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1-(4-Nitrophenyl)-3-pivaloylthiourea

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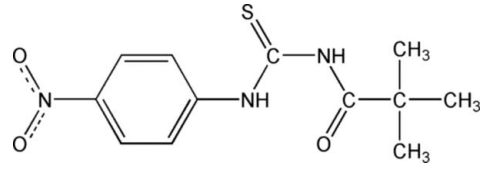
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.003 Å; R factor = 0.053; wR factor = 0.102; data-to-parameter ratio = 16.6.

In the title compound [systematic name: 1-(2,2-dimethylpropionyl)-3-(4-nitrophenyl)thiourea], $C_{12}H_{15}N_3O_3S$, the molecule exists in the thione form with typical thiourea C—S and C—O bonds, as well as shortened C—N bond lengths. The planes containing the thiourea N atoms form dihedral angles of 27.12 (7) and 1.6 (2)°, respectively, with the benzene ring. The molecule exhibits only an intramolecular N—H···O hydrogen bond and no intermolecular N—H···S hydrogen bonds. This is in contrast to the usual behaviour of this class of compounds.

Related literature

The bond lengths and angles are quite typical for *N*,*N*′-disubstituted thiourea compounds found in the Cambridge Structural Database (Version 5.28, Allen, 2002; Khawar Rauf *et al.*, 2006).

For related literature, see: Baily *et al.* (1996); Koch (2001); Maryanoff *et al.* (1986); Namgun *et al.* (2001); Patil & Chedekel (1984); Shoukat *et al.* (2007).



Experimental

Crystal data

$C_{12}H_{15}N_3O_3S$
M_r = 281.33
Monoclinic, $P2_1/n$
a = 6.207 (3) Å
b = 10.878 (5) Å
c = 19.990 (9) Å
β = 96.706 (6)°
V = 1340.5 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 113 (2) K
0.40 × 0.22 × 0.20 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
Absorption correction: none
10513 measured reflections
3029 independent reflections
2622 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.102
S = 1.19
3029 reflections
183 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.85 (2)	1.82 (2)	2.590 (3)	150 (2)

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *TEXSAN*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WK2052).

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supplementary materials

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1-(4-Nitrophenyl)-3-pivaloylthiourea

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Comment

N-Aryl-*N*′-aroyl thiourea derivatives are very useful building blocks for the synthesis of a wide range of aliphatic macromolecular and heterocyclic compounds. Thus, benzothiazoles have been prepared from arylthioureas in the presence of bromine (Patil & Chedekel, 1984), and condensation of thiourea with α-halocarbonyl compounds form 2-aminothiazoles (Baily *et al.*, 1996). 2-Methylaminothiazolines have been synthesized by cyclization of *N*-(2-hydroxyethyl)-*N*'-methylthioureas (Namgun *et al.*, 2001). Thioureas are efficient guanylating agents (Maryanoff *et al.*, 1986). N, *N*-dialkyl-*N*-aroylthioureas have been efficiently used for the extraction of nickel, palladium and platinum metals (Koch, 2001). Herein, as a continuation of these studies, the structure of the title compound (I) is described, Fig. 1 & Table 1. Bond lengths and angles can be regarded as normal (Allen, 2002; Shoukat *et al.*, 2007) and show the molecule to exist in the thione form with typical thiourea C—S and C—O bonds, as well as shortened C—N bond lengths. The thiocarbonyl and carbonyl groups are almost coplanar, as reflected by the torsion angles of 3.1 (3)° for O(1)—C(2)—N(2)—C(1), -4.9 (3)° for N(1)—C(1)—N(2)—C(2). This is associated with the expected intramolecular N—H···O hydrogen bonds (Table 2)

Experimental

Freshly prepared pivaloylisothiocyanate (1.43 g, 10 mmol) was dissolved in acetone (30 ml) and stirred for 20 minutes. Neat 4-nitroaniline (1.38 g, 10 mmol) was then added and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into acidified water and stirred well. The solid product was separated and washed with deionized water and purified by recrystallization from ethanol/1,1-dichloromethane (1:1 *v/v*) to give fine crystals of (I), with an overall yield 85%.

