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1-(3-Bromophenyl)-3-pivaloylthiourea

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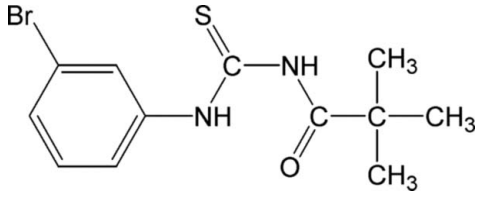
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.006 Å; disorder in main residue; R factor = 0.041; wR factor = 0.082; data-to-parameter ratio = 16.3.

The crystal structure of the title compound, $C_{12}H_{15}BrN_2OS$, is composed of discrete molecules with bond lengths and angles quite typical for thiourea compounds of this class. The molecule exists in the solid state in its thione form with typical thiourea C—S and C—O bonds lengths, as well as shortened C—N bonds. Stabilized by an intramolecular N—H···O hydrogen bond, the thiocarbonyl and carbonyl groups are almost coplanar. The three methyl groups are disordered over two positions with occupancy factors in an approximate 4:1 ratio.

Related literature

For related literature, see: Shoukat *et al.* (2007); Khawar Rauf *et al.* (2006); Allen (2002).



Experimental

Crystal data

$C_{12}H_{15}BrN_2OS$
M_r = 315.23
Orthorhombic, $P2_12_12_1$
a = 6.188 (4) Å
b = 10.250 (7) Å
c = 21.268 (14) Å
V = 1348.9 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.19 mm^{-1}
T = 113 (2) K
0.51 × 0.42 × 0.21 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
Absorption correction: integration (*NUMABS*; Higashi, 1999)
T_{min} = 0.537, T_{max} = 0.715
10869 measured reflections
3073 independent reflections
2965 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.082
S = 1.21
3073 reflections
189 parameters
66 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Absolute structure: Flack (1983), 1275 Friedel pairs
Flack parameter: 0.012 (12)

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.334 (5)	N1—C3	1.439 (5)
C1—N2	1.399 (5)	C2—O1	1.224 (5)
C1—S1	1.674 (4)	C2—N2	1.381 (5)
O1—C2—N2—C1	0.5 (7)	N1—C1—N2—C2	−5.8 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.88	1.88	2.586 (5)	136

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, 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: ZL2018).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Khawar Rauf, M., Badshah, A. & Flörke, U. (2006). *Acta Cryst.* E**62**, o3823–o3825.
Molecular Structure Corporation & Rigaku (2001). *CrystalClear*. Version 1.3. MSC, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
Molecular Structure Corporation & Rigaku (2004). *TEXSAN*. Version 2.0. MSC, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Shoukat, N., Khawar Rauf, M., Bolte, M. & Badshah, A. (2007). *Acta Cryst.* E**63**, o920–o922.

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supplementary materials

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1-(3-Bromophenyl)-3-pivaloylthiourea

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Comment

The background to this study has been set out in our previous work for the structural chemistry of *N*,*N*′-disubstituted thioureas (Shoukat *et al.*, 2007). Herein, as a continuation of these studies, the structure of the title compound (I) is described. A depiction of the molecule is given in Fig. 1. Bond lengths and angles, see the selected geometric parameters table, can be regarded as typical for *N*,*N*′-disubstituted thiourea compounds as found in the Cambridge Structural Database v5.28 (Allen, 2002; Khawar Rauf *et al.*, 2006). The molecule exists in its thione form with typical thiourea C—S and C—O bond distances, as well as shortened C—N bonds (See selected geometric parameters table). The molecule also features an intramolecular N—H···O hydrogen bond (See hydrogen-bond geometry table) which stears the thiocarbonyl and carbonyl groups to be almost coplanar, as reflected by the torsion angles of 0.5 (7)° for O(1)—C(2)—N(2)—C(1) and -5.8 (6)° for N(1)—C(1)—N(2)—C(2). The plane containing the S1, O1, N1, N2, C1 & C2 atoms is almost perpendicular to the phenyl ring with a dihedral angle of 86.13 (11)°.

