IUCrData

ISSN 2414-3146

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

Aisyah Kadir,[a] Normyzatul Akmal Abd Malek,[b] Hamizah Mohd Zaki,[b]* Siti Aishah Hasbullah[a] and Bohari M. Yamin[a]

[a]School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor D.E., Malaysia, and [b]School of Chemistry, Faculty of Applied Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor D.E., Malaysia. *Correspondence e-mail: hamiz410@salam.uitm.edu.my

Received 25 May 2016
Accepted 21 July 2016

Edited by A. J. Lough, University of Toronto, Canada

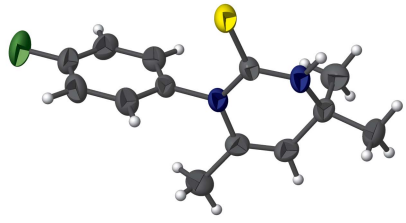
Keywords: crystal structure; 1-(4-fluorophenyl)-4,4,6-trimethyltetrahydropyrimidine-2(1*H*)-thione; tetrahydropyrimidine; twisted; envelope.

CCDC reference: 1495083

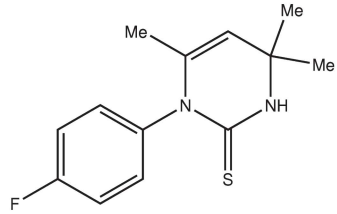
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_{13}H_{15}FN_2S$, the dihydropyrimidine ring is in a flattened boat conformation with deviations of 0.135 (2) and 0.371 (2) Å for the fluorophenyl-substituted N atom and the dimethyl-substituted C atom, respectively, from the four other essentially co-planar atoms. In the crystal, pairs of molecules related by twofold rotation axes are linked by N—H···S hydrogen bonds, forming dimers.

3D view



Chemical scheme



Structure description

The title compound is related to 4,4,6-trimethyl-1-phenyl-3,4- dihydropyrimidne-2-(1*H*)-thione (Yamin *et al.*, 2005; Ismail *et al.*, 2007), and isomeric to (*S*)-1-(3-fluorophenyl)-4,4,6-trimethyltetrahydropyrimidine-2(1*H*)-thione (Yamin *et al.*, 2011) in which the dihydropyrimidine rings are in flattened sofa conformations. The dihydropyrimidine ring (N1/N2/C7–C10) in the title compound (Fig. 1) is in a flattened boat conformation with deviations of 0.135 (2) and 0.371 (2) Å for atoms N1 and C10, respectively, from the mean plane through atoms C7/C8/C9/N2. The benzene (C1–C6) and four planar atoms (C7/C8/C9/N2) of the dihydropyrimidine ring form a dihedral angle of 85.78 (13)°. The bond length and angles are in normal ranges and comparable to those in the above mentioned analogs. In the crystal, pairs of molecules related by twofold rotation axes are linked by N—H···S hydrogen bonds, forming dimers (Table 1 and Fig. 2).

Synthesis and crystallization

A procedure similar to that used for the preparation of 1-(3-fluorophenyl)-4,4,6-trimethyl-3,4-dihydropyrimidine-2(1*H*)-thione (Yamin *et al.*, 2011) was followed. Equi-

