398 (10)	0.52664 (19)	0.0383 (5)
C2	0.54607 (15)	0.07863 (9)	0.63901 (19)	0.0363 (5)
C3	0.49773 (15)	0.04386 (10)	0.72025 (19)	0.0373 (5)
C4	0.41299 (17)	0.04978 (11)	0.7732 (2)	0.0511 (7)
H4	0.3727	0.0809	0.7631	0.061*
C5	0.53365 (15)	−0.00752 (10)	0.75801 (19)	0.0377 (5)
C6	0.65913 (16)	−0.00200 (10)	0.6605 (2)	0.0413 (6)
H6	0.7162	−0.0164	0.6392	0.050*
C7	0.69620 (18)	0.07699 (12)	0.5361 (2)	0.0554 (7)
H7A	0.7560	0.0814	0.5700	0.066*
H7B	0.6733	0.1158	0.5199	0.066*
C8	0.7081 (3)	0.04447 (17)	0.4342 (3)	0.1022 (13)
H8A	0.7498	0.0654	0.3884	0.153*
H8B	0.6495	0.0406	0.3992	0.153*
H8C	0.7327	0.0064	0.4492	0.153*
C9	0.4750 (2)	−0.08616 (13)	0.8837 (3)	0.0726 (9)
H9A	0.4554	−0.0814	0.9576	0.087*
H9B	0.5377	−0.1009	0.8841	0.087*
C10	0.4139 (3)	−0.12911 (14)	0.8295 (3)	0.0962 (13)
H10A	0.4166	−0.1657	0.8668	0.144*
H10B	0.4340	−0.1345	0.7568	0.144*
H10C	0.3517	−0.1148	0.8298	0.144*
C11	0.61067 (15)	0.15818 (10)	0.76316 (19)	0.0383 (6)
C12	0.66082 (17)	0.11905 (11)	0.8257 (2)	0.0478 (6)
H12	0.6632	0.0797	0.8072	0.057*
C13	0.70698 (17)	0.13906 (13)	0.9156 (2)	0.0538 (7)
H13	0.7404	0.1128	0.9571	0.065*
C14	0.70444 (18)	0.19696 (13)	0.9449 (2)	0.0576 (8)
H14	0.7357	0.2099	1.0054	0.069*
C15	0.65481 (18)	0.23514 (13)	0.8829 (2)	0.0577 (8)
H15	0.6524	0.2744	0.9021	0.069*
C16	0.60827 (16)	0.21655 (11)	0.7924 (2)	0.0479 (7)
H16	0.5753	0.2432	0.7512	0.058*
C17	0.43453 (15)	0.20319 (10)	0.4501 (2)	0.0399 (6)
C18	0.39468 (17)	0.18210 (12)	0.3574 (2)	0.0505 (7)
H18	0.3970	0.1423	0.3424	0.061*
C19	0.35137 (19)	0.21958 (14)	0.2866 (2)	0.0623 (8)
H19	0.3252	0.2051	0.2239	0.075*
C20	0.3471 (2)	0.27838 (14)	0.3090 (3)	0.0665 (9)

