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3-(2-Hydroxyethyl)-3-methyl-1-(4-methylbenzoyl)thiourea

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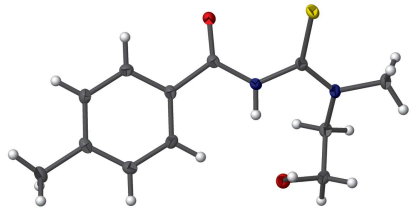
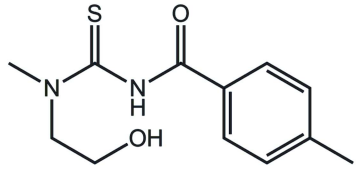
Structural data: full structural data are available from iucrdata.iucr.org

The title thiourea derivative, $C_{12}H_{16}N_2O_2S$, has a twisted conformation with the dihedral angle between the NC(=S)N and O=CC_6 planes being 35.45 (5)°. The observed conformation allows for an intramolecular N—H···O hydrogen bond. In the molecular packing, supramolecular aggregation is based on hydroxy-O—H···O(carbonyl) hydrogen bonding and leads to supramolecular helical chains along the *a* axis; chains are reinforced by *N*-methylene-C—H···S and *N*-methyl-C—H···π(arene) interactions. Supramolecular layers in the *ab* plane are formed as a result of tolyl-methyl-C—H···π(arene) interactions.

3D view



Chemical scheme



Structure description

Interest in the title compound arises from promising cytotoxicity profiles exhibited by palladium(II) (Selvakumaran *et al.*, 2011) and copper(I) (Rauf *et al.*, 2009) complexes of related *N*,*N*-di(alkyl/aryl)-*N*′-benzoylthiourea derivatives. The molecular structure of the title compound, Fig. 1, comprises planar NC(=S)N (r.m.s. deviation = 0.0130 Å) and O=CC_6 (r.m.s. deviation = 0.0068 Å) residues which form a dihedral angle of 35.45 (5)°. The N1—C2—C3—O1 torsion of 66.9 (2)° places the hydroxy-O1 atom in close proximity to the amide enabling the formation of an intramolecular N2—H···O1 hydrogen bond, Table 1.

In the crystal, supramolecular helical chains are formed along the *a* axis and are sustained by a combination of hydroxy-O—H···O(carbonyl) hydrogen bonding, and N-methylene-C—H···S and N-methyl-C—H···π(arene) interactions. Connections between the chains are of the type tolyl-methyl-C—H···π(arene) and occur along the *b* axis

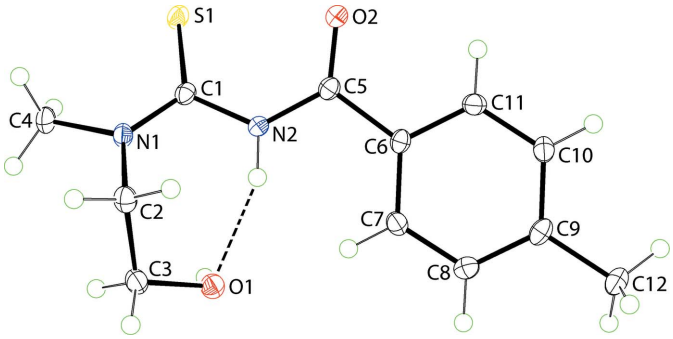


Figure 1
The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. The dashed line represents the intramolecular N—H···O hydrogen bond.

resulting in a supramolecular layer, Fig. 2. The layers pack along the *c* axis with no directional interactions between them.

The most closely related molecule in the literature, *i.e.* with *N*-ethyl, rather than *N*-methyl, and 2-tolyl rather than 4-tolyl (Yamin *et al.*, 2014), has an almost identical conformation with the exception of the relative orientation of the tolyl rings. Thus, the dihedral angle between the NC(=S)N and O=CC$_6$ planes in the literature structure is 22.75 (5)° *cf.* 35.45 (5)° in the title compound. The molecular packing differs also in that although hydroxy-O—H···O(carbonyl) hydrogen bonding persist, they lead to zigzag chains (glide symmetry).

Synthesis and crystallization

A procedure based on a literature precedent (Rauf *et al.*, 2009) was employed in the synthesis of the title compound. Thus, an excess of thionyl chloride was mixed with 4-methylbenzoic acid (1 mmol) and the solution refluxed until a pale-yellow solution was obtained. The excess thionyl chloride was removed on a water bath, leaving only 4-methylbenzoyl chloride, which is a viscous, yellow liquid. Ammonium thiocyanate (1 mmol) was added to a stirred acetone solution of 4-methylbenzoyl chloride (1 mmol), yielding a pink solution which turned yellow upon stirring for 2 h. The white precipitate (ammonium chloride) was isolated upon filtration and to the yellow filtrate, *N*-methyl-*N*-(hydroxyethyl)amine was carefully added and stirring continued for another 1 h. Upon the addition of water, a yellow precipitate was obtained. This was collected by filtration and recrystallized from hot acetone solution, yielding yellow blocks.

