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1-(3-Fluorophenyl)-4,4,6-trimethyl-3,4-dihydropyrimidine-2(1*H*)-thione

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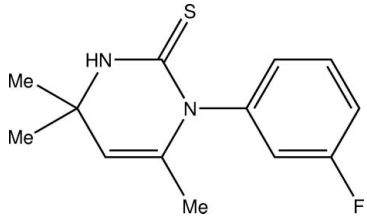
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.059; wR factor = 0.153; data-to-parameter ratio = 15.9.

In the title compound, $C_{13}H_{15}FN_2S$, the dihydropyrimidine ring is essentially planar, with a maximum deviation of 0.086 (3) Å from the mean plane of the rest of the ring for the dimethylated C atom. The benzene ring is almost perpendicular to the dihydropyrimidine ring, with a dihedral angle of 83.97 (14)°. The crystal packing is characterized by centrosymmetric dimers resulting from pairs of intermolecular N—H···S hydrogen bonds. There are also C—H···π interactions.

Related literature

For the biological properties of related compounds, see: Rovnyak *et al.* (1995); Kappe (2000); Alam *et al.* (2005); Sriram *et al.* (2006); Leite *et al.* (2006). For related structures, see: Yamin *et al.* (2005); Ismail *et al.* (2007); Saeed *et al.* (2010); Yamin & Salem (2011). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{13}H_{15}FN_2S$
M_r = 250.33
Monoclinic, $P2_1/c$
a = 8.814 (3) Å
b = 14.997 (5) Å
c = 10.215 (3) Å
β = 95.711 (6)°
V = 1343.6 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.23 mm^{-1}
T = 298 K
0.50 × 0.29 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.892, T_{max} = 0.954
7116 measured reflections
2497 independent reflections
1764 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.153
S = 1.06
2497 reflections
157 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

*Cg*1 is the centroid of the N1/N2/C1–C4 pyrimidine ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*A*···S1^{i}	0.86	2.57	3.400 (3)	162
C9—H9*A*···*Cg*1^{ii}	0.93	2.89	3.788 (4)	163

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LD2016).

References

Alam, O., Imran, M. & Khan, S. A. (2005). *Indian J. Heterocycl. Chem.* **14**, 293–296.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2000). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Ismail, N. L., Othman, E. & Yamin, B. M. (2007). *Acta Cryst.* E**63**, o2442–o2443.
Kappe, C. O. (2000). *Acc. Chem. Res.* **33**, 879–888.
Leite, A. C. L., Lima, R. S., Moreira, D. R. M., Cardoso, M. V. O., Brito, A. C. G., Santos, L. M. F., Hernandes, M. Z., Kiperstok, A. C., Lima, R. S. & Soares, M. B. P. (2006). *Bioorg. Med. Chem.* **14**, 3749–3757.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Rovnyak, G. C., Kimball, S. D., Beyer, B., Cucinotta, G., DiMarco, J. D., Gougoutas, J., Hedberg, A., Malley, M., McCarthy, J. P., Zhang, R. & Moreland, S. (1995). *J. Med. Chem.* **38**, 119–129.
Saeed, A., Khera, R. A. & Parvez, M. (2010). *Acta Cryst.* E**66**, o635.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Sriram, D., Yogeeswari, P. & Devakaram, R. V. (2006). *Bioorg. Med. Chem.* **14**, 3113–3118.
Yamin, B. M., Kasim, N. A. M. & Hamzah, N. (2005). *Acta Cryst.* E**61**, o55–o57.
Yamin, B. M. & Salem, H. F. (2011). *Acta Cryst.* E**67**, o282.

supporting information

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1-(3-Fluorophenyl)-4,4,6-trimethyl-3,4-dihydropyrimidine-2(1*H*)-thione