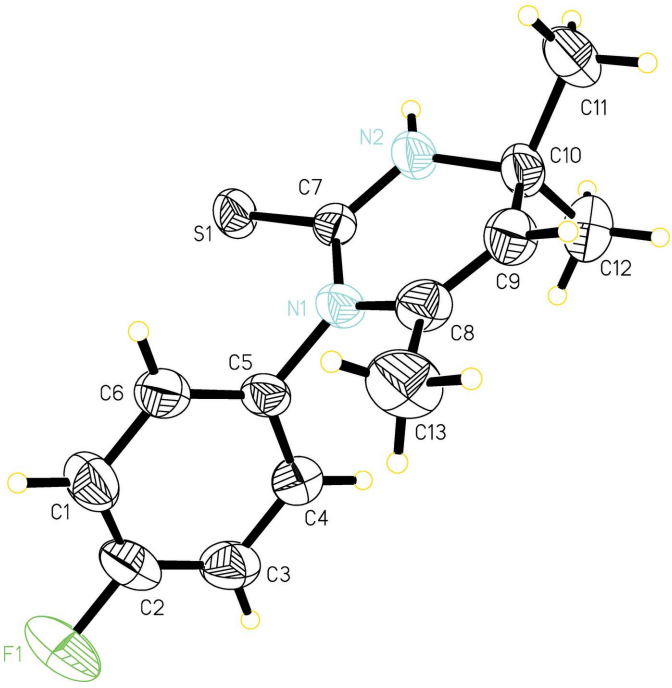


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

molar quantities of thiocyanic acid and 4-fluoro-aniline (5.4 mmol) in acetone were stirred for 2–3 h. Colourless crystals of 78% yield were obtained after three days by evaporation at room temperature. Melting point 456.8–458.9 K. Analysis calculated for $C_{13}H_{15}F_1N_2S_1$: C, 58.53; H, 5.67; N,10.50; S, 12.02%; found: C, 62.32; H, 5.99; F, 7.59; N, 11.19; S, 12.78, IR(KBr), ν (cm^{-1}) 1535 (C═S), 1591 (C═C), 3184 (N—H). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 (6*H*, *s*, $2CH_3$), 1.49 (3*H*, *s*, CH_3), 4.83 (1*H*, *s*, CH), 11.50 (1*H*, *s*, NH), 7.06–7.50 (C_6H_5 ring); $^{13}C\{^1H\}$: δ 20.9 (CH_3), 31.6 ($2CH_3$), 52.4, 112.3, 132.4 ($3C_{quaternary}$), 128–130.1 (C_6H_5 ring) and 177.4 (C═S).

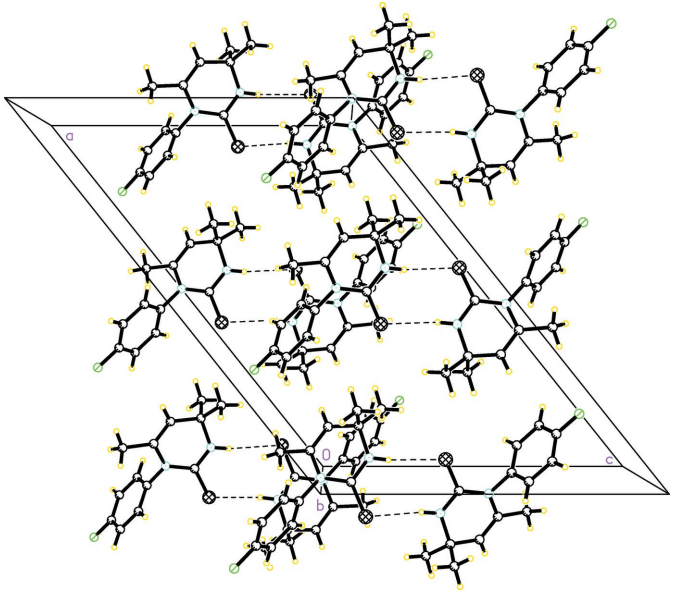


Figure 2
The crystal packing of the title compound viewed along the *b* axis. The dashed lines indicate hydrogen bonds.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H14*A*···S1^{i}	0.86 (2)	2.57 (2)	3.422 (2)	172 (2)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{15}FN_2S$
M_r	250.33
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	303
a, *b*, *c* (Å)	21.231 (3), 10.8714 (14), 14.589 (4)
β (°)	128.524 (3)
V (Å^3)	2634.3 (8)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.24
Crystal size (mm)	0.47 × 0.46 × 0.19
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2000)
T_{min}, T_{max}	0.897, 0.956
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35963, 2452, 2017
R_{int}	0.043
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.039, 0.102, 1.10
No. of reflections	2452
No. of parameters	158
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})	0.21, −0.27

Computer programs: *SMART* and *SAINT* (Bruker, 2000), *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors thank the Ministry of Higher Education of Malaysia and Universiti Kebangsaan Malaysia for the research grant FRGS 1/2015/ST01/UKM/02/2 and Universiti Teknologi MARA FRGS/2/2014/SKK03/UITM/02/1 for the publication.