Refinement

C-bound H atoms were included in the riding model approximation with C—H 0.95 - 0.98 Å, and with $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $U_{iso}(H) = 1.5\ U_{eq}(C_{methyl})$. The N-bound H atoms were refined isotropically, see Table 2 for distances.

Figures

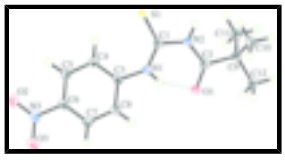

Fig. 1. Molecular structure of (I) showing atom labelling and displacement ellipsoids drawn at the 50% probability level. The hydrogen bond is shown as dashed lines.

1-(2,2-dimethylpropionyl)-3-(4-nitrophenyl)thiourea

Crystal data

$C_{12}H_{15}N_3O_3S$ $F_{000} = 592$

M_r = 281.33	D_x = 1.394 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71070 Å
Hall symbol: -P 2yn	Cell parameters from 3440 reflections
a = 6.207 (3) Å	θ = 3.1–27.5º
b = 10.878 (5) Å	μ = 0.25 mm^{-1}
c = 19.990 (9) Å	T = 113 (2) K
β = 96.706 (6)º	Block, light yellow
V = 1340.5 (10) Å^3	0.40 × 0.22 × 0.20 mm
Z = 4	

Data collection

Rigaku/MSC Mercury CCD diffractometer	3029 independent reflections
Radiation source: fine-focus sealed tube	2622 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.043
Detector resolution: 14.62 pixels mm^{-1}	θ_{max} = 27.5º
T = 113(2) K	θ_{min} = 3.3º
ω scans	h = −8→6
Absorption correction: none	k = −13→14
10513 measured reflections	l = −25→22

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.6155P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.053	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.102	$\Delta\rho_{max}$ = 0.29 e Å^{-3}
S = 1.19	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
3029 reflections	Extinction correction: none
183 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.1277 (3)	0.00927 (18)	0.57635 (9)	0.0176 (4)
S1	−0.24312 (8)	0.12580 (5)	0.53185 (3)	0.02278 (14)
N1	0.0525 (2)	0.01268 (16)	0.62050 (8)	0.0184 (3)
H1	0.088 (3)	−0.060 (2)	0.6322 (11)	0.022 (6)*
C2	−0.1402 (3)	−0.21796 (18)	0.59510 (9)	0.0179 (4)
O1	0.0266 (2)	−0.22339 (13)	0.63433 (7)	0.0222 (3)
N2	−0.2195 (2)	−0.10775 (15)	0.56787 (9)	0.0187 (4)
H2	−0.336 (3)	−0.1095 (19)	0.5394 (11)	0.019 (5)*
C3	0.1814 (3)	0.11237 (18)	0.64588 (9)	0.0175 (4)
C4	0.1056 (3)	0.23198 (19)	0.65144 (10)	0.0207 (4)
H4	−0.0403	0.2519	0.6353	0.025*
C5	0.2443 (3)	0.32160 (19)	0.68060 (10)	0.0211 (4)
H5	0.1947	0.4035	0.6848	0.025*
C6	0.4560 (3)	0.29053 (18)	0.70352 (10)	0.0185 (4)
C7	0.5339 (3)	0.17179 (19)	0.69980 (10)	0.0224 (4)
H7	0.6793	0.1522	0.7167	0.027*
C8	0.3949 (3)	0.08264 (19)	0.67092 (10)	0.0217 (4)
H8	0.4445	0.0004	0.6680	0.026*
N3	0.6011 (3)	0.38608 (16)	0.73402 (8)	0.0221 (4)
O2	0.5311 (2)	0.49171 (13)	0.73614 (7)	0.0281 (3)
O3	0.7875 (2)	0.35722 (15)	0.75618 (8)	0.0318 (4)
C9	−0.2745 (3)	−0.33191 (18)	0.57417 (10)	0.0195 (4)
C10	−0.2978 (3)	−0.34397 (19)	0.49716 (10)	0.0248 (4)
H10A	−0.3774	−0.2729	0.4768	0.037*
H10B	−0.3775	−0.4195	0.4837	0.037*
H10C	−0.1536	−0.3473	0.4819	0.037*
C11	−0.4969 (3)	−0.3203 (2)	0.60073 (11)	0.0232 (4)
H11A	−0.4758	−0.3102	0.6498	0.035*
H11B	−0.5824	−0.3947	0.5892	0.035*
H11C	−0.5740	−0.2486	0.5801	0.035*
C12	−0.1541 (3)	−0.44494 (19)	0.60566 (11)	0.0261 (5)
H12A	−0.0134	−0.4525	0.5883	0.039*
H12B	−0.2406	−0.5189	0.5940	0.039*
H12C	−0.1316	−0.4356	0.6547	0.039*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0178 (9)	0.0195 (10)	0.0159 (10)	−0.0011 (7)	0.0032 (7)	−0.0016 (8)