Experimental

Freshly prepared pivaloylisothiocyanate (1.43 g, 10 mmol) in acetone (30 ml) was stirred for 15 minutes. Neat 3-bromoaniline (1.72 g, 10 mmol) was then added and the resulting mixture was stirred for 1 h. The reaction mixture was poured into acidified water and stirred well. The solid product was separated and washed with deionized water and purified by recrystallization from methanol/ 1,1-dichloromethane (1:1 *v/v*) to give fine crystals of (I), with an overall yield of 85%.

Refinement

The C atoms of the *t*-butyl group were found to be disordered over two sites and were refined using similarity restraints (DELU and SIMU). Refinement of the occupancies converged to 0.819 (12) for C10 to C12 and 0.191 (12) for C13 to C15. H atoms were included using the riding model approximation with N—H 0.88 and C—H 0.95 - 0.98 Å, and with U_{iso}(H) = 1.2 U_{eq}(C and N) or U_{iso}(H) = 1.5 U_{eq}(C_{methyl}).

Figures

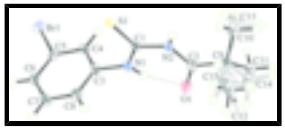

Fig. 1. The molecular structure of (I) showing the atom labelling scheme. Thermal displacement ellipsoids are drawn at the 50% probability level. The hydrogen bond is shown as a dashed line and the white/unfilled bonds depict the minor disordered moiety of the *t*-butyl group.

1-(3-Bromophenyl)-3-pivaloylthiourea

Crystal data

$C_{12}H_{15}BrN_2OS$	F_{000} = 640
M_r = 315.23	D_x = 1.552 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71070 Å
Hall symbol: P 2ac 2ab	Cell parameters from 4509 reflections
a = 6.188 (4) Å	θ = 3.3–27.5º
b = 10.250 (7) Å	μ = 3.19 mm^{-1}
c = 21.268 (14) Å	T = 113 (2) K
V = 1348.9 (15) Å^3	Block, colorless
Z = 4	0.51 × 0.42 × 0.21 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer	3073 independent reflections
Monochromator: graphite	2965 reflections with $I > 2\sigma(I)$
Detector resolution: 14.62 pixels mm^{-1}	R_{int} = 0.051
T = 113(2) K	θ_{max} = 27.5º
ω scans	θ_{min} = 3.4º
Absorption correction: integration (NUMABS; Higashi, 1999)	h = −8→5
T_{min} = 0.537, T_{max} = 0.715	k = −13→12
10869 measured reflections	l = −26→27

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.042	$w = 1/[\sigma^2(F_o^2) + 2.2104P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.082	$(\Delta/\sigma)_{max}$ = 0.003
S = 1.21	$\Delta\rho_{max}$ = 0.66 e Å^{-3}
3073 reflections	$\Delta\rho_{min}$ = −0.45 e Å^{-3}
189 parameters	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
66 restraints	Extinction coefficient: 0.0030 (8)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1275 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.012 (12)