References

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.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Yamin, B. M., Kasim, N. A. M. & Hamzah, N. (2005). *Acta Cryst.* E**61**, o55–o57.
Yamin, B. M., Lawi, R. L. & Salem, H. F. (2011). *Acta Cryst.* E**67**, o1810.

full crystallographic data

IUCrData (2016). **1**, x161189 [https://doi.org/10.1107/S2414314616011895]

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

Aisyah Kadir, Normyzatul Akmal Abd Malek, Hamizah Mohd Zaki, Siti Aishah Hasbullah and Bohari M. Yamin

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

Crystal data

$C_{13}H_{15}FN_2S$
M_r = 250.33
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 21.231 (3) Å
b = 10.8714 (14) Å
c = 14.589 (4) Å
β = 128.524 (3)°
V = 2634.3 (8) Å^3
Z = 8
F(000) = 1056
D_x = 1.262 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 9935 reflections
θ = 3.3–28.1°
μ = 0.24 mm^{-1}
T = 303 K
Block, colourless
0.47 × 0.46 × 0.19 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 83.66 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.897, T_{max} = 0.956
35963 measured reflections
2452 independent reflections
2017 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.5°, θ_{min} = 3.3°
h = −25→25
k = −13→13
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.102
S = 1.10
2452 reflections
158 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 2.1835P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.07442 (3)	0.80412 (5)	0.43577 (4)	0.04451 (17)
N1	−0.02089 (8)	0.72028 (14)	0.48345 (12)	0.0373 (3)
N2	−0.07352 (8)	0.71633 (15)	0.29028 (12)	0.0420 (4)
F1	0.19803 (9)	0.90181 (15)	0.93207 (11)	0.0869 (5)
C1	0.16002 (12)	0.7460 (2)	0.79555 (16)	0.0543 (5)
H1A	0.2064	0.7022	0.8522	0.065*
C2	0.14420 (13)	0.8571 (2)	0.82123 (16)	0.0531 (5)
C3	0.07749 (13)	0.92469 (19)	0.74188 (18)	0.0528 (5)
H3A	0.0686	0.9998	0.7627	0.063*
C4	0.02300 (11)	0.87899 (18)	0.62920 (16)	0.0447 (4)
H4A	−0.0231	0.9235	0.5730	0.054*
C5	0.03739 (10)	0.76731 (16)	0.60068 (14)	0.0364 (4)
C6	0.10517 (12)	0.70054 (18)	0.68297 (16)	0.0467 (5)
H6A	0.1142	0.6250	0.6631	0.056*
C7	−0.01163 (10)	0.74492 (16)	0.40060 (14)	0.0338 (4)
C8	−0.08797 (11)	0.65017 (17)	0.45490 (16)	0.0431 (4)
C9	−0.15077 (11)	0.63413 (18)	0.34358 (16)	0.0455 (4)
H9A	−0.1926	0.5838	0.3253	0.055*
C10	−0.15696 (10)	0.69430 (17)	0.24567 (15)	0.0414 (4)
C11	−0.19692 (13)	0.6099 (2)	0.13948 (17)	0.0592 (6)
H11A	−0.1681	0.5335	0.1627	0.089*
H11B	−0.1963	0.6486	0.0809	0.089*
H11C	−0.2516	0.5945	0.1080	0.089*
C12	−0.20189 (12)	0.8167 (2)	0.2106 (2)	0.0599 (6)
H12A	−0.1762	0.8688	0.2782	0.090*
H12B	−0.2566	0.8020	0.1791	0.090*
H12C	−0.2011	0.8560	0.1524	0.090*
C13	−0.07976 (15)	0.5930 (2)	0.55542 (19)	0.0670 (7)
H13A	−0.1280	0.5485	0.5262	0.100*
H13B	−0.0713	0.6563	0.6079	0.100*
H13C	−0.0347	0.5376	0.5964	0.100*
H14A	−0.0688 (12)	0.7351 (19)	0.2377 (14)	0.052 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0318 (2)	0.0689 (3)	0.0334 (3)	−0.0048 (2)	0.0206 (2)	−0.0011 (2)
N1	0.0375 (8)	0.0477 (9)	0.0288 (7)	−0.0032 (6)	0.0216 (6)	−0.0019 (6)
N2	0.0330 (8)	0.0655 (10)	0.0288 (7)	−0.0041 (7)	0.0199 (7)	−0.0017 (7)
F1	0.0906 (10)	0.0940 (11)	0.0403 (7)	−0.0210 (8)	0.0233 (7)	−0.0230 (7)
C1	0.0508 (12)	0.0621 (13)	0.0353 (10)	0.0047 (10)	0.0197 (9)	0.0064 (9)
C2	0.0574 (12)	0.0620 (13)	0.0343 (10)	−0.0166 (10)	0.0257 (10)	−0.0112 (9)
C3	0.0612 (13)	0.0486 (11)	0.0534 (12)	−0.0070 (10)	0.0381 (11)	−0.0144 (9)
C4	0.0450 (10)	0.0464 (11)	0.0439 (10)	0.0026 (8)	0.0283 (9)	−0.0017 (8)
C5	0.0392 (9)	0.0445 (10)	0.0302 (8)	−0.0030 (7)	0.0238 (8)	−0.0014 (7)
C6	0.0520 (11)	0.0482 (11)	0.0388 (10)	0.0062 (9)	0.0277 (9)	0.0000 (8)
C7	0.0328 (8)	0.0401 (9)	0.0294 (8)	0.0041 (7)	0.0197 (7)	0.0017 (7)
C8	0.0468 (10)	0.0472 (10)	0.0458 (10)	−0.0068 (8)	0.0340 (9)	−0.0027 (8)
C9	0.0415 (10)	0.0505 (11)	0.0486 (11)	−0.0093 (8)	0.0301 (9)	−0.0042 (9)
C10	0.0304 (9)	0.0504 (11)	0.0377 (9)	−0.0061 (8)	0.0184 (8)	−0.0033 (8)
C11	0.0513 (12)	0.0700 (14)	0.0408 (11)	−0.0159 (10)	0.0211 (10)	−0.0114 (10)
C12	0.0440 (11)	0.0606 (13)	0.0680 (14)	0.0035 (10)	0.0314 (11)	0.0068 (11)
C13	0.0764 (16)	0.0826 (17)	0.0574 (13)	−0.0205 (13)	0.0493 (13)	0.0003 (12)