S1	0.0226 (2)	0.0190 (3)	0.0248 (3)	−0.00128 (19)	−0.00565 (18)	0.0035 (2)
N1	0.0184 (8)	0.0156 (9)	0.0202 (9)	0.0010 (6)	−0.0023 (6)	0.0008 (7)
C2	0.0172 (9)	0.0200 (10)	0.0172 (10)	0.0014 (7)	0.0045 (7)	0.0004 (8)
O1	0.0186 (7)	0.0219 (8)	0.0247 (8)	0.0006 (5)	−0.0035 (5)	0.0034 (6)
N2	0.0157 (8)	0.0180 (9)	0.0210 (9)	−0.0005 (6)	−0.0035 (6)	0.0015 (7)
C3	0.0176 (8)	0.0194 (10)	0.0152 (10)	−0.0021 (7)	0.0009 (7)	0.0011 (8)
C4	0.0181 (9)	0.0214 (11)	0.0218 (11)	0.0029 (7)	−0.0009 (7)	−0.0002 (8)
C5	0.0234 (9)	0.0190 (10)	0.0205 (11)	0.0007 (8)	0.0012 (8)	−0.0006 (8)
C6	0.0197 (9)	0.0213 (10)	0.0147 (10)	−0.0048 (7)	0.0018 (7)	−0.0004 (8)
C7	0.0183 (9)	0.0243 (11)	0.0238 (11)	−0.0001 (8)	−0.0014 (7)	0.0018 (9)
C8	0.0213 (9)	0.0197 (10)	0.0231 (11)	0.0027 (8)	−0.0010 (7)	0.0017 (8)
N3	0.0241 (8)	0.0240 (10)	0.0184 (9)	−0.0056 (7)	0.0026 (6)	−0.0001 (7)
O2	0.0351 (8)	0.0205 (8)	0.0284 (9)	−0.0052 (6)	0.0028 (6)	−0.0031 (6)
O3	0.0215 (7)	0.0356 (9)	0.0363 (9)	−0.0054 (6)	−0.0046 (6)	−0.0037 (7)
C9	0.0188 (9)	0.0189 (10)	0.0206 (10)	−0.0011 (7)	0.0013 (7)	0.0005 (8)
C10	0.0296 (10)	0.0192 (11)	0.0253 (12)	−0.0028 (8)	0.0026 (8)	−0.0033 (9)
C11	0.0198 (9)	0.0237 (11)	0.0264 (12)	−0.0026 (8)	0.0035 (8)	0.0020 (9)
C12	0.0257 (10)	0.0174 (11)	0.0347 (13)	0.0003 (8)	0.0010 (9)	0.0027 (9)

Geometric parameters (Å, °)