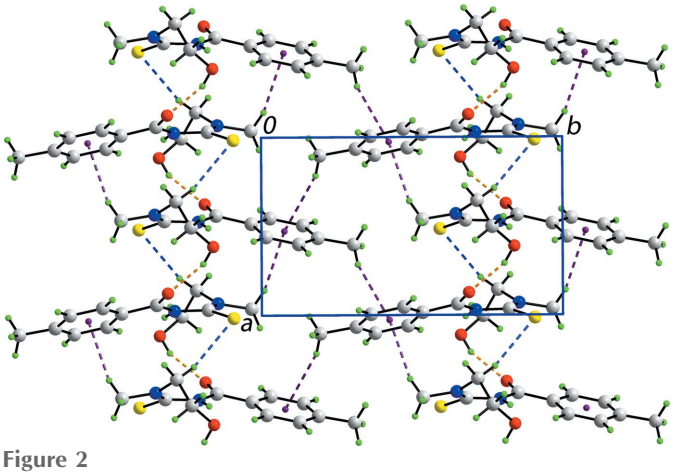


Figure 2
A view of the supramolecular layer in the *ab* plane in the crystal structure of the title compound shown in projection down the *c* axis. The O—H···O, C—H···S and C—H···π interactions are shown as orange, blue and purple dashed lines, respectively.

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

*Cg*1 is the centroid of the C6–C11 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···O1	0.87 (2)	2.02 (2)	2.838 (3)	157 (2)
O1—H1*O*···O2^{i}	0.84 (2)	1.95 (2)	2.750 (2)	160 (2)
C2—H2*B*···S1^{ii}	0.97	2.83	3.783 (3)	167
C4—H4*B*···*Cg*1^{iii}	0.96	2.67	3.605 (3)	164
C12—H12*A*···*Cg*1^{iv}	0.96	3.00	3.932 (3)	164

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

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{16}N_2O_2S$
M_r	252.33
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, *b*, *c* (Å)	7.351 (3), 12.452 (4), 13.423 (5)
V (Å^3)	1228.8 (7)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.26
Crystal size (mm)	0.20 × 0.16 × 0.15
Data collection	
Diffractometer	Bruker SMART APEX diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.951, 0.963
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7036, 2790, 2637
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.031, 0.073, 1.02
No. of reflections	2790
No. of parameters	162
No. of restraints	2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.25
Absolute structure	Flack *x* determined using 1054 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.10 (4)

Computer programs: *SMART* (Bruker, 2009), *SAINT* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006), *publCIF* (Westrip, 2010).