Bohari M. Yamin, Ruhana L. Lawi and Halima F. Salem

S1. Comment

Pyrimidine-2(1*H*)-ones/thiones are calcium channel blocker compounds (Rovnyak *et al.*, 1995). They also have other biological activities such as antibacterial, antifungal and antiviral (Kappe, 2000; Alam *et al.*, 2005; Sriram *et al.*, 2006; Leite *et al.*, 2006). The 4,4,6-trimethyl-1-aryl-3,4-dihydropyrimidine-2-(1*H*)-thiones open a new series of 3,4-dihydro pyrimidine-2-(1*H*)-thione derivatives following publication of 4,4,6- trimethyl-1-phenyl-3,4-dihydropyrimidine-2-(1*H*)-thione (Yamin *et al.*, 2005; Ismail *et al.*, 2007). The title compound is isomorphous to 4,4,6-trimethyl-1-(3-chloro-phenyl)-3,4-dihydropyrimidine-2-(1*H*)-thione (Yamin & Salem, 2011) and 4,4,6-trimethyl-1-(3-methylphenyl)-3,4-di-hydropyrimidine-2-(1*H*)-thione (Saeed *et al.*, 2010). The dihydropyrimidine (N1,N2,C1—C4) ring is planar with maximum deviation of 0.086 (3)Å for C4 atom from the least square plane. The benzene ring is perpendicular to the di-hydropyrimidine with dihedral angle of 83.97 (14)°, slightly smaller than that in the *meta*- chloro analog (86.62 (13)°). The bond lenghts and angles are in normal ranges (Allen *et al.*, 1987) and are comparable to those in the above mentioned analogs. In the crystal, the molecules are linked by N1—H1A···S1 intermolecular hydrogen bonds (see symmetry code in Table 2) to form centrosymmetric dimers parallel to the *ab* face (Fig 2). There is also a C9—H9A···π interaction involving the pyrimidine (C_g1: N1/N2/(C1—C4)) ring (Table 2).

S2. Experimental

A procedure similar to that used for the preparation of 4,4,6-Trimethyl-1-(3-chlorophenyl)-3,4-dihydro-pyrimidine-2-(1*H*)-thione (Yamin & Salem,2011) was followed. Equimolar quantities of thiocyanic acid and 3-fluoro-aniline (5.4 mmol) in acetone were stirred for 2–3 h. Colourless crystals of 78% yield were obtained after 3 days by evaporation at room temperature. Melting point 456.8–458.9 K.

S3. Refinement

H atoms on the C and N atoms were positioned geometrically with C—H= 0.93 (aromatic and olefinic), 0.96 Å (methyl) and N—H = 0.86 Å respectively, and constrained to ride and rotate (for Me groups) on their parent atoms with U_{iso}=x_{eq}(parent atom) where x=1.2 for N, aromatic C and olefinic C and x=1.5 for methyl C. There is a highest peak and deepest hole of 0.45 from H10 and 0.76Å from F1 atom the respectively.

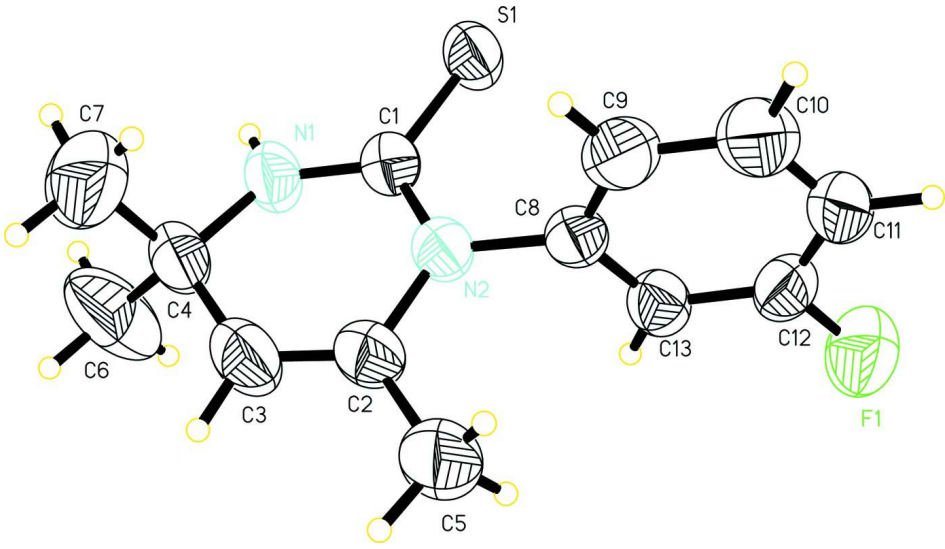

Figure 1

Molecular structure of (1), with the atomic-labelling scheme. Displacement ellipsoid are drawn at the 50% probablity level.

