

N-(3-Nitrophenyl)-N'-pivaloylthiourea

M. Sukeri M. Yusof,^{a*} Siti Hajar Muharam,^a M. B. Kassim^b and Bohari M. Yamin^b^aDepartment of Chemical Sciences, Faculty of Science and Technology, Universiti Malaysia Terengganu, Mengabang Telipot, 21030 Kuala Terengganu, Malaysia, and^bSchool of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Correspondence e-mail: mohdsukeri@umt.edu.my

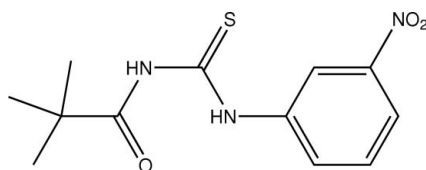
Received 23 April 2008; accepted 14 May 2008

Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.042; wR factor = 0.103; data-to-parameter ratio = 17.6.

In the title compound, $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$, there is an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. The crystal structure is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{S}$ and $\text{C}-\text{H}\cdots\text{S}$ hydrogen bonds, forming a two-dimensional network parallel to the ac plane.

Related literature

For related crystal structures, see: Saeed & Flörke (2007); Sultana *et al.* (2007).



Experimental

Crystal data

 $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$ $M_r = 281.33$ Orthorhombic, $Pna2_1$ $a = 20.400$ (5) Å $b = 10.886$ (3) Å $c = 6.2120$ (15) Å $V = 1379.5$ (6) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.24$ mm⁻¹ $T = 273$ (2) K $0.48 \times 0.18 \times 0.12$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2000)

 $T_{\min} = 0.893$, $T_{\max} = 0.972$

8152 measured reflections

3020 independent reflections

2321 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.032$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.042$ $wR(F^2) = 0.103$ $S = 0.91$

3020 reflections

172 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.14$ e Å⁻³

Absolute structure: Flack (1983),

1296 Friedel pairs

Flack parameter: 0.07 (9)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2A}\cdots\text{O1}$	0.86	1.92	2.605 (3)	135
$\text{N1}-\text{H1A}\cdots\text{S1}^{\text{i}}$	0.86	2.76	3.582 (2)	160
$\text{C3}-\text{H3A}\cdots\text{S1}^{\text{i}}$	0.96	2.83	3.742 (3)	159
$\text{N2}-\text{H2A}\cdots\text{O2}^{\text{ii}}$	0.86	2.52	3.197 (3)	137

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

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, 2003).

The authors thank the Malaysian Government, Universiti Kebangsaan Malaysia, Universiti Malaysia Terengganu and the Ministry of Higher Education, Malaysia, for research grants OUP UKM OUP-BIT-28/20076 and UMT-FRGS-59001.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SG2240).

References

- Bruker (2000). SADABS, SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Saeed, A. & Flörke, U. (2007). *Acta Cryst.* **E63**, o4259.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Sultana, S., Khawar Rauf, M., Ebihara, M. & Badshah, A. (2007). *Acta Cryst.* **E63**, o2801.

supplementary materials

Acta Cryst. (2008). E64, o1137 [doi:10.1107/S1600536808014530]

N-(3-Nitrophenyl)-*N'*-pivaloylthiourea

M. S. M. Yusof, S. H. Muharam, M. B. Kassim and B. M. Yamin

Comment

Two isomers of *N*-nitrophenyl-*N'*-pivaloylthiourea were reported by Saeed & Flörke, (2007) (nitro group at *ortho* position) and Sultana *et al.*, (2007) (nitro group at *para* position). Here, the molecule with a nitro group in the *meta* position, (I), has been successfully synthesized (Fig. 1). The molecule displays similar bond distances and angles to the related compounds.

The carbonylthiourea (S1/N1/N2/O1/C4–C7) and 3-nitrophenyl fragments are essentially planar, with maximum deviation of 0.077 Å for atom O2 from the least square plane. The carbonylthiourea fragment makes a dihedral angle of 85.64 (7)° to the nitrophenyl fragment. There is an intramolecular hydrogen bond, N2—H2···O1 leading to a pseudo-six membered ring (O1···H2—N2—C6—N1—C5—O1). In the crystal structure, the molecules are linked by intermolecular interactions, N—H···O, N—H···S and C—H···S (symmetry codes as in Table 1) forming a two dimensional network along the *ac* plane (Fig.2).

Experimental

To a stirring acetone solution (75 ml) of pivaloyl chloride (5.0 g, 0.04 mol) and ammonium thiocyanate (3.15 g, 0.04 mol), 3-nitroaniline (5.73 g, 0.04 mol) in 40 ml of acetone was added dropwise. The solution mixture was refluxed for 1 h. The resulting solution was poured into a beaker containing some ice blocks. The white precipitate was filtered off and washed with distilled water and cold ethanol before being dried under vacuum. Good quality crystals were obtained by recrystallization from THF.

