Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

4,4,6-Trimethyl-1-phenyl-3,4-dihydropyrimidine-2(1*H*)-thione

Bohari M. Yamin,*
Noor Azilah M. Kasim and
Noraini Hamzah

School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Correspondence e-mail:
bohari@pkrisc.cc.ukm.my

Received 19 October 2004
Accepted 29 November 2004
Online 11 December 2004

Key indicators

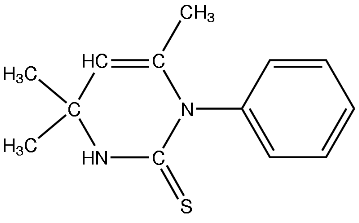
Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.058
wR factor = 0.164
Data-to-parameter ratio = 19.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The reaction of cinnamoyl isothiocyanate and aniline gave a the title cyclized thiourea, $C_{13}H_{16}N_2S$. There are two molecules in the asymmetric unit. The pyrimidine-2-thione moiety in each molecule is almost perpendicular to the phenyl group. The molecules are linked by two intermolecular N—H···S hydrogen bonds to form a dimer.

Comment

Under normal condition, benzoyl isothiocyanate reacts with aniline to give *N*-benzoyl-*N*′-phenylthiourea (Yamin & Yusof, 2003). However, the product of the reaction between cinnamoyl isothiocyanate and aniline, (I), showed not only the presence of the expected thiourea and phenyl chemical shifts but also the methyl protons and the disappearance of the carbonyl group. Therefore, an X-ray investigation was carried out.



(I)

The asymmetric unit of (I) consists of two molecules (Fig. 1). The 3,4-dihydro-pyrimidine-2(1*H*)-thione rings have phenyl, methyl and dimethyl substituents at N1/N3, C2/C15 and C4/C17, respectively. The S1═C1, S2═C14, N1—C1, N2—C1, N3—C14 and N4—C14 bond lengths (Table 1) are comparable with those in other thiourea derivatives, such as *N*-benzoyl-*N*′-phenylthiourea (Yamin & Yusof, 2003) and 1-ethyl-5-(4-methoxybenzoyl)-4-(4-methoxyphenyl)pyrimidine-2(1*H*)-thione (Özçelik *et al.*, 2004). Other bond lengths and angles are in normal ranges (Allen *et al.*, 1987). The pyrimidine-2-thione rings, N1/N2/C1—C4/S1 and N3/N4/C14—C17/S2 are essentially planar with maximum deviation of 0.091 (3) Å for atom C4. The dihedral angle between the benzene and pyrimidine-2-thione rings in these molecules are 89.79 (12) and 84.42 (15)°. In the crystal structure, the molecules are stabilized by intermolecular hydrogen bonds, N2—H2*A*···S2 and N4—H4*A*···S1 (Table 2), forming dimers. The dimers are arranged nearly parallel to (400).

Experimental

Cinnamoyl isothiocyanate was first prepared by the reaction of ammonium thiocyanate with cinnamoyl chloride. A solution of

doi:10.1107/S1600536804031320

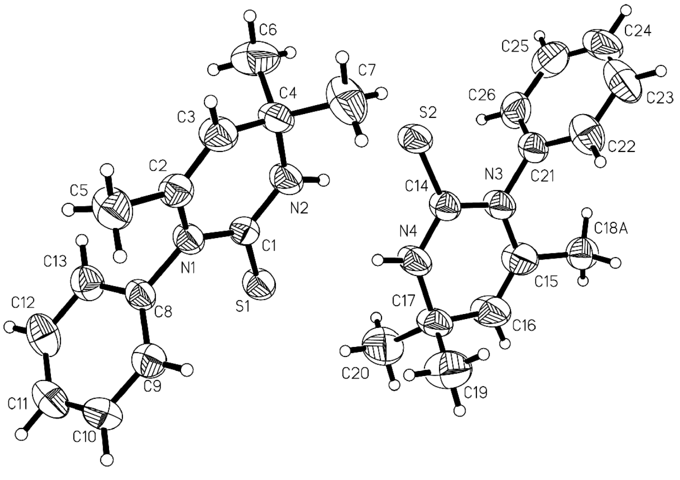


Figure 1
The structure of the asymmetric unit of (I), shown with 50% probability displacement ellipsoids for non-H atoms. Only one disorder component of atom C18 is shown (C18*A*).