H20	0.3182	0.3037	0.2614	0.080*
C21	0.38543 (19)	0.29943 (13)	0.4014 (3)	0.0646 (8)
H21	0.3823	0.3392	0.4165	0.077*
C22	0.42870 (18)	0.26235 (11)	0.4724 (2)	0.0527 (7)
H22	0.4540	0.2771	0.5354	0.063*
N1	0.52713 (13)	0.18375 (8)	0.60593 (16)	0.0414 (5)
N2	0.56296 (14)	0.14038 (8)	0.67014 (16)	0.0444 (5)
N3	0.63253 (12)	0.04874 (8)	0.61271 (16)	0.0396 (5)
N4	0.61620 (13)	−0.03289 (9)	0.73112 (17)	0.0430 (5)
N5	0.47290 (14)	−0.02945 (9)	0.82976 (18)	0.0523 (6)
N6	0.39730 (15)	0.00565 (10)	0.8391 (2)	0.0618 (7)
S1	0.47272 (5)	0.08793 (3)	0.51716 (6)	0.0486 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0362 (12)	0.0355 (13)	0.0431 (14)	0.0013 (10)	−0.0001 (11)	0.0032 (11)
C2	0.0380 (12)	0.0283 (12)	0.0425 (14)	0.0008 (10)	−0.0069 (10)	−0.0008 (10)
C3	0.0362 (12)	0.0305 (12)	0.0453 (15)	0.0006 (10)	−0.0020 (10)	−0.0003 (11)
C4	0.0440 (14)	0.0471 (16)	0.0621 (19)	0.0096 (12)	0.0070 (12)	0.0006 (14)
C5	0.0365 (12)	0.0331 (13)	0.0435 (14)	−0.0019 (10)	−0.0020 (10)	0.0033 (11)
C6	0.0332 (12)	0.0411 (14)	0.0496 (15)	0.0055 (11)	−0.0048 (11)	−0.0022 (12)
C7	0.0491 (15)	0.0602 (18)	0.0568 (19)	−0.0083 (13)	0.0078 (12)	0.0152 (15)
C8	0.127 (3)	0.107 (3)	0.073 (3)	−0.015 (2)	0.048 (2)	−0.004 (2)
C9	0.070 (2)	0.066 (2)	0.082 (2)	0.0031 (17)	0.0156 (17)	0.0367 (18)
C10	0.118 (3)	0.054 (2)	0.117 (3)	−0.008 (2)	0.038 (3)	0.014 (2)
C11	0.0373 (12)	0.0403 (14)	0.0372 (14)	−0.0053 (10)	0.0004 (10)	−0.0034 (11)
C12	0.0557 (15)	0.0409 (15)	0.0469 (16)	−0.0021 (13)	−0.0091 (12)	0.0008 (12)
C13	0.0506 (15)	0.068 (2)	0.0425 (16)	−0.0036 (14)	−0.0098 (12)	0.0037 (14)
C14	0.0461 (15)	0.075 (2)	0.0516 (18)	−0.0088 (15)	−0.0046 (12)	−0.0178 (15)
C15	0.0515 (15)	0.0553 (18)	0.066 (2)	−0.0024 (14)	−0.0024 (14)	−0.0238 (15)
C16	0.0451 (14)	0.0396 (15)	0.0591 (18)	0.0003 (11)	−0.0071 (12)	−0.0098 (13)
C17	0.0360 (12)	0.0388 (14)	0.0449 (15)	0.0055 (11)	0.0022 (10)	0.0085 (11)
C18	0.0537 (15)	0.0487 (16)	0.0491 (17)	0.0087 (13)	−0.0019 (13)	0.0070 (13)
C19	0.0596 (17)	0.074 (2)	0.0532 (19)	0.0092 (15)	−0.0122 (14)	0.0101 (16)
C20	0.0640 (18)	0.061 (2)	0.074 (2)	0.0148 (16)	−0.0108 (16)	0.0262 (17)
C21	0.0640 (18)	0.0450 (17)	0.085 (2)	0.0131 (14)	−0.0074 (17)	0.0128 (16)
C22	0.0547 (15)	0.0406 (16)	0.0627 (19)	0.0054 (13)	−0.0086 (13)	0.0080 (13)
N1	0.0478 (11)	0.0308 (11)	0.0457 (12)	0.0023 (9)	−0.0042 (10)	0.0065 (9)
N2	0.0595 (13)	0.0278 (11)	0.0461 (13)	−0.0011 (9)	−0.0168 (10)	0.0046 (9)
N3	0.0373 (10)	0.0369 (11)	0.0446 (12)	−0.0005 (9)	0.0006 (8)	0.0041 (9)
N4	0.0377 (11)	0.0395 (12)	0.0519 (14)	0.0061 (9)	−0.0012 (9)	0.0091 (10)
N5	0.0481 (12)	0.0468 (13)	0.0619 (15)	0.0026 (10)	0.0098 (11)	0.0169 (11)
N6	0.0516 (13)	0.0624 (16)	0.0714 (17)	0.0052 (12)	0.0180 (12)	0.0111 (13)
S1	0.0567 (4)	0.0362 (4)	0.0531 (4)	−0.0001 (3)	−0.0217 (3)	0.0025 (3)

Geometric parameters (Å, º)