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}	Occ. (<1)
C1	0.6304 (6)	0.3939 (4)	0.97247 (17)	0.0152 (7)	
S1	0.70985 (18)	0.32987 (9)	1.04111 (5)	0.0182 (2)	
N1	0.4986 (5)	0.4961 (3)	0.96633 (15)	0.0172 (7)	
H1	0.4677	0.5232	0.9281	0.021*	
C2	0.6416 (7)	0.3735 (4)	0.85578 (18)	0.0191 (8)	
O1	0.5088 (6)	0.4596 (3)	0.84607 (13)	0.0300 (8)	
N2	0.7040 (6)	0.3399 (3)	0.91598 (15)	0.0156 (7)	
H2	0.8010	0.2774	0.9192	0.019*	
C3	0.4040 (7)	0.5643 (4)	1.01863 (18)	0.0176 (8)	
C4	0.5135 (6)	0.6714 (3)	1.04368 (18)	0.0166 (8)	
H4	0.6531	0.6954	1.0291	0.020*	
C5	0.4098 (7)	0.7419 (3)	1.09107 (18)	0.0174 (8)	
C6	0.2083 (7)	0.7088 (4)	1.11360 (18)	0.0201 (8)	
H6	0.1426	0.7581	1.1463	0.024*	
C7	0.1024 (7)	0.6014 (4)	1.08742 (19)	0.0223 (9)	
H7	−0.0371	0.5776	1.1021	0.027*	
C8	0.2004 (8)	0.5286 (4)	1.03973 (19)	0.0203 (8)	
H8	0.1283	0.4555	1.0220	0.024*	
Br1	0.55861 (7)	0.88797 (4)	1.125472 (19)	0.02269 (12)	
C9	0.7379 (8)	0.2956 (4)	0.80096 (19)	0.0210 (8)	
C10	0.9613 (13)	0.2404 (8)	0.8134 (3)	0.0386 (17)	0.819 (12)
H10A	1.0588	0.3110	0.8261	0.058*	0.819 (12)
H10B	1.0166	0.1992	0.7751	0.058*	0.819 (12)
H10C	0.9530	0.1753	0.8471	0.058*	0.819 (12)
C11	0.7487 (14)	0.3872 (6)	0.7432 (3)	0.0330 (15)	0.819 (12)
H11A	0.8357	0.4642	0.7535	0.049*	0.819 (12)
H11B	0.6023	0.4146	0.7316	0.049*	0.819 (12)
H11C	0.8151	0.3408	0.7078	0.049*	0.819 (12)
C12	0.5761 (14)	0.1849 (6)	0.7871 (3)	0.0336 (15)	0.819 (12)
H12A	0.6288	0.1327	0.7517	0.050*	0.819 (12)
H12B	0.4351	0.2225	0.7764	0.050*	0.819 (12)
H12C	0.5615	0.1293	0.8243	0.050*	0.819 (12)
C13	0.995 (5)	0.303 (3)	0.8023 (15)	0.030 (3)	0.181 (12)