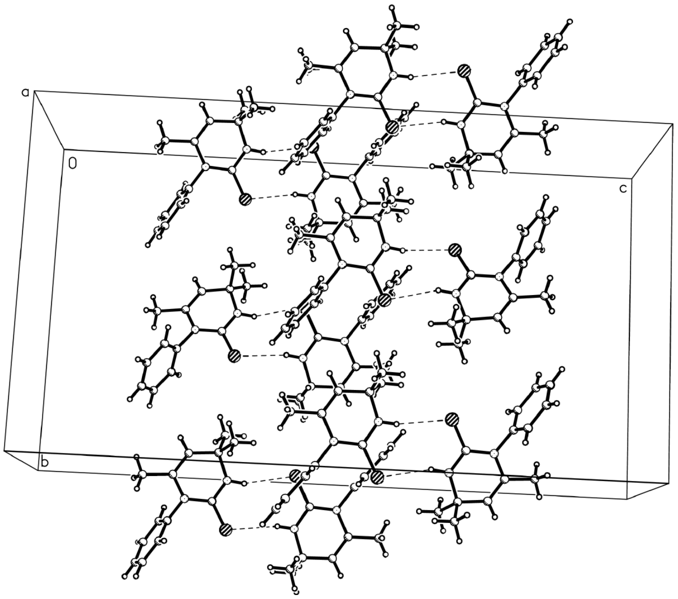


Figure 2
Packing diagram of (I), viewed down the *a* axis. The dashed lines denote N—H⋯S hydrogen bonds.

aniline (0.753 g, 8.10 mmol) in acetone (20 ml) was added dropwise with stirring to the freshly prepared acetone solution of cinnamoyl isothiocyanate. The mixture was refluxed for 1 h. After cooling, the solution was poured into a beaker containing crushed ice with vigorous stirring. The precipitate which formed was filtered off and washed with distilled water and dried under vacuum. Recrystallization from ethanol yielded colourless crystals suitable for X-ray investigation (yield 75%; m.p. 459.3–460.4 K). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.36 (6H, *s*, 2CH$_3$), 1.49 (3H, *s*, CH$_3$), 4.83 (1H, *s*, CH), 11.61 (1H, *s*, NH), 7.06–7.50 (C$_6$H$_5$ ring); ^{13}C{^{1}H}: δ 20.9 (CH$_3$), 31.6 (2CH$_3$), 52.6, 112.1, 132.6 (3C$_{\rm quaternary}$), 128–131.11 (C$_6$H$_5$ ring) and 177.8 (C═S).

Crystal data

$C_{13}H_{16}N_2S$
$M_r = 232.34$
Orthorhombic, *Pbca*
$a = 10.0407\ (16)$ Å
$b = 17.007\ (3)$ Å
$c = 30.197\ (5)$ Å
$V = 5156.6\ (14)$ Å^3
$Z = 16$
$D_x = 1.197$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 5295 reflections
$\theta = 1.3$–$27.5°$
$\mu = 0.23$ mm^{-1}
$T = 273\ (2)$ K
Block, colourless
0.47 × 0.46 × 0.33 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.900$, $T_{\rm max} = 0.928$
28481 measured reflections

5628 independent reflections
4954 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\rm max} = 27.0°$
$h = -7 \rightarrow 12$
$k = -21 \rightarrow 21$
$l = -38 \rightarrow 37$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.164$
$S = 1.13$
5628 reflections
289 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 4.7245P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.46$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.688 (2)	N3—C14	1.363 (3)
S2—C14	1.685 (2)	N3—C15	1.426 (3)
N1—C1	1.371 (3)	N3—C21	1.438 (3)
N1—C2	1.427 (3)	N4—C14	1.324 (3)
N1—C8	1.447 (3)	N4—C17	1.474 (3)
N2—C1	1.327 (3)	C2—C3	1.317 (3)
N2—C4	1.465 (3)	C15—C16	1.312 (4)
N4—C14—N3	117.6 (2)	N3—C14—S2	121.76 (18)
N4—C14—S2	120.62 (18)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H2*A*⋯S2	0.86	2.61	3.422 (2)	158
N4—H4*A*⋯S1	0.86	2.64	3.479 (2)	167

After the location of the H atoms in a difference map, they were positioned geometrically and fixed at ideal positions. The H atoms were allowed to ride on their parent C atoms [C—H = 0.93–0.96 Å, N—H = 0.86 Å, and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for CH$_3$, 1.2$U_{\rm eq}$(C) for CH and 1.2$U_{\rm eq}$(N) for NH groups]. The large U_{11} values of several atoms, in particular C15, C16, C18, C23, C24 and C25, compared to their U_{22} and U_{33} values may indicate that the molecule suffers from dynamic disorder or static disorder due to the librational motion of the molecule. Atom C18 was refined in two alternative positions with occupancy factors 0.54 (2):0.46 (2) and with isotropic displacement parameters of 0.054 (2) and 0.057 (3) Å^2, respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

The authors thank the Malaysian Government for the research grant IRPA No. 09-02-02-0163 and a referee for useful comments.

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