Refinement

After their location in the difference map, all H-atoms were fixed geometrically at ideal positions and allowed to ride on the parent C or N atoms with C—H = 0.93–0.97 Å and N—H = 0.86 Å with $U_{\text{iso}}(\text{H}) = 1.2$ (CH₂ and NH) or 1.5 $U_{\text{eq}}(\text{C})(\text{CH}_3)$.

Figures

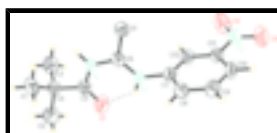


Fig. 1. : The molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bond.

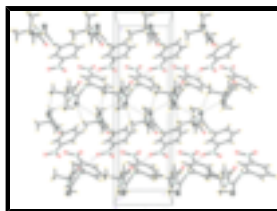


Fig. 2. : Packing diagram of compound,(I), viewed down the *b* axis. The dashed lines denote the N—H···O, N—H···S and C—H···S hydrogen bonds.

N-(3-Nitrophenyl)-*N'*-pivaloylthiourea

Crystal data

$C_{12}H_{15}N_3O_3S$

$M_r = 281.33$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$a = 20.400$ (5) Å

$b = 10.886$ (3) Å

$c = 6.2120$ (15) Å

$V = 1379.5$ (6) Å³

$Z = 4$

$F_{000} = 592$

$D_x = 1.355$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 925 reflections

$\theta = 2.0$ – 27.5°

$\mu = 0.24$ mm⁻¹

$T = 273$ (2) K

Block, colourless

$0.48 \times 0.18 \times 0.12$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 83.66 pixels mm⁻¹

$T = 298$ (2) K

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2000)

$T_{\min} = 0.893$, $T_{\max} = 0.972$

8152 measured reflections

3020 independent reflections

2321 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 2.0^\circ$

$h = -21 \rightarrow 26$

$k = -13 \rightarrow 14$

$l = -7 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.103$

$S = 0.91$

3020 reflections

172 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-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 0.0515P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.28$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.14$ e Å⁻³

Extinction correction: none

Absolute structure: Flack (1983), 1296 Friedel pairs

Flack parameter: 0.07 (9)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.97040 (3)	0.39600 (5)	0.62603 (13)	0.04412 (17)
O3	0.72971 (13)	0.0240 (2)	0.9230 (4)	0.0936 (8)
O2	0.73374 (10)	0.13216 (17)	0.6346 (5)	0.0791 (6)
O1	0.84682 (10)	0.73243 (15)	0.7556 (4)	0.0694 (6)
N2	0.86872 (9)	0.49974 (16)	0.8218 (3)	0.0422 (5)
H2A	0.8456	0.5640	0.8480	0.051*
N1	0.92866 (9)	0.62483 (14)	0.5965 (3)	0.0394 (5)
H1A	0.9603	0.6304	0.5055	0.047*
C11	0.79218 (11)	0.2008 (2)	0.9299 (4)	0.0414 (5)
C10	0.81336 (11)	0.1747 (2)	1.1350 (5)	0.0490 (6)
H10A	0.7999	0.1035	1.2052	0.059*
C9	0.85486 (13)	0.2563 (2)	1.2331 (5)	0.0521 (6)
H9A	0.8704	0.2395	1.3708	0.062*
C8	0.87392 (11)	0.36328 (19)	1.1304 (5)	0.0463 (5)
H8A	0.9018	0.4187	1.1985	0.056*
C7	0.85101 (11)	0.38661 (19)	0.9253 (4)	0.0387 (5)
C12	0.80979 (11)	0.3062 (2)	0.8226 (4)	0.0413 (5)
H12A	0.7942	0.3224	0.6848	0.050*
N3	0.74809 (11)	0.11334 (19)	0.8218 (5)	0.0557 (6)
C6	0.91904 (11)	0.50999 (19)	0.6876 (4)	0.0375 (5)
C5	0.89385 (11)	0.73105 (18)	0.6338 (5)	0.0421 (5)
C4	0.91691 (13)	0.8460 (2)	0.5166 (4)	0.0451 (6)
C3	0.90038 (15)	0.8322 (3)	0.2772 (5)	0.0635 (8)
H3A	0.9239	0.7634	0.2189	0.095*
H3B	0.9128	0.9056	0.2019	0.095*
H3C	0.8541	0.8188	0.2610	0.095*
C2	0.87985 (15)	0.9559 (2)	0.6113 (7)	0.0733 (8)
H2B	0.8905	0.9641	0.7611	0.110*
H2C	0.8335	0.9430	0.5958	0.110*
H2D	0.8923	1.0294	0.5363	0.110*
C1	0.99039 (14)	0.8627 (2)	0.5451 (6)	0.0625 (8)
H1B	1.0130	0.7938	0.4834	0.094*
H1C	1.0005	0.8681	0.6957	0.094*