H13A	1.0447	0.3064	0.8460	0.045*	0.181 (12)
H13B	1.0432	0.3809	0.7799	0.045*	0.181 (12)
H13C	1.0547	0.2249	0.7819	0.045*	0.181 (12)
C14	0.645 (6)	0.350 (3)	0.7436 (13)	0.028 (3)	0.181 (12)
H14A	0.6911	0.4404	0.7386	0.042*	0.181 (12)
H14B	0.4866	0.3461	0.7462	0.042*	0.181 (12)
H14C	0.6935	0.2984	0.7073	0.042*	0.181 (12)
C15	0.650 (6)	0.160 (3)	0.8086 (16)	0.033 (3)	0.181 (12)
H15A	0.6254	0.1212	0.7671	0.049*	0.181 (12)
H15B	0.5132	0.1633	0.8318	0.049*	0.181 (12)
H15C	0.7541	0.1065	0.8320	0.049*	0.181 (12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0096 (17)	0.0164 (15)	0.0195 (18)	−0.0053 (15)	0.0030 (13)	0.0002 (16)
S1	0.0173 (5)	0.0204 (4)	0.0171 (5)	0.0018 (4)	−0.0001 (4)	0.0012 (4)
N1	0.0178 (19)	0.0157 (14)	0.0182 (16)	0.0035 (12)	0.0013 (13)	−0.0010 (12)
C2	0.019 (2)	0.0200 (18)	0.0186 (19)	−0.0002 (16)	0.0028 (15)	−0.0007 (15)
O1	0.037 (2)	0.0329 (16)	0.0199 (15)	0.0177 (14)	−0.0019 (13)	−0.0036 (12)
N2	0.0150 (17)	0.0140 (13)	0.0177 (16)	0.0019 (13)	0.0001 (14)	−0.0034 (12)
C3	0.022 (2)	0.0170 (15)	0.0137 (18)	0.0051 (15)	0.0039 (16)	0.0008 (14)
C4	0.014 (2)	0.0164 (16)	0.0193 (18)	0.0037 (14)	0.0029 (15)	0.0028 (15)
C5	0.021 (2)	0.0158 (16)	0.0152 (18)	0.0016 (16)	−0.0041 (17)	−0.0010 (14)
C6	0.020 (2)	0.0239 (18)	0.017 (2)	0.0050 (16)	0.0047 (17)	−0.0005 (15)
C7	0.020 (2)	0.0239 (19)	0.023 (2)	−0.0046 (18)	0.0061 (16)	0.0000 (17)
C8	0.024 (2)	0.0168 (18)	0.020 (2)	−0.0010 (16)	0.0006 (18)	−0.0021 (15)
Br1	0.0280 (2)	0.01807 (17)	0.02199 (19)	−0.00228 (18)	−0.00135 (19)	−0.00341 (17)
C9	0.027 (2)	0.0192 (16)	0.0172 (18)	0.0047 (15)	−0.0005 (16)	−0.0038 (14)
C10	0.034 (3)	0.057 (4)	0.025 (3)	0.019 (3)	−0.003 (3)	−0.016 (3)
C11	0.052 (4)	0.023 (2)	0.024 (2)	0.009 (3)	0.014 (3)	0.001 (2)
C12	0.039 (3)	0.032 (3)	0.030 (3)	−0.009 (3)	0.004 (3)	−0.009 (2)
C13	0.028 (4)	0.039 (7)	0.024 (7)	0.006 (5)	−0.001 (5)	−0.009 (7)
C14	0.036 (7)	0.031 (6)	0.018 (5)	0.018 (6)	0.002 (6)	−0.008 (5)
C15	0.044 (7)	0.025 (5)	0.029 (7)	−0.003 (5)	0.004 (7)	−0.009 (5)

Geometric parameters (Å, °)

C1—N1	1.334 (5)	C9—C10	1.517 (8)
C1—N2	1.399 (5)	C9—C12	1.542 (8)
C1—S1	1.674 (4)	C9—C11	1.548 (7)
N1—C3	1.439 (5)	C9—C13	1.59 (3)
N1—H1	0.8800	C10—H10A	0.9800
C2—O1	1.224 (5)	C10—H10B	0.9800
C2—N2	1.381 (5)	C10—H10C	0.9800
C2—C9	1.533 (5)	C11—H11A	0.9800
N2—H2	0.8800	C11—H11B	0.9800
C3—C8	1.387 (6)	C11—H11C	0.9800
C3—C4	1.396 (5)	C12—H12A	0.9800