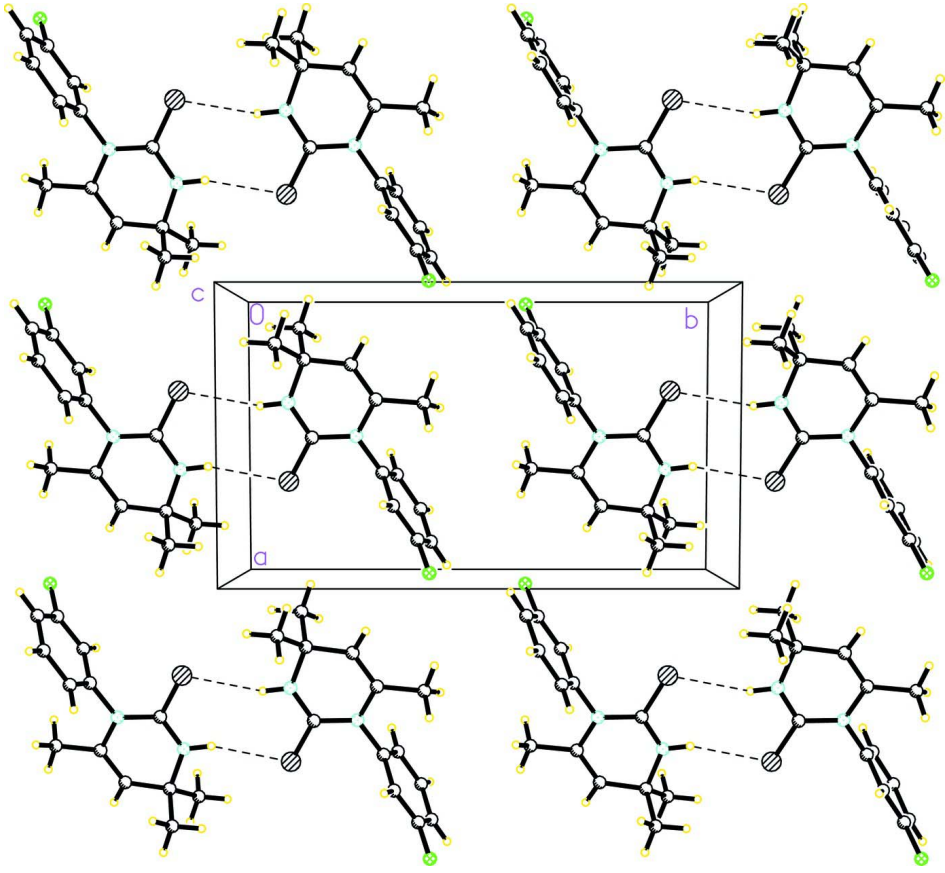

Figure 2

The packing of (1) viewed down the *c* axis. Hydrogen bonds are shown by dashed lines.

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Crystal data

$C_{13}H_{15}FN_2S$
$M_r = 250.33$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.814$ (3) Å
$b = 14.997$ (5) Å
$c = 10.215$ (3) Å
$\beta = 95.711$ (6)°
$V = 1343.6$ (7) Å^3
$Z = 4$
$F(000) = 528$
$D_x = 1.238$ Mg m^{-3}
Melting point = 458.9–456.8 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2497 reflections
$\theta = 2.3$–25.5°
$\mu = 0.23$ mm^{-1}
$T = 298$ K
Block, colourless
0.50 × 0.29 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.892$, $T_{max} = 0.954$
7116 measured reflections
2497 independent reflections
1764 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.3°$
$h = -10 \rightarrow 10$
$k = -16 \rightarrow 18$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.153$
$S = 1.06$
2497 reflections
157 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
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.4935P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ 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 $F^2 > \sigma(F^2)$ 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}
F1	0.9699 (2)	0.40143 (14)	0.6648 (2)	0.0938 (7)
S1	0.65807 (8)	0.11011 (5)	0.47356 (8)	0.0623 (3)
N1	0.3831 (3)	0.11471 (16)	0.5539 (2)	0.0620 (7)
H1A	0.3939	0.0577	0.5561	0.074*