C1—N1	1.342 (2)	C7—C8	1.379 (3)
C1—N2	1.397 (2)	C7—H7	0.9500
C1—S1	1.662 (2)	C8—H8	0.9500
N1—C3	1.407 (2)	N3—O3	1.230 (2)
N1—H1	0.85 (2)	N3—O2	1.231 (2)
C2—O1	1.225 (2)	C9—C10	1.535 (3)
C2—N2	1.383 (3)	C9—C12	1.535 (3)
C2—C9	1.525 (3)	C9—C11	1.541 (3)
N2—H2	0.86 (2)	C10—H10A	0.9800
C3—C4	1.392 (3)	C10—H10B	0.9800
C3—C8	1.399 (3)	C10—H10C	0.9800
C4—C5	1.384 (3)	C11—H11A	0.9800
C4—H4	0.9500	C11—H11B	0.9800
C5—C6	1.382 (3)	C11—H11C	0.9800
C5—H5	0.9500	C12—H12A	0.9800
C6—C7	1.384 (3)	C12—H12B	0.9800
C6—N3	1.461 (2)	C12—H12C	0.9800
N1—C1—N2	113.70 (17)	C3—C8—H8	119.7
N1—C1—S1	127.24 (15)	O3—N3—O2	123.14 (17)
N2—C1—S1	119.06 (14)	O3—N3—C6	118.48 (17)
C1—N1—C3	130.83 (17)	O2—N3—C6	118.39 (16)
C1—N1—H1	109.0 (15)	C2—C9—C10	109.23 (16)
C3—N1—H1	120.2 (15)	C2—C9—C12	108.32 (15)
O1—C2—N2	121.93 (18)	C10—C9—C12	109.11 (17)
O1—C2—C9	122.04 (18)	C2—C9—C11	108.78 (16)
N2—C2—C9	116.02 (16)	C10—C9—C11	111.65 (16)
C2—N2—C1	128.37 (16)	C12—C9—C11	109.69 (17)
C2—N2—H2	118.1 (14)	C9—C10—H10A	109.5

C1—N2—H2	113.4 (14)	C9—C10—H10B	109.5
C4—C3—C8	120.16 (18)	H10A—C10—H10B	109.5
C4—C3—N1	124.45 (17)	C9—C10—H10C	109.5
C8—C3—N1	115.22 (17)	H10A—C10—H10C	109.5
C5—C4—C3	119.49 (18)	H10B—C10—H10C	109.5
C5—C4—H4	120.3	C9—C11—H11A	109.5
C3—C4—H4	120.3	C9—C11—H11B	109.5
C6—C5—C4	119.23 (19)	H11A—C11—H11B	109.5
C6—C5—H5	120.4	C9—C11—H11C	109.5
C4—C5—H5	120.4	H11A—C11—H11C	109.5
C5—C6—C7	122.34 (18)	H11B—C11—H11C	109.5
C5—C6—N3	118.71 (18)	C9—C12—H12A	109.5
C7—C6—N3	118.94 (17)	C9—C12—H12B	109.5
C8—C7—C6	118.25 (18)	H12A—C12—H12B	109.5
C8—C7—H7	120.9	C9—C12—H12C	109.5
C6—C7—H7	120.9	H12A—C12—H12C	109.5
C7—C8—C3	120.50 (19)	H12B—C12—H12C	109.5
C7—C8—H8	119.7		
N2—C1—N1—C3	−175.10 (18)	N3—C6—C7—C8	179.96 (17)
S1—C1—N1—C3	6.2 (3)	C6—C7—C8—C3	0.3 (3)
O1—C2—N2—C1	3.1 (3)	C4—C3—C8—C7	−1.6 (3)
C9—C2—N2—C1	−177.76 (18)	N1—C3—C8—C7	−177.15 (18)
N1—C1—N2—C2	−4.9 (3)	C5—C6—N3—O3	177.85 (18)
S1—C1—N2—C2	173.91 (15)	C7—C6—N3—O3	−0.9 (3)
C1—N1—C3—C4	27.2 (3)	C5—C6—N3—O2	−2.3 (3)
C1—N1—C3—C8	−157.51 (19)	C7—C6—N3—O2	178.91 (18)
C8—C3—C4—C5	1.4 (3)	O1—C2—C9—C10	−123.10 (19)
N1—C3—C4—C5	176.48 (18)	N2—C2—C9—C10	57.8 (2)
C3—C4—C5—C6	0.2 (3)	O1—C2—C9—C12	−4.4 (2)
C4—C5—C6—C7	−1.5 (3)	N2—C2—C9—C12	176.48 (16)
C4—C5—C6—N3	179.80 (17)	O1—C2—C9—C11	114.8 (2)
C5—C6—C7—C8	1.3 (3)	N2—C2—C9—C11	−64.3 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.85 (2)	1.82 (2)	2.590 (3)	150 (2)

Fig. 1