C4—C5	1.396 (5)	C12—H12B	0.9800
C4—H4	0.9500	C12—H12C	0.9800
C5—C6	1.378 (6)	C13—H13A	0.9800
C5—Br1	1.904 (4)	C13—H13B	0.9800
C6—C7	1.397 (6)	C13—H13C	0.9800
C6—H6	0.9500	C14—H14A	0.9800
C7—C8	1.397 (6)	C14—H14B	0.9800
C7—H7	0.9500	C14—H14C	0.9800
C8—H8	0.9500	C15—H15A	0.9800
C9—C14	1.46 (3)	C15—H15B	0.9800
C9—C15	1.50 (3)	C15—H15C	0.9800
N1—C1—N2	115.2 (3)	C2—C9—C12	106.0 (4)
N1—C1—S1	124.9 (3)	C10—C9—C11	109.0 (5)
N2—C1—S1	119.9 (3)	C2—C9—C11	107.8 (4)
C1—N1—C3	123.7 (3)	C12—C9—C11	108.8 (4)
C1—N1—H1	118.1	C14—C9—C13	113.1 (17)
C3—N1—H1	118.1	C15—C9—C13	113.7 (18)
O1—C2—N2	121.6 (4)	C2—C9—C13	110.6 (11)
O1—C2—C9	120.5 (4)	C9—C10—H10A	109.5
N2—C2—C9	117.8 (3)	C9—C10—H10B	109.5
C2—N2—C1	127.3 (3)	C9—C10—H10C	109.5
C2—N2—H2	116.3	C9—C11—H11A	109.5
C1—N2—H2	116.3	C9—C11—H11B	109.5
C8—C3—C4	121.7 (4)	C9—C11—H11C	109.5
C8—C3—N1	119.4 (4)	C9—C12—H12A	109.5
C4—C3—N1	118.7 (4)	C9—C12—H12B	109.5
C3—C4—C5	117.3 (4)	C9—C12—H12C	109.5
C3—C4—H4	121.3	C9—C13—H13A	109.5
C5—C4—H4	121.3	C9—C13—H13B	109.5
C6—C5—C4	122.6 (4)	H13A—C13—H13B	109.5
C6—C5—Br1	119.8 (3)	C9—C13—H13C	109.5
C4—C5—Br1	117.5 (3)	H13A—C13—H13C	109.5
C5—C6—C7	118.7 (4)	H13B—C13—H13C	109.5
C5—C6—H6	120.7	C9—C14—H14A	109.5
C7—C6—H6	120.7	C9—C14—H14B	109.5
C6—C7—C8	120.5 (4)	H14A—C14—H14B	109.5
C6—C7—H7	119.8	C9—C14—H14C	109.5
C8—C7—H7	119.8	H14A—C14—H14C	109.5
C3—C8—C7	119.2 (4)	H14B—C14—H14C	109.5
C3—C8—H8	120.4	C9—C15—H15A	109.5
C7—C8—H8	120.4	C9—C15—H15B	109.5
C14—C9—C15	107.3 (18)	H15A—C15—H15B	109.5
C14—C9—C2	106.6 (11)	C9—C15—H15C	109.5
C15—C9—C2	105.0 (12)	H15A—C15—H15C	109.5
C10—C9—C2	114.6 (4)	H15B—C15—H15C	109.5
C10—C9—C12	110.5 (5)		
N2—C1—N1—C3	179.3 (3)	C4—C3—C8—C7	−0.2 (6)
S1—C1—N1—C3	−0.9 (5)	N1—C3—C8—C7	−175.3 (4)

O1—C2—N2—C1	0.5 (7)	C6—C7—C8—C3	0.0 (6)
C9—C2—N2—C1	−177.3 (4)	O1—C2—C9—C14	1.7 (17)
N1—C1—N2—C2	−5.8 (6)	N2—C2—C9—C14	179.5 (17)
S1—C1—N2—C2	174.4 (3)	O1—C2—C9—C15	−112.0 (17)
C1—N1—C3—C8	−93.5 (5)	N2—C2—C9—C15	65.8 (17)
C1—N1—C3—C4	91.3 (4)	O1—C2—C9—C10	153.2 (5)
C8—C3—C4—C5	−0.1 (6)	N2—C2—C9—C10	−29.0 (6)
N1—C3—C4—C5	175.0 (3)	O1—C2—C9—C12	−84.6 (6)
C3—C4—C5—C6	0.6 (6)	N2—C2—C9—C12	93.2 (5)
C3—C4—C5—Br1	179.9 (3)	O1—C2—C9—C11	31.7 (6)
C4—C5—C6—C7	−0.8 (6)	N2—C2—C9—C11	−150.5 (5)
Br1—C5—C6—C7	179.9 (3)	O1—C2—C9—C13	125.0 (14)
C5—C6—C7—C8	0.5 (6)	N2—C2—C9—C13	−57.2 (14)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.88	1.88	2.586 (5)	136

Fig. 1