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1-(2-Nitrophenyl)-3-pivaloylthiourea

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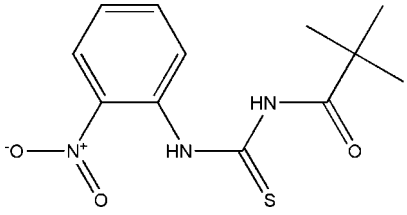
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.039; wR factor = 0.104; data-to-parameter ratio = 19.4.

In the structure of the title compound, $C_{12}H_{15}N_3O_3S$, the thioamide and amide groups are almost coplanar with the benzene ring. The planes of the NO_2 group and the benzene ring form a dihedral angle of 40.8 (2)°. The crystal packing shows intermolecular N—H···S hydrogen bonds, forming centrosymmetric dimers which are stacked along [001].

Related literature

For related literature, see: Saeed & Flörke (2006, 2007).



Experimental

Crystal data

$C_{12}H_{15}N_3O_3S$
M_r = 281.33
Monoclinic, $P2_1/c$
a = 10.8491 (14) Å
b = 11.8882 (16) Å
c = 11.1206 (15) Å
β = 103.723 (3)°
V = 1393.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 120 (2) K
0.50 × 0.41 × 0.25 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.890, T_{max} = 0.933
11932 measured reflections
3329 independent reflections
2954 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.104
S = 1.05
3329 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1	0.88	1.90	2.5953 (16)	134
N1—H1A···S1^{i}	0.88	2.59	3.4614 (12)	171
C4—H4B···S1^{i}	0.98	2.75	3.6486 (18)	153
C5—H5C···S1^{i}	0.98	2.84	3.7121 (18)	149

Symmetry code: (i) $-x+2, -y, -z+2$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2060).

References

Bruker (2002). *SMART* (Version 5.62), *SAINT* (Version 6.02), *SHELXTL* (Version 6.10) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
Saeed, A. & Flörke, U. (2006). *Acta Cryst.* E**62**, o2924–o2925.
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supplementary materials

Acta Cryst. (2007). E**63**, o4259 [**doi:10.1107/S160053680704593X**]

1-(2-Nitrophenyl)-3-pivaloylthiourea

A. Saeed and U. Flörke

Comment

The coplanarity of thioamide and amide groups with the phenyl ring are reflected by the torsion angles C6–N1–C1–O1 of −6.1 (2)° and C8–N2–C6–N2 of 1.4 (2)°. This is a common feature for this type of compounds (Saeed & Flörke, 2006) as well as the intermolecular N–H···S hydrogen bonds (Table 2, Fig. 2), forming centrosymmetric dimers which are stacked along [001]. Two intermolecular C–H···S interactions with somewhat longer H···S distances are also present (see the hydrogen bonding table). Additionally, the typical (Saeed & Flörke, 2006) intramolecular N–H···O hydrogen bond is formed with the carbonyl function.

Experimental

A solution of freshly distilled pivaloyl chloride (1.20 g, 10 mmol) in acetone (50 ml) was added dropwise to a suspension of potassium thiocyanate (0.97 g,10 mmol) in acetone (30 ml) and the reaction mixture was refluxed for 30 min. After cooling to room temperature, a solution of 3-methoxyaniline (10 mmol) in acetone (10 ml) was added and the resulting mixture refluxed for 2.0 h. The reaction mixture was poured into cold water and the resulting precipitate was isolated by filtration followed by recrystallization from ethanol to afford the title thiourea compound as colourless crystals (2.33 g, 83.0 mmol, 83%). m.p. 352 K. IR (KBr) cm^{-1}: 3351 (free NH), 3200 (assoc. NH), 1667 (CO), 1610 (arom.), 1529, 1325, 1160, 744, 762; ^{1}H NMR ($CDCl_3$) 1.27 (9*H*, s, pivaloyl), 3.89 (3*H*, s, $ArOCH_3$), 7.31–7.75 (aromatic), 9.19 (1*H*, s, broad, NH); 12.76 (1*H*, s, broad, NH); EIMS m/e: 281, 283, 149, 119, 91, 64.9; Analysis calculated for $C_{12}H_{15}N_3O_3S$ C, 51.23; H, 5.37; N, 14.94; S, 11.40 found C, 64.01; H, 5.32; N, 9..10; O, S, 10.65.