Acknowledgements

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full crystallographic data

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Crystal data

$C_{12}H_{16}N_2O_2S$
$M_r = 252.33$
Orthorhombic, $P2_12_12_1$
$a = 7.351$ (3) Å
$b = 12.452$ (4) Å
$c = 13.423$ (5) Å
$V = 1228.8$ (7) Å^3
$Z = 4$
$F(000) = 536$
$D_x = 1.364$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2964 reflections
$\theta = 2.2$–$29.9°$
$\mu = 0.26$ mm^{-1}
$T = 296$ K
Block, yellow
0.20 × 0.16 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.951$, $T_{max} = 0.963$
7036 measured reflections
2790 independent reflections
2637 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.2°$
$h = -9\rightarrow9$
$k = -16\rightarrow16$
$l = -17\rightarrow10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.073$
$S = 1.02$
2790 reflections
162 parameters
2 restraints
Hydrogen site location: mixed
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.2556P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Absolute structure: Flack *x* determined using 1054 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.10 (4)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	1.01508 (8)	0.90725 (4)	0.57485 (4)	0.01773 (14)
O1	1.1122 (2)	0.66072 (11)	0.30188 (12)	0.0179 (3)
H1O	1.208 (3)	0.6932 (19)	0.3173 (19)	0.027*
O2	0.8730 (2)	0.68828 (12)	0.65388 (11)	0.0188 (3)
N1	0.9313 (2)	0.85435 (14)	0.38890 (14)	0.0151 (4)
N2	0.9723 (3)	0.71025 (12)	0.49351 (13)	0.0154 (4)
H2N	1.007 (3)	0.6768 (17)	0.4400 (12)	0.019*
C1	0.9672 (3)	0.82250 (15)	0.48229 (15)	0.0143 (4)
C2	0.8567 (3)	0.78372 (17)	0.31094 (16)	0.0170 (5)
H2A	0.7743	0.8249	0.2694	0.020*
H2B	0.7871	0.7268	0.3422	0.020*
C3	1.0032 (3)	0.73413 (16)	0.24575 (15)	0.0183 (4)
H3B	0.9468	0.6965	0.1905	0.022*
H3C	1.0798	0.7904	0.2187	0.022*
C4	0.9624 (3)	0.96612 (16)	0.35912 (17)	0.0190 (5)
H4A	1.0689	0.9931	0.3921	0.028*
H4B	0.8590	1.0089	0.3774	0.028*
H4C	0.9797	0.9696	0.2883	0.028*
C5	0.9380 (3)	0.65102 (16)	0.57733 (17)	0.0142 (4)
C6	0.9851 (3)	0.53401 (15)	0.57083 (16)	0.0140 (4)
C7	1.0600 (3)	0.48527 (17)	0.48678 (16)	0.0158 (4)
H7	1.0827	0.5258	0.4299	0.019*
C8	1.1007 (3)	0.37630 (16)	0.48775 (17)	0.0172 (5)
H8	1.1518	0.3448	0.4315	0.021*
C9	1.0662 (3)	0.31339 (16)	0.57154 (18)	0.0164 (4)
C10	0.9946 (3)	0.36278 (16)	0.65533 (16)	0.0170 (4)
H10	0.9732	0.3224	0.7124	0.020*
C11	0.9544 (3)	0.47186 (16)	0.65537 (17)	0.0161 (4)
H11	0.9066	0.5036	0.7124	0.019*
C12	1.1028 (3)	0.19392 (16)	0.56988 (19)	0.0201 (5)
H12A	1.2151	0.1804	0.5356	0.030*
H12B	1.0053	0.1579	0.5360	0.030*
H12C	1.1113	0.1676	0.6370	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0235 (3)	0.0120 (2)	0.0178 (3)	0.0004 (2)	−0.0022 (3)	−0.00127 (19)
O1	0.0193 (8)	0.0168 (8)	0.0176 (8)	−0.0015 (6)	−0.0009 (7)	0.0000 (6)
O2	0.0250 (8)	0.0139 (7)	0.0177 (8)	0.0026 (6)	0.0046 (7)	0.0007 (6)
N1	0.0182 (9)	0.0122 (8)	0.0148 (9)	0.0000 (7)	−0.0014 (7)	0.0019 (7)
N2	0.0218 (10)	0.0111 (7)	0.0134 (8)	0.0009 (7)	0.0018 (8)	−0.0009 (6)
C1	0.0124 (10)	0.0130 (9)	0.0175 (10)	0.0009 (8)	0.0014 (8)	0.0008 (8)
C2	0.0178 (10)	0.0165 (10)	0.0167 (12)	−0.0017 (8)	−0.0040 (9)	0.0012 (8)
C3	0.0242 (11)	0.0165 (9)	0.0142 (10)	−0.0019 (9)	−0.0018 (10)	0.0014 (7)

C4	0.0237 (12)	0.0131 (9)	0.0202 (11)	0.0003 (9)	0.0022 (10)	0.0053 (8)
C5	0.0132 (9)	0.0131 (9)	0.0163 (10)	0.0006 (7)	−0.0016 (9)	−0.0003 (8)
C6	0.0131 (9)	0.0125 (8)	0.0163 (10)	0.0001 (8)	−0.0023 (10)	0.0011 (7)
C7	0.0184 (11)	0.0159 (9)	0.0132 (11)	−0.0026 (8)	−0.0009 (9)	0.0014 (8)
C8	0.0177 (11)	0.0169 (10)	0.0170 (12)	0.0008 (8)	−0.0006 (9)	−0.0028 (8)
C9	0.0136 (9)	0.0122 (9)	0.0234 (11)	−0.0003 (7)	−0.0043 (9)	−0.0013 (9)
C10	0.0179 (10)	0.0151 (9)	0.0182 (10)	0.0001 (9)	0.0005 (10)	0.0037 (8)
C11	0.0165 (10)	0.0167 (9)	0.0150 (10)	0.0003 (8)	0.0017 (9)	−0.0014 (8)
C12	0.0218 (11)	0.0129 (9)	0.0257 (12)	0.0016 (8)	0.0003 (10)	0.0003 (10)

Geometric parameters (Å, º)

