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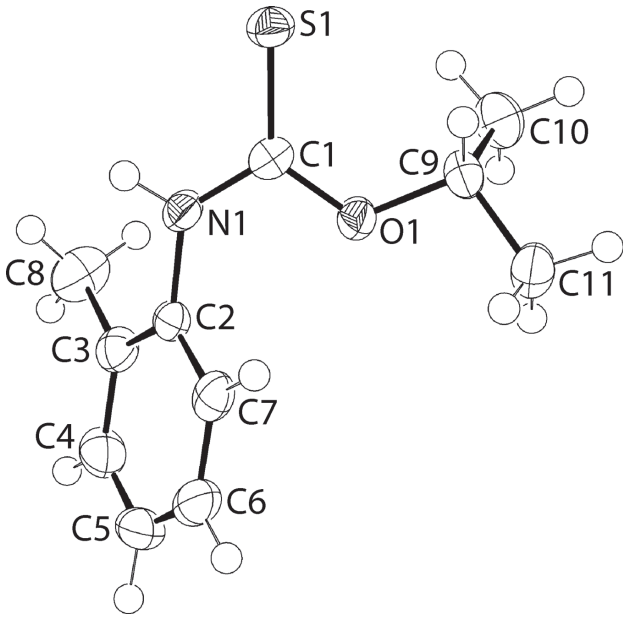
Crystal structure of *N*-(2-methylphenyl)(propan-2-yloxy)carbothioamide, $C_{11}H_{15}NOS$



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Abstract

$C_{11}H_{15}NOS$, monoclinic, $P2_1/n$ (no. 14), $a = 7.3979(4)$ Å, $b = 8.5384(4)$ Å, $c = 18.2771(10)$ Å, $\beta = 90.999(3)°$, $V = 1154.32(10)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0409$, $wR_{ref}(F^2) = 0.1093$, $T = 100(2)$ K.

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The title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.27 \times 0.11 \times 0.11$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.25 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX, ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10515, 2649, 0.058
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2186
$N(param)_{refined}$:	133
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

Source of material

All chemicals and solvents were used as purchased without purification. All reactions were carried out under ambient conditions. The melting point was determined on a Krüss KSP1N melting point meter. The IR spectrum was obtained on a Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR spectrophotometer from 4000 to 400 cm^{-1}; abbreviation: s, strong. Elemental analyses were performed on a Perkin Elmer PE 2400 CHN Elemental Analyser.

o-Tolyl isothiocyanate (Sigma Aldrich; 2.5 mmol, 0.33 mL) was added to NaOH (Merck; 2.5 mmol, 0.10 g) in *i*PrOH (Merck; 5 mL) and the mixture was left stirring at room temperature for 2 h, followed by the addition of excess 5 *M* HCl solution. The resulting mixture was stirred for another 1.5 h. The final product was extracted with chloroform (Merck; 20 mL) and left for evaporation at room temperature, yielding colourless crystal after 4 weeks. *M*.pt: 323−324 K. IR (cm^{-1}): 3208 (*s*) ν(N—H), 1459 (*s*) ν(C—N), 1204 (*s*) (C= S), 1094 (*s*) ν(C—O). Anal. Calc. for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69%. Found: C, 63.15; H, 7.42; N, 6.92%.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95−1.00 Å) and refined as riding with $U_{iso}(H) = 1.2$−$1.5U_{eq}(C)$. The N-bound H-atom was located in a difference Fourier map but refined with a distance restraint of N—H = 0.88 ±0.01 Å, and with $U_{iso}(H)$ set to $1.2U_{equiv}(N)$.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.31646(5)	0.92776(5)	1.08505(2)	0.02241(14)
O1	0.08168(14)	0.74832(13)	1.00997(6)	0.0207(3)
N1	0.30848(17)	0.84343(16)	0.94626(7)	0.0204(3)
H1N	0.4082(17)	0.8953(19)	0.9436(10)	0.025*
C1	0.23022(19)	0.83559(18)	1.01114(8)	0.0184(3)
C2	0.2401(2)	0.78416(18)	0.87761(8)	0.0183(3)
C3	0.3557(2)	0.69622(19)	0.83442(9)	0.0233(4)
C4	0.2909(3)	0.6479(2)	0.76591(10)	0.0311(4)
H4	0.3679	0.5893	0.7351	0.037*
C5	0.1177(3)	0.6831(2)	0.74184(9)	0.0340(4)
H5	0.0767	0.6491	0.6949	0.041*
C6	0.0044(2)	0.7679(2)	0.78616(10)	0.0312(4)
H6	−0.1154	0.7909	0.7700	0.037*
C7	0.0651(2)	0.81951(19)	0.85417(9)	0.0228(3)
H7	−0.0123	0.8787	0.8845	0.027*
C8	0.5424(2)	0.6509(2)	0.86049(11)	0.0352(4)
H8A	0.5997	0.5855	0.8234	0.053*
H8B	0.5343	0.5922	0.9064	0.053*
H8C	0.6149	0.7456	0.8687	0.053*
C9	−0.0271(2)	0.73030(19)	1.07634(8)	0.0209(3)
H9	−0.0288	0.8313	1.1040	0.025*
C10	0.0529(2)	0.6032(2)	1.12380(10)	0.0303(4)
H10A	0.1774	0.6310	1.1377	0.045*
H10B	0.0527	0.5042	1.0967	0.045*
H10C	−0.0192	0.5916	1.1680	0.045*
C11	−0.2154(2)	0.6921(2)	1.04822(10)	0.0287(4)
H11A	−0.2581	0.7762	1.0158	0.043*
H11B	−0.2970	0.6821	1.0896	0.043*
H11C	−0.2129	0.5932	1.0210	0.043*