Refinement

Hydrogen atoms were located in difference syntheses, refined at idealized positions riding on the C (C–H = 0.95–0.99 Å) or N (N–H = 0.88 Å) atoms with isotropic displacement parameters U_{iso}(H) = 1.2U(C_{eq} / N_{eq}) and 1.5(methyl-C). Methyl H atoms were refined on the basis of rigid groups allowed to rotate but not tip.

Figures

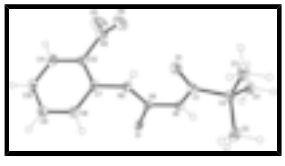

Fig. 1. Molecular structure of title compound. Displacement ellipsoids are drawn at the 50% probability level.

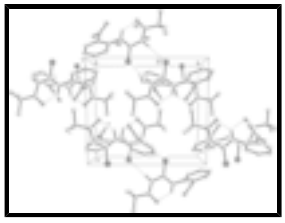

Fig. 2. Crystal packing viewed along [001] with the intra- and N–H···S intermolecular hydrogen bonding pattern indicated as dashed lines. H-atoms not involved in hydrogen bonding are omitted.

1-(2-Nitrophenyl)-3-pivaloylthiourea

Crystal data

$C_{12}H_{15}N_3O_3S$	F_{000} = 592
M_r = 281.33	D_x = 1.341 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 981 reflections
a = 10.8491 (14) Å	θ = 2.5–28.2º
b = 11.8882 (16) Å	μ = 0.24 mm^{-1}
c = 11.1206 (15) Å	T = 120 (2) K
β = 103.723 (3)º	Block, yellow
V = 1393.4 (3) Å^3	0.50 × 0.41 × 0.25 mm
Z = 4	

Data collection

Bruker SMART APEX diffractometer	3329 independent reflections
Radiation source: sealed tube	2954 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.025
T = 120(2) K	θ_{max} = 27.9º
φ and ω scans	θ_{min} = 1.9º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	h = −14→12
T_{min} = 0.890, T_{max} = 0.933	k = −15→15
11932 measured reflections	l = −14→14

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.039	H-atom parameters constrained
$wR(F^2)$ = 0.104	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.5774P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max} < 0.001$
3329 reflections	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
172 parameters	$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.99549 (3)	0.16750 (3)	0.98065 (4)	0.02415 (12)
O1	0.57778 (10)	0.08899 (9)	0.84219 (10)	0.0276 (2)
O2	0.76929 (17)	0.45204 (15)	1.14489 (13)	0.0606 (4)
O3	0.63077 (16)	0.34998 (13)	1.02002 (15)	0.0545 (4)
N1	0.78505 (11)	0.04492 (9)	0.92321 (10)	0.0190 (2)
H1A	0.8365	−0.0104	0.9549	0.023*
N2	0.76148 (11)	0.23423 (10)	0.87778 (11)	0.0215 (2)
H2A	0.6795	0.2209	0.8544	0.026*
N3	0.72498 (15)	0.40959 (12)	1.04339 (13)	0.0347 (3)
C1	0.65778 (13)	0.01695 (12)	0.87845 (12)	0.0195 (3)
C2	0.62599 (13)	−0.10813 (12)	0.87869 (13)	0.0221 (3)
C3	0.48233 (15)	−0.12139 (14)	0.83176 (17)	0.0346 (4)
H3A	0.4394	−0.0816	0.8874	0.052*
H3B	0.4601	−0.2014	0.8296	0.052*
H3C	0.4555	−0.0897	0.7483	0.052*
C4	0.66637 (15)	−0.15607 (13)	1.01035 (14)	0.0264 (3)
H4A	0.6226	−0.1153	1.0646	0.040*
H4B	0.7583	−0.1475	1.0413	0.040*
H4C	0.6440	−0.2360	1.0092	0.040*
C5	0.69320 (16)	−0.17063 (13)	0.79120 (15)	0.0307 (3)
H5A	0.6660	−0.1391	0.7077	0.046*
H5B	0.6711	−0.2507	0.7892	0.046*
H5C	0.7852	−0.1620	0.8210	0.046*
C6	0.83936 (13)	0.14998 (11)	0.92322 (12)	0.0181 (3)
C7	0.80631 (13)	0.34525 (11)	0.86576 (13)	0.0205 (3)
C8	0.86926 (14)	0.36909 (12)	0.77407 (14)	0.0248 (3)
H8A	0.8819	0.3113	0.7192	0.030*
C9	0.91413 (15)	0.47677 (13)	0.76166 (14)	0.0278 (3)
H9A	0.9563	0.4926	0.6978	0.033*
C10	0.89742 (15)	0.56134 (13)	0.84252 (15)	0.0303 (3)
H10A	0.9281	0.6350	0.8336	0.036*