N2	0.4991 (2)	0.25140 (15)	0.5427 (2)	0.0519 (6)
C1	0.5038 (3)	0.1608 (2)	0.5251 (3)	0.0506 (7)
C2	0.3725 (3)	0.2932 (2)	0.5938 (3)	0.0601 (8)
C3	0.2523 (4)	0.2442 (2)	0.6138 (4)	0.0780 (10)
H3A	0.1727	0.2723	0.6507	0.094*
C4	0.2343 (3)	0.1480 (2)	0.5824 (3)	0.0644 (8)
C5	0.3852 (4)	0.3902 (2)	0.6208 (4)	0.0895 (12)
H5A	0.2904	0.4120	0.6471	0.134*
H5B	0.4085	0.4209	0.5428	0.134*
H5C	0.4650	0.4006	0.6902	0.134*
C6	0.1856 (5)	0.0964 (3)	0.6999 (5)	0.1206 (18)
H6A	0.2611	0.1035	0.7736	0.181*
H6B	0.1757	0.0343	0.6777	0.181*
H6C	0.0895	0.1188	0.7222	0.181*
C7	0.1209 (5)	0.1335 (3)	0.4636 (5)	0.1154 (16)
H7A	0.1512	0.1673	0.3908	0.173*
H7B	0.0217	0.1525	0.4832	0.173*
H7C	0.1177	0.0713	0.4412	0.173*
C8	0.6272 (3)	0.30394 (18)	0.5099 (3)	0.0493 (7)
C9	0.6358 (4)	0.3306 (2)	0.3822 (3)	0.0653 (8)
H9A	0.5581	0.3160	0.3174	0.078*
C10	0.7597 (5)	0.3789 (2)	0.3506 (4)	0.0802 (11)
H10A	0.7663	0.3960	0.2638	0.096*
C11	0.8726 (4)	0.4018 (2)	0.4449 (4)	0.0747 (10)
H11A	0.9569	0.4341	0.4238	0.090*
C12	0.8593 (3)	0.3763 (2)	0.5706 (3)	0.0606 (8)
C13	0.7392 (3)	0.32727 (19)	0.6068 (3)	0.0538 (7)
H13A	0.7338	0.3104	0.6938	0.065*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0710 (13)	0.0981 (17)	0.1111 (16)	−0.0189 (11)	0.0028 (12)	−0.0109 (12)
S1	0.0536 (4)	0.0493 (5)	0.0878 (6)	−0.0031 (3)	0.0263 (4)	−0.0071 (4)
N1	0.0512 (14)	0.0491 (15)	0.0893 (18)	−0.0086 (11)	0.0249 (13)	−0.0059 (13)
N2	0.0487 (12)	0.0461 (14)	0.0630 (14)	−0.0021 (11)	0.0151 (11)	−0.0044 (11)
C1	0.0491 (15)	0.0509 (18)	0.0527 (16)	−0.0045 (13)	0.0093 (13)	−0.0007 (13)
C2	0.0531 (17)	0.0572 (19)	0.0717 (19)	0.0065 (14)	0.0151 (15)	−0.0071 (16)
C3	0.0562 (18)	0.072 (2)	0.110 (3)	0.0044 (17)	0.0322 (19)	−0.011 (2)
C4	0.0487 (16)	0.066 (2)	0.082 (2)	−0.0057 (15)	0.0223 (16)	−0.0062 (17)
C5	0.073 (2)	0.063 (2)	0.137 (3)	0.0071 (17)	0.032 (2)	−0.021 (2)
C6	0.125 (4)	0.109 (4)	0.142 (4)	0.007 (3)	0.086 (3)	0.021 (3)
C7	0.071 (3)	0.134 (4)	0.137 (4)	−0.004 (2)	−0.010 (3)	−0.038 (3)
C8	0.0523 (16)	0.0392 (16)	0.0582 (17)	−0.0004 (12)	0.0142 (14)	−0.0044 (13)
C9	0.079 (2)	0.060 (2)	0.0577 (18)	−0.0084 (17)	0.0093 (16)	−0.0043 (15)
C10	0.116 (3)	0.059 (2)	0.071 (2)	−0.019 (2)	0.034 (2)	0.0013 (17)
C11	0.090 (2)	0.053 (2)	0.088 (3)	−0.0223 (17)	0.042 (2)	−0.0133 (18)
C12	0.0552 (17)	0.0483 (18)	0.079 (2)	−0.0063 (14)	0.0102 (16)	−0.0146 (15)

C13	0.0556 (16)	0.0470 (17)	0.0605 (17)	−0.0005 (13)	0.0138 (14)	0.0029 (14)

Geometric parameters (Å, º)

