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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]

**Mohammed El Fal,ᵃ Youssef Ramli,ᵇ El Mokhtar Essassi,ᵃ\* Mohamed Saadiᶜ and Lahcen El Ammariᶜ**

ᵃLaboratoire de Chimie Organique Hétérocyclique URAC 21, Pôle de Compétence Pharmacochimie, Av. Ibn Battouta, BP 1014, Faculté des Sciences, Université Mohammed V, Rabat, Morocco, ᵇLaboratory of Medicinal Chemistry, Faculty of Medicine and Pharmacy, University Mohammed V, Rabat, Morocco, and ᶜLaboratoire de Chimie du Solide Appliquée, Faculté des Sciences, Université Mohammed V, Avenue Ibn Battouta, BP 1014, Rabat, Morocco. *Correspondence e-mail: em_essassi@yahoo.fr

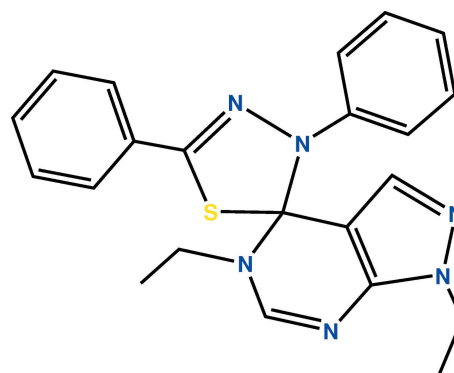In the title compound, $C_{22}H_{22}N_6S$, the pyrazolo[3,4-*d*]pyrimi-]pyrimidine rings system is almost planar, with the r.m.s. deviation for the fitted atoms being 0.011 Å. The two phenyl groups linked to the thiadiazole ring are nearly perpendicular to the fused-ring system as indicated by the dihedral 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.

## 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

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

### 2.2. Data collection

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

### 2.3. Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | 262 parameters |
| $wR(F^2) = 0.138$ | H-atom parameters constrained |
| $S = 1.00$ | $\Delta\rho_{max} = 0.31$ e $Å^{-3}$ |
| 4224 reflections | $\Delta\rho_{min} = -0.30$ 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⋯$Cg1^i$ | 0.93 | 2.75 | 3.615 (3) | 155 |
| C20—H20⋯$Cg2^{ii}$ | 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

# data reports

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# supporting information

# 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).
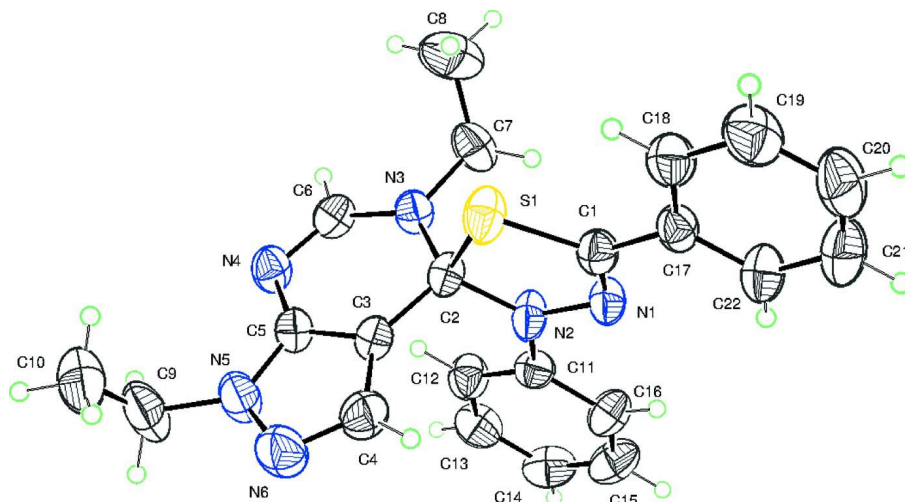
   The molecule of the title compound is built up from two fused five- and six-membered heterocycles linked to two ethyls and to two phenyl rings *via* the thiadiazole ring as shown in Fig. 1. The pyrazolo[3,4-*d*]pyrimidine system is virtually planar with the largest deviation from the mean plane being 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*

| | |
|---|---|
| $C_{22}H_{22}N_6S$ | $D_x = 1.292$ Mg m$^{-3}$ |
| $M_r = 402.51$ | Melting point: 468 K |
| Orthorhombic, *Pbca* | Mo *Kα* radiation, $\lambda = 0.71073$ Å |
| $a = 14.501$ (5) Å | Cell parameters from 4224 reflections |
| $b = 22.898$ (5) Å | $\theta = 2.3–26.4°$ |
| $c = 12.468$ (4) Å | $\mu = 0.18$ mm$^{-1}$ |
| $V = 4140$ (2) Å$^3$ | $T = 296$ K |
| $Z = 8$ | Block, yellow |
| $F(000) = 1696$ | $0.37 \times 0.34 \times 0.29$ mm |

*Data collection*

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

*Refinement*

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

|  | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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.