C11	0.83692 (16)	0.53913 (13)	0.93514 (15)	0.0298 (3)
H11A	0.8270	0.5964	0.9917	0.036*
C12	0.79046 (14)	0.43159 (12)	0.94491 (13)	0.0236 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01774 (18)	0.01579 (18)	0.0359 (2)	−0.00065 (12)	0.00039 (14)	0.00073 (13)
O1	0.0191 (5)	0.0235 (5)	0.0392 (6)	0.0015 (4)	0.0049 (4)	0.0041 (4)
O2	0.0804 (12)	0.0730 (11)	0.0350 (7)	−0.0148 (9)	0.0270 (7)	−0.0147 (7)
O3	0.0623 (10)	0.0499 (8)	0.0642 (10)	−0.0193 (7)	0.0408 (8)	−0.0105 (7)
N1	0.0188 (5)	0.0144 (5)	0.0227 (6)	0.0003 (4)	0.0026 (4)	0.0016 (4)
N2	0.0180 (5)	0.0168 (6)	0.0286 (6)	0.0003 (4)	0.0035 (5)	0.0026 (4)
N3	0.0458 (9)	0.0285 (7)	0.0348 (7)	−0.0016 (6)	0.0194 (6)	−0.0027 (6)
C1	0.0194 (6)	0.0208 (6)	0.0186 (6)	−0.0017 (5)	0.0048 (5)	−0.0001 (5)
C2	0.0210 (7)	0.0191 (7)	0.0245 (7)	−0.0039 (5)	0.0022 (5)	0.0002 (5)
C3	0.0248 (8)	0.0289 (8)	0.0443 (9)	−0.0091 (6)	−0.0034 (7)	0.0035 (7)
C4	0.0259 (7)	0.0250 (7)	0.0280 (7)	−0.0023 (5)	0.0057 (6)	0.0055 (6)
C5	0.0396 (9)	0.0231 (7)	0.0287 (8)	−0.0025 (6)	0.0066 (6)	−0.0062 (6)
C6	0.0201 (6)	0.0168 (6)	0.0176 (6)	−0.0004 (5)	0.0053 (5)	−0.0007 (5)
C7	0.0190 (6)	0.0171 (6)	0.0234 (7)	0.0019 (5)	0.0012 (5)	0.0031 (5)
C8	0.0271 (7)	0.0223 (7)	0.0249 (7)	0.0014 (6)	0.0057 (6)	0.0008 (6)
C9	0.0286 (8)	0.0278 (7)	0.0278 (7)	−0.0008 (6)	0.0082 (6)	0.0067 (6)
C10	0.0340 (8)	0.0190 (7)	0.0361 (8)	−0.0040 (6)	0.0049 (6)	0.0060 (6)
C11	0.0363 (8)	0.0192 (7)	0.0334 (8)	0.0002 (6)	0.0073 (6)	−0.0026 (6)
C12	0.0256 (7)	0.0216 (7)	0.0236 (7)	0.0010 (5)	0.0059 (5)	0.0018 (5)