F1—C12	1.353 (3)	C6—H6A	0.9600
S1—C1	1.687 (3)	C6—H6B	0.9600
N1—C1	1.326 (3)	C6—H6C	0.9600
N1—C4	1.460 (4)	C7—H7A	0.9600
N1—H1A	0.8600	C7—H7B	0.9600
N2—C1	1.372 (4)	C7—H7C	0.9600
N2—C2	1.423 (3)	C8—C13	1.372 (4)
N2—C8	1.443 (3)	C8—C9	1.374 (4)
C2—C3	1.321 (4)	C9—C10	1.376 (5)
C2—C5	1.483 (4)	C9—H9A	0.9300
C3—C4	1.483 (5)	C10—C11	1.359 (5)
C3—H3A	0.9300	C10—H10A	0.9300
C4—C7	1.509 (5)	C11—C12	1.356 (5)
C4—C6	1.526 (5)	C11—H11A	0.9300
C5—H5A	0.9600	C12—C13	1.369 (4)
C5—H5B	0.9600	C13—H13A	0.9300
C5—H5C	0.9600		
C1—N1—C4	128.5 (3)	H6A—C6—H6B	109.5
C1—N1—H1A	115.7	C4—C6—H6C	109.5
C4—N1—H1A	115.7	H6A—C6—H6C	109.5
C1—N2—C2	121.3 (2)	H6B—C6—H6C	109.5
C1—N2—C8	118.4 (2)	C4—C7—H7A	109.5
C2—N2—C8	120.3 (2)	C4—C7—H7B	109.5
N1—C1—N2	116.8 (2)	H7A—C7—H7B	109.5
N1—C1—S1	121.6 (2)	C4—C7—H7C	109.5
N2—C1—S1	121.5 (2)	H7A—C7—H7C	109.5
C3—C2—N2	118.8 (3)	H7B—C7—H7C	109.5
C3—C2—C5	124.3 (3)	C13—C8—C9	120.5 (3)
N2—C2—C5	116.9 (3)	C13—C8—N2	119.7 (2)
C2—C3—C4	125.3 (3)	C9—C8—N2	119.8 (3)
C2—C3—H3A	117.4	C8—C9—C10	119.8 (3)
C4—C3—H3A	117.4	C8—C9—H9A	120.1
N1—C4—C3	107.3 (2)	C10—C9—H9A	120.1
N1—C4—C7	109.1 (3)	C11—C10—C9	120.6 (3)
C3—C4—C7	111.3 (3)	C11—C10—H10A	119.7
N1—C4—C6	108.1 (3)	C9—C10—H10A	119.7
C3—C4—C6	110.9 (3)	C12—C11—C10	118.3 (3)
C7—C4—C6	110.1 (3)	C12—C11—H11A	120.9
C2—C5—H5A	109.5	C10—C11—H11A	120.9
C2—C5—H5B	109.5	F1—C12—C11	118.0 (3)
H5A—C5—H5B	109.5	F1—C12—C13	118.7 (3)
C2—C5—H5C	109.5	C11—C12—C13	123.3 (3)
H5A—C5—H5C	109.5	C12—C13—C8	117.5 (3)

H5B—C5—H5C	109.5	C12—C13—H13A	121.2
C4—C6—H6A	109.5	C8—C13—H13A	121.2
C4—C6—H6B	109.5		

C4—N1—C1—N2	10.7 (4)	C2—C3—C4—C7	−107.0 (4)
C4—N1—C1—S1	−171.0 (2)	C2—C3—C4—C6	130.1 (4)
C2—N2—C1—N1	2.1 (4)	C1—N2—C8—C13	−96.2 (3)
C8—N2—C1—N1	−178.8 (2)	C2—N2—C8—C13	82.9 (3)
C2—N2—C1—S1	−176.1 (2)	C1—N2—C8—C9	84.1 (3)
C8—N2—C1—S1	2.9 (3)	C2—N2—C8—C9	−96.8 (3)
C1—N2—C2—C3	−5.8 (4)	C13—C8—C9—C10	1.8 (5)
C8—N2—C2—C3	175.2 (3)	N2—C8—C9—C10	−178.5 (3)
C1—N2—C2—C5	174.3 (3)	C8—C9—C10—C11	−1.1 (5)
C8—N2—C2—C5	−4.7 (4)	C9—C10—C11—C12	−0.4 (5)
N2—C2—C3—C4	−2.6 (5)	C10—C11—C12—F1	−178.1 (3)
C5—C2—C3—C4	177.3 (4)	C10—C11—C12—C13	1.2 (5)
C1—N1—C4—C3	−16.9 (4)	F1—C12—C13—C8	178.9 (2)
C1—N1—C4—C7	103.7 (4)	C11—C12—C13—C8	−0.5 (5)
C1—N1—C4—C6	−136.5 (3)	C9—C8—C13—C12	−1.0 (4)
C2—C3—C4—N1	12.2 (5)	N2—C8—C13—C12	179.3 (2)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the N1/N2/C1–C4 pyrimidine ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···S1^{i}	0.86	2.57	3.400 (3)	162
C9—H9*A*···*Cg*1^{ii}	0.93	2.89	3.788 (4)	163

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