C1—N1	1.281 (3)	C10—H10B	0.9600
C1—C17	1.469 (3)	C10—H10C	0.9600
C1—S1	1.749 (2)	C11—C16	1.386 (3)
C2—N3	1.466 (3)	C11—C12	1.393 (3)
C2—C3	1.467 (3)	C11—N2	1.411 (3)
C2—N2	1.487 (3)	C12—C13	1.383 (3)
C2—S1	1.867 (2)	C12—H12	0.9300
C3—C5	1.370 (3)	C13—C14	1.376 (4)
C3—C4	1.401 (3)	C13—H13	0.9300
C4—N6	1.323 (3)	C14—C15	1.371 (4)
C4—H4	0.9300	C14—H14	0.9300
C5—N5	1.352 (3)	C15—C16	1.381 (4)
C5—N4	1.372 (3)	C15—H15	0.9300
C6—N4	1.290 (3)	C16—H16	0.9300
C6—N3	1.361 (3)	C17—C18	1.379 (4)
C6—H6	0.9300	C17—C22	1.386 (3)
C7—N3	1.478 (3)	C18—C19	1.382 (4)
C7—C8	1.482 (4)	C18—H18	0.9300
C7—H7A	0.9700	C19—C20	1.377 (4)
C7—H7B	0.9700	C19—H19	0.9300
C8—H8A	0.9600	C20—C21	1.368 (4)
C8—H8B	0.9600	C20—H20	0.9300
C8—H8C	0.9600	C21—C22	1.378 (4)
C9—N5	1.463 (3)	C21—H21	0.9300
C9—C10	1.486 (5)	C22—H22	0.9300
C9—H9A	0.9700	N1—N2	1.377 (3)
C9—H9B	0.9700	N5—N6	1.364 (3)
C10—H10A	0.9600		
N1—C1—C17	121.6 (2)	C12—C11—N2	122.1 (2)
N1—C1—S1	115.96 (18)	C13—C12—C11	119.6 (2)
C17—C1—S1	122.39 (18)	C13—C12—H12	120.2
N3—C2—C3	108.05 (18)	C11—C12—H12	120.2
N3—C2—N2	111.20 (18)	C14—C13—C12	121.4 (3)
C3—C2—N2	114.5 (2)	C14—C13—H13	119.3
N3—C2—S1	111.02 (16)	C12—C13—H13	119.3
C3—C2—S1	110.59 (15)	C15—C14—C13	118.6 (3)
N2—C2—S1	101.41 (14)	C15—C14—H14	120.7
C5—C3—C4	104.8 (2)	C13—C14—H14	120.7
C5—C3—C2	121.5 (2)	C14—C15—C16	121.3 (3)
C4—C3—C2	133.8 (2)	C14—C15—H15	119.3
N6—C4—C3	111.7 (2)	C16—C15—H15	119.3
N6—C4—H4	124.2	C15—C16—C11	120.0 (3)
C3—C4—H4	124.2	C15—C16—H16	120.0
N5—C5—C3	107.4 (2)	C11—C16—H16	120.0
N5—C5—N4	124.9 (2)	C18—C17—C22	119.0 (2)

C3—C5—N4	127.7 (2)	C18—C17—C1	121.3 (2)
N4—C6—N3	129.0 (2)	C22—C17—C1	119.6 (2)
N4—C6—H6	115.5	C17—C18—C19	120.6 (3)
N3—C6—H6	115.5	C17—C18—H18	119.7
N3—C7—C8	114.0 (2)	C19—C18—H18	119.7
N3—C7—H7A	108.8	C20—C19—C18	119.9 (3)
C8—C7—H7A	108.8	C20—C19—H19	120.1
N3—C7—H7B	108.8	C18—C19—H19	120.1
C8—C7—H7B	108.8	C21—C20—C19	119.8 (3)
H7A—C7—H7B	107.6	C21—C20—H20	120.1
C7—C8—H8A	109.5	C19—C20—H20	120.1
C7—C8—H8B	109.5	C20—C21—C22	120.6 (3)
H8A—C8—H8B	109.5	C20—C21—H21	119.7
C7—C8—H8C	109.5	C22—C21—H21	119.7
H8A—C8—H8C	109.5	C21—C22—C17	120.1 (3)
H8B—C8—H8C	109.5	C21—C22—H22	120.0
N5—C9—C10	111.5 (3)	C17—C22—H22	120.0
N5—C9—H9A	109.3	C1—N1—N2	113.15 (19)
C10—C9—H9A	109.3	N1—N2—C11	117.04 (18)
N5—C9—H9B	109.3	N1—N2—C2	118.15 (18)
C10—C9—H9B	109.3	C11—N2—C2	124.77 (19)
H9A—C9—H9B	108.0	C6—N3—C2	122.90 (19)
C9—C10—H10A	109.5	C6—N3—C7	118.6 (2)
C9—C10—H10B	109.5	C2—N3—C7	118.34 (19)
H10A—C10—H10B	109.5	C6—N4—C5	110.84 (19)
C9—C10—H10C	109.5	C5—N5—N6	111.18 (19)
H10A—C10—H10C	109.5	C5—N5—C9	128.3 (2)
H10B—C10—H10C	109.5	N6—N5—C9	120.0 (2)
C16—C11—C12	119.1 (2)	C4—N6—N5	105.0 (2)
C16—C11—N2	118.9 (2)	C1—S1—C2	91.28 (10)

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the ring centroids of the C17–C22 and C11–C16 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···*Cg*1^{i}	0.93	2.75	3.615 (3)	155
C20—H20···*Cg*2^{ii}	0.93	2.77	3.564 (4)	144

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