Geometric parameters (Å, °)

S1—C6	1.6754 (14)	C3—H3C	0.9800
O1—C1	1.2180 (17)	C4—H4A	0.9800
O2—N3	1.226 (2)	C4—H4B	0.9800
O3—N3	1.220 (2)	C4—H4C	0.9800
N1—C6	1.3809 (17)	C5—H5A	0.9800
N1—C1	1.3924 (17)	C5—H5B	0.9800
N1—H1A	0.8800	C5—H5C	0.9800
N2—C6	1.3304 (17)	C7—C8	1.385 (2)
N2—C7	1.4238 (17)	C7—C12	1.389 (2)
N2—H2A	0.8800	C8—C9	1.388 (2)
N3—C12	1.4634 (19)	C8—H8A	0.9500
C1—C2	1.5266 (19)	C9—C10	1.389 (2)
C2—C3	1.530 (2)	C9—H9A	0.9500
C2—C4	1.535 (2)	C10—C11	1.372 (2)
C2—C5	1.539 (2)	C10—H10A	0.9500
C3—H3A	0.9800	C11—C12	1.388 (2)
C3—H3B	0.9800	C11—H11A	0.9500
C6—N1—C1	127.08 (11)	H4B—C4—H4C	109.5
C6—N1—H1A	116.5	C2—C5—H5A	109.5

C1—N1—H1A	116.5	C2—C5—H5B	109.5
C6—N2—C7	122.22 (12)	H5A—C5—H5B	109.5
C6—N2—H2A	118.9	C2—C5—H5C	109.5
C7—N2—H2A	118.9	H5A—C5—H5C	109.5
O3—N3—O2	124.13 (15)	H5B—C5—H5C	109.5
O3—N3—C12	118.38 (14)	N2—C6—N1	116.64 (12)
O2—N3—C12	117.49 (15)	N2—C6—S1	123.01 (10)
O1—C1—N1	121.25 (13)	N1—C6—S1	120.35 (10)
O1—C1—C2	122.81 (12)	C8—C7—C12	118.18 (13)
N1—C1—C2	115.93 (12)	C8—C7—N2	119.87 (13)
C1—C2—C3	108.19 (12)	C12—C7—N2	121.95 (13)
C1—C2—C4	110.48 (11)	C7—C8—C9	120.52 (14)
C3—C2—C4	108.92 (12)	C7—C8—H8A	119.7
C1—C2—C5	109.15 (12)	C9—C8—H8A	119.7
C3—C2—C5	109.38 (13)	C8—C9—C10	120.03 (14)
C4—C2—C5	110.68 (12)	C8—C9—H9A	120.0
C2—C3—H3A	109.5	C10—C9—H9A	120.0
C2—C3—H3B	109.5	C11—C10—C9	120.38 (14)
H3A—C3—H3B	109.5	C11—C10—H10A	119.8
C2—C3—H3C	109.5	C9—C10—H10A	119.8
H3A—C3—H3C	109.5	C10—C11—C12	118.91 (14)
H3B—C3—H3C	109.5	C10—C11—H11A	120.5
C2—C4—H4A	109.5	C12—C11—H11A	120.5
C2—C4—H4B	109.5	C11—C12—C7	121.95 (14)
H4A—C4—H4B	109.5	C11—C12—N3	118.23 (13)
C2—C4—H4C	109.5	C7—C12—N3	119.81 (13)
H4A—C4—H4C	109.5		
C6—N1—C1—O1	−6.1 (2)	N2—C7—C8—C9	−179.64 (13)
C6—N1—C1—C2	174.25 (12)	C7—C8—C9—C10	0.8 (2)
O1—C1—C2—C3	−1.98 (19)	C8—C9—C10—C11	0.2 (2)
N1—C1—C2—C3	177.68 (12)	C9—C10—C11—C12	−1.4 (2)
O1—C1—C2—C4	−121.13 (15)	C10—C11—C12—C7	1.7 (2)
N1—C1—C2—C4	58.53 (16)	C10—C11—C12—N3	−179.36 (14)
O1—C1—C2—C5	116.95 (15)	C8—C7—C12—C11	−0.8 (2)
N1—C1—C2—C5	−63.38 (15)	N2—C7—C12—C11	178.37 (13)
C7—N2—C6—N1	−176.23 (12)	C8—C7—C12—N3	−179.70 (13)
C7—N2—C6—S1	4.82 (19)	N2—C7—C12—N3	−0.6 (2)
C1—N1—C6—N2	1.4 (2)	O3—N3—C12—C11	140.14 (17)
C1—N1—C6—S1	−179.60 (10)	O2—N3—C12—C11	−40.3 (2)
C6—N2—C7—C8	73.24 (18)	O3—N3—C12—C7	−40.9 (2)
C6—N2—C7—C12	−105.88 (16)	O2—N3—C12—C7	138.65 (17)
C12—C7—C8—C9	−0.5 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O1	0.88	1.90	2.5953 (16)	134
N1—H1A···S1^{i}	0.88	2.59	3.4614 (12)	171