supplementary materials

H1D 1.0041 0.9368 0.4742 0.094*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0528 (3)	0.0349 (3)	0.0446 (3)	0.0050 (2)	0.0020 (3)	0.0025 (3)
O3	0.124 (2)	0.0680 (13)	0.0885 (16)	-0.0522 (13)	0.0132 (15)	-0.0002 (13)
O2	0.0909 (15)	0.0660 (12)	0.0804 (15)	-0.0173 (10)	-0.0336 (15)	0.0052 (14)
O1	0.0707 (13)	0.0443 (10)	0.0930 (16)	0.0126 (9)	0.0308 (12)	0.0156 (10)
N2	0.0457 (10)	0.0311 (9)	0.0497 (11)	0.0041 (8)	0.0075 (10)	0.0086 (8)
N1	0.0440 (10)	0.0325 (9)	0.0416 (13)	-0.0003 (7)	0.0044 (10)	0.0064 (8)
C11	0.0378 (12)	0.0376 (12)	0.0488 (14)	-0.0003 (10)	0.0062 (11)	0.0013 (11)
C10	0.0557 (14)	0.0387 (11)	0.0526 (14)	-0.0019 (10)	0.0128 (15)	0.0136 (15)
C9	0.0650 (16)	0.0508 (14)	0.0404 (13)	0.0030 (13)	-0.0015 (12)	0.0109 (12)
C8	0.0488 (12)	0.0427 (11)	0.0474 (13)	-0.0016 (9)	-0.0003 (15)	-0.0004 (14)
C7	0.0396 (13)	0.0366 (12)	0.0399 (13)	0.0020 (9)	0.0051 (10)	0.0043 (10)
C12	0.0423 (13)	0.0409 (12)	0.0409 (13)	0.0024 (10)	0.0016 (11)	0.0056 (11)
N3	0.0540 (13)	0.0435 (12)	0.0695 (16)	-0.0055 (10)	0.0068 (12)	-0.0009 (11)
C6	0.0391 (11)	0.0367 (12)	0.0366 (14)	-0.0034 (10)	-0.0084 (9)	0.0029 (9)
C5	0.0441 (12)	0.0350 (10)	0.0471 (12)	0.0004 (9)	0.0006 (13)	0.0067 (13)
C4	0.0520 (15)	0.0313 (11)	0.0519 (15)	-0.0003 (11)	0.0008 (12)	0.0078 (10)
C3	0.0761 (19)	0.0570 (16)	0.0575 (19)	-0.0034 (14)	-0.0070 (15)	0.0183 (14)
C2	0.093 (2)	0.0359 (12)	0.091 (2)	0.0162 (13)	0.020 (2)	0.0097 (18)
C1	0.0643 (18)	0.0414 (14)	0.082 (2)	-0.0118 (13)	-0.0026 (15)	0.0018 (13)

Geometric parameters (\AA , $^\circ$)

S1—C6	1.668 (2)	C8—C7	1.381 (4)
O3—N3	1.217 (3)	C8—H8A	0.9300
O2—N3	1.216 (3)	C7—C12	1.371 (3)
O1—C5	1.222 (3)	C12—H12A	0.9300
N2—C6	1.327 (3)	C5—C4	1.523 (3)
N2—C7	1.435 (3)	C4—C1	1.520 (4)
N2—H2A	0.8600	C4—C3	1.532 (4)
N1—C5	1.377 (3)	C4—C2	1.532 (4)
N1—C6	1.386 (3)	C3—H3A	0.9600
N1—H1A	0.8600	C3—H3B	0.9600
C11—C10	1.375 (4)	C3—H3C	0.9600
C11—C12	1.375 (3)	C2—H2B	0.9600
C11—N3	1.472 (3)	C2—H2C	0.9600
C10—C9	1.370 (4)	C2—H2D	0.9600
C10—H10A	0.9300	C1—H1B	0.9600
C9—C8	1.384 (3)	C1—H1C	0.9600
C9—H9A	0.9300	C1—H1D	0.9600
C6—N2—C7	123.23 (18)	N1—C6—S1	119.22 (17)
C6—N2—H2A	118.4	O1—C5—N1	121.3 (2)
C7—N2—H2A	118.4	O1—C5—C4	121.9 (2)
C5—N1—C6	128.0 (2)	N1—C5—C4	116.8 (2)