Geometric parameters (Å, º)

S1—C7	1.6875 (17)	C6—H6A	0.9300
N1—C7	1.366 (2)	C8—C9	1.322 (3)
N1—C8	1.430 (2)	C8—C13	1.499 (3)
N1—C5	1.443 (2)	C9—C10	1.501 (3)
N2—C7	1.334 (2)	C9—H9A	0.9300
N2—C10	1.477 (2)	C10—C11	1.524 (3)
N2—H14A	0.858 (9)	C10—C12	1.528 (3)
F1—C2	1.362 (2)	C11—H11A	0.9600
C1—C2	1.367 (3)	C11—H11B	0.9600
C1—C6	1.384 (3)	C11—H11C	0.9600
C1—H1A	0.9300	C12—H12A	0.9600
C2—C3	1.358 (3)	C12—H12B	0.9600
C3—C4	1.385 (3)	C12—H12C	0.9600
C3—H3A	0.9300	C13—H13A	0.9600
C4—C5	1.378 (3)	C13—H13B	0.9600
C4—H4A	0.9300	C13—H13C	0.9600
C5—C6	1.374 (2)		
C7—N1—C8	120.85 (14)	N1—C8—C13	116.62 (16)
C7—N1—C5	119.30 (14)	C8—C9—C10	122.35 (16)
C8—N1—C5	119.84 (14)	C8—C9—H9A	118.8
C7—N2—C10	125.38 (14)	C10—C9—H9A	118.8
C7—N2—H14A	116.6 (14)	N2—C10—C9	106.33 (14)
C10—N2—H14A	114.8 (14)	N2—C10—C11	107.52 (16)
C2—C1—C6	118.16 (19)	C9—C10—C11	111.60 (16)