C4—H4B···S1^{i}	0.98	2.75	3.6486 (18)	153
C5—H5C···S1^{i}	0.98	2.84	3.7121 (18)	149

Symmetry codes: (i) −*x*+2, −*y*, −*z*+2.

Fig. 1

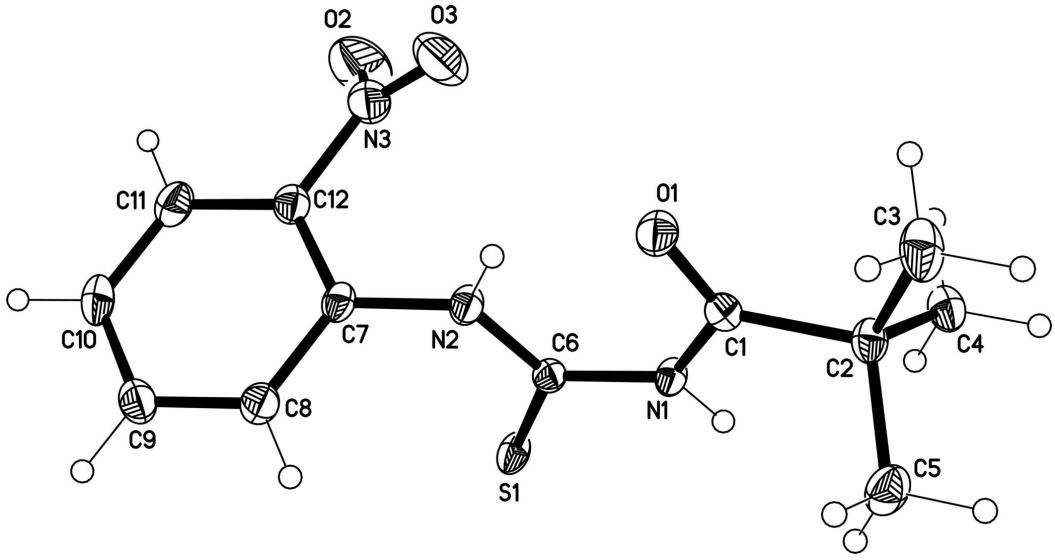

Fig. 2