C5—N1—H1A	116.0	C1—C4—C5	110.3 (2)
C6—N1—H1A	116.0	C1—C4—C3	110.0 (2)
C10—C11—C12	122.7 (2)	C5—C4—C3	108.4 (2)
C10—C11—N3	118.8 (2)	C1—C4—C2	110.4 (2)
C12—C11—N3	118.6 (2)	C5—C4—C2	107.8 (2)
C9—C10—C11	118.2 (2)	C3—C4—C2	109.9 (3)
C9—C10—H10A	120.9	C4—C3—H3A	109.5
C11—C10—H10A	120.9	C4—C3—H3B	109.5
C10—C9—C8	120.9 (3)	H3A—C3—H3B	109.5
C10—C9—H9A	119.5	C4—C3—H3C	109.5
C8—C9—H9A	119.5	H3A—C3—H3C	109.5
C7—C8—C9	119.0 (2)	H3B—C3—H3C	109.5
C7—C8—H8A	120.5	C4—C2—H2B	109.5
C9—C8—H8A	120.5	C4—C2—H2C	109.5
C12—C7—C8	121.3 (2)	H2B—C2—H2C	109.5
C12—C7—N2	119.6 (2)	C4—C2—H2D	109.5
C8—C7—N2	119.1 (2)	H2B—C2—H2D	109.5
C7—C12—C11	117.9 (2)	H2C—C2—H2D	109.5
C7—C12—H12A	121.1	C4—C1—H1B	109.5
C11—C12—H12A	121.1	C4—C1—H1C	109.5
O2—N3—O3	123.7 (3)	H1B—C1—H1C	109.5
O2—N3—C11	118.3 (2)	C4—C1—H1D	109.5
O3—N3—C11	118.0 (3)	H1B—C1—H1D	109.5
N2—C6—N1	116.21 (19)	H1C—C1—H1D	109.5
N2—C6—S1	124.57 (17)		
C12—C11—C10—C9	-1.5 (4)	C10—C11—N3—O3	3.4 (3)
N3—C11—C10—C9	179.4 (2)	C12—C11—N3—O3	-175.7 (2)
C11—C10—C9—C8	1.2 (4)	C7—N2—C6—N1	178.4 (2)
C10—C9—C8—C7	-0.6 (4)	C7—N2—C6—S1	-2.2 (3)
C9—C8—C7—C12	0.2 (4)	C5—N1—C6—N2	2.6 (4)
C9—C8—C7—N2	177.6 (2)	C5—N1—C6—S1	-176.9 (2)
C6—N2—C7—C12	-87.3 (3)	C6—N1—C5—O1	-2.1 (4)
C6—N2—C7—C8	95.2 (3)	C6—N1—C5—C4	177.8 (2)
C8—C7—C12—C11	-0.4 (3)	O1—C5—C4—C1	130.5 (3)
N2—C7—C12—C11	-177.81 (19)	N1—C5—C4—C1	-49.4 (3)
C10—C11—C12—C7	1.0 (3)	O1—C5—C4—C3	-109.0 (3)
N3—C11—C12—C7	-179.9 (2)	N1—C5—C4—C3	71.1 (3)
C10—C11—N3—O2	-174.3 (2)	O1—C5—C4—C2	9.9 (4)
C12—C11—N3—O2	6.6 (3)	N1—C5—C4—C2	-170.0 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2A \cdots O1	0.86	1.92	2.605 (3)	135
N1—H1A \cdots S1 ⁱ	0.86	2.76	3.582 (2)	160
C3—H3A \cdots S1 ⁱ	0.96	2.83	3.742 (3)	159
N2—H2A \cdots O2 ⁱⁱ	0.86	2.52	3.197 (3)	137

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

Fig. 1

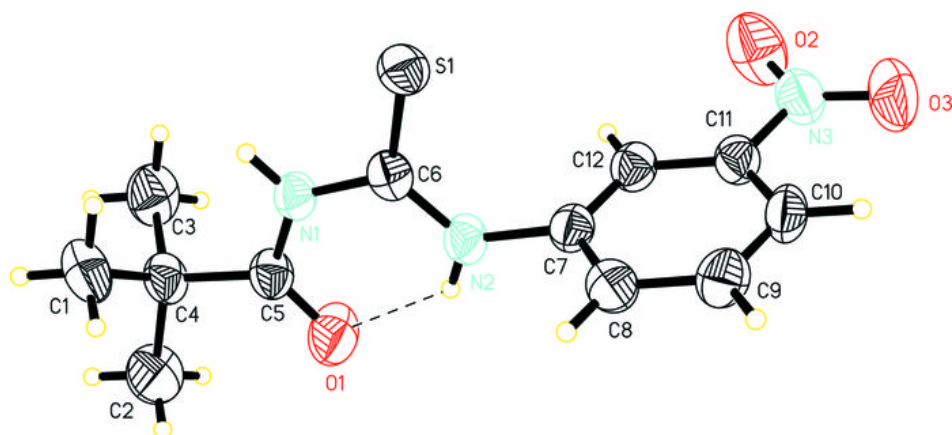


Fig. 2