S1—C1	1.668 (2)	C4—H4C	0.9600
O1—C3	1.430 (3)	C5—C6	1.500 (3)
O1—H1O	0.838 (13)	C6—C11	1.392 (3)
O2—C5	1.225 (3)	C6—C7	1.394 (3)
N1—C1	1.341 (3)	C7—C8	1.390 (3)
N1—C4	1.466 (3)	C7—H7	0.9300
N1—C2	1.473 (3)	C8—C9	1.394 (3)
N2—C5	1.369 (3)	C8—H8	0.9300
N2—C1	1.406 (2)	C9—C10	1.386 (3)
N2—H2N	0.868 (12)	C9—C12	1.512 (3)
C2—C3	1.518 (3)	C10—C11	1.390 (3)
C2—H2A	0.9700	C10—H10	0.9300
C2—H2B	0.9700	C11—H11	0.9300
C3—H3B	0.9700	C12—H12A	0.9600
C3—H3C	0.9700	C12—H12B	0.9600
C4—H4A	0.9600	C12—H12C	0.9600
C4—H4B	0.9600		
C3—O1—H1O	107.1 (18)	O2—C5—N2	123.87 (18)
C1—N1—C4	120.34 (18)	O2—C5—C6	120.45 (19)
C1—N1—C2	124.11 (17)	N2—C5—C6	115.68 (18)
C4—N1—C2	115.54 (17)	C11—C6—C7	118.79 (18)
C5—N2—C1	128.23 (18)	C11—C6—C5	117.08 (19)
C5—N2—H2N	118.4 (15)	C7—C6—C5	124.11 (19)
C1—N2—H2N	113.3 (15)	C8—C7—C6	120.2 (2)
N1—C1—N2	113.53 (18)	C8—C7—H7	119.9
N1—C1—S1	123.42 (15)	C6—C7—H7	119.9
N2—C1—S1	122.93 (15)	C7—C8—C9	121.1 (2)
N1—C2—C3	112.86 (18)	C7—C8—H8	119.4
N1—C2—H2A	109.0	C9—C8—H8	119.4
C3—C2—H2A	109.0	C10—C9—C8	118.33 (19)
N1—C2—H2B	109.0	C10—C9—C12	121.1 (2)
C3—C2—H2B	109.0	C8—C9—C12	120.6 (2)
H2A—C2—H2B	107.8	C9—C10—C11	121.0 (2)
O1—C3—C2	110.70 (17)	C9—C10—H10	119.5
O1—C3—H3B	109.5	C11—C10—H10	119.5

C2—C3—H3B	109.5	C10—C11—C6	120.6 (2)
O1—C3—H3C	109.5	C10—C11—H11	119.7
C2—C3—H3C	109.5	C6—C11—H11	119.7
H3B—C3—H3C	108.1	C9—C12—H12A	109.5
N1—C4—H4A	109.5	C9—C12—H12B	109.5
N1—C4—H4B	109.5	H12A—C12—H12B	109.5
H4A—C4—H4B	109.5	C9—C12—H12C	109.5
N1—C4—H4C	109.5	H12A—C12—H12C	109.5
H4A—C4—H4C	109.5	H12B—C12—H12C	109.5
H4B—C4—H4C	109.5		

C4—N1—C1—N2	−165.77 (19)	O2—C5—C6—C7	−179.8 (2)
C2—N1—C1—N2	15.5 (3)	N2—C5—C6—C7	0.4 (3)
C4—N1—C1—S1	10.3 (3)	C11—C6—C7—C8	0.8 (3)
C2—N1—C1—S1	−168.40 (16)	C5—C6—C7—C8	179.46 (19)
C5—N2—C1—N1	−153.5 (2)	C6—C7—C8—C9	0.7 (3)
C5—N2—C1—S1	30.4 (3)	C7—C8—C9—C10	−1.8 (3)
C1—N1—C2—C3	−94.6 (2)	C7—C8—C9—C12	177.1 (2)
C4—N1—C2—C3	86.6 (2)	C8—C9—C10—C11	1.4 (3)
N1—C2—C3—O1	66.9 (2)	C12—C9—C10—C11	−177.5 (2)
C1—N2—C5—O2	10.2 (4)	C9—C10—C11—C6	0.1 (3)
C1—N2—C5—C6	−170.0 (2)	C7—C6—C11—C10	−1.2 (3)
O2—C5—C6—C11	−1.1 (3)	C5—C6—C11—C10	−179.9 (2)
N2—C5—C6—C11	179.1 (2)		

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C6–C11 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···O1	0.87 (2)	2.02 (2)	2.838 (3)	157 (2)
O1—H1*O*···O2^{i}	0.84 (2)	1.95 (2)	2.750 (2)	160 (2)
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C4—H4*B*···*Cg*1^{iii}	0.96	2.67	3.605 (3)	164
C12—H12*A*···*Cg*1^{iv}	0.96	3.00	3.932 (3)	164

Symmetry codes: (i) *x*+1/2, −*y*+3/2, −*z*+1; (ii) *x*−1/2, −*y*+3/2, −*z*+1; (iii) −*x*−1, *y*+3/2, −*z*+3/2; (iv) −*x*, *y*+1/2, −*z*+3/2.