C2—C1—H1A	120.9	N2—C10—C12	109.50 (15)
C6—C1—H1A	120.9	C9—C10—C12	111.38 (17)
C3—C2—F1	118.5 (2)	C11—C10—C12	110.33 (16)
C3—C2—C1	123.24 (18)	C10—C11—H11A	109.5
F1—C2—C1	118.21 (19)	C10—C11—H11B	109.5
C2—C3—C4	118.33 (19)	H11A—C11—H11B	109.5
C2—C3—H3A	120.8	C10—C11—H11C	109.5
C4—C3—H3A	120.8	H11A—C11—H11C	109.5
C5—C4—C3	119.74 (18)	H11B—C11—H11C	109.5
C5—C4—H4A	120.1	C10—C12—H12A	109.5
C3—C4—H4A	120.1	C10—C12—H12B	109.5
C6—C5—C4	120.68 (16)	H12A—C12—H12B	109.5
C6—C5—N1	120.46 (16)	C10—C12—H12C	109.5
C4—C5—N1	118.85 (16)	H12A—C12—H12C	109.5
C5—C6—C1	119.84 (18)	H12B—C12—H12C	109.5
C5—C6—H6A	120.1	C8—C13—H13A	109.5
C1—C6—H6A	120.1	C8—C13—H13B	109.5
N2—C7—N1	116.45 (15)	H13A—C13—H13B	109.5
N2—C7—S1	121.47 (13)	C8—C13—H13C	109.5
N1—C7—S1	122.06 (12)	H13A—C13—H13C	109.5
C9—C8—N1	119.19 (16)	H13B—C13—H13C	109.5
C9—C8—C13	124.10 (18)		

C6—C1—C2—C3	0.0 (3)	C8—N1—C7—N2	9.5 (2)
C6—C1—C2—F1	179.83 (19)	C5—N1—C7—N2	−169.62 (15)
F1—C2—C3—C4	179.86 (18)	C8—N1—C7—S1	−168.57 (14)
C1—C2—C3—C4	−0.3 (3)	C5—N1—C7—S1	12.3 (2)
C2—C3—C4—C5	0.2 (3)	C7—N1—C8—C9	−16.1 (3)
C3—C4—C5—C6	0.2 (3)	C5—N1—C8—C9	163.03 (17)
C3—C4—C5—N1	178.83 (16)	C7—N1—C8—C13	160.48 (18)
C7—N1—C5—C6	−88.4 (2)	C5—N1—C8—C13	−20.4 (3)
C8—N1—C5—C6	92.4 (2)	N1—C8—C9—C10	−4.4 (3)
C7—N1—C5—C4	93.0 (2)	C13—C8—C9—C10	179.3 (2)
C8—N1—C5—C4	−86.2 (2)	C7—N2—C10—C9	−34.3 (2)
C4—C5—C6—C1	−0.5 (3)	C7—N2—C10—C11	−153.97 (18)
N1—C5—C6—C1	−179.11 (17)	C7—N2—C10—C12	86.1 (2)
C2—C1—C6—C5	0.4 (3)	C8—C9—C10—N2	26.1 (3)
C10—N2—C7—N1	18.2 (3)	C8—C9—C10—C11	143.1 (2)
C10—N2—C7—S1	−163.71 (14)	C8—C9—C10—C12	−93.1 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H14*A*···S1^{i}	0.86 (2)	2.57 (2)	3.422 (2)	172 (2)

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