Comment

The title compound was investigated as part of continuing and systematic crystal chemical studies of alkoxycarbothioamides [6–9], *i.e.* molecules of the general formula ROC(=S)N(H)*R*′ (*R*/*R*′ = alkyl and/or aryl). Continued synthesis of these molecules is also motivated by the exciting biological activity exhibited by their phosphanegold(I) derivatives, *e.g.* as anti-microbial [10] and anti-cancer [11] agents, and the observed dependence of biological potential upon the nature of *R* and *R*′. In the present communication, the crystal and molecular structures of the title compound, *i*PrOC(=S)N(H)C_6H_4Me-2, are described.

The molecular structure is shown in the figure (70% displacement ellipsoids) and features the normally observed [6–9] *syn*-disposition of the thione-S and thioamide-N—H atoms. The central residue is strictly planar with the [r.m.s. deviation of the S1, O1, N1, C1 atoms = 0.0011 Å] and forms a dihedral angle of 53.63(4)° with the appended 2-tolyl group. The key geometric parameters are C1 = S1 = 1.6796(15) Å, C1—O1 = 1.3275(18) Å, C1—N1 = 1.330(2) Å, S1—C1—O1 = 125.35(11)°, S1—C1—N1 = 121.88(12)° and O1—C1—N1 = 112.77(13)°. These follow the expected trends [6–9].

The molecular packing features thioamide-N—H···S(thione) hydrogen bonds [N1–H1n···S1^{i}: H1n···S1^{i} = 2.597(14) Å, N1···S.^{i} = 3.4494(14) Å with angle at H1n = 170.0(15)° for symmetry operation (i) $1-x$, $2-y$, $2-z$] between centrosymmetrically related molecules to generate an eight-membered $\{\cdots HNCS\}_2$ synthon. Globally, the dimeric aggregates thus formed stack in columns along the *a*-axis. The connections between the columns leading to a three-dimensional architecture are of the type tolyl-C—H···S(thione) [C5–H5···S1^{ii}: H5···S1^{ii} = 2.83 Å, C5···S1^{ii} = 3.7218(19) Å with angle at H5 = 156°; C7—H7···S1^{iii}: H7···S1^{iii} = 2.85 Å, C7···S1^{iii} = 3.7374(16) Å with angle at H7 = 155°, for symmetry operations: (ii) -1/2 + *x*, 3/2 − *y*, -1/2 + *z*; (iii) − *x*, 2 − *y*, 2 − *z*].

The present structure determination completes the series of structures of general formula ROC(=S)N(H)C_6H_4Me-2, *i.e.* for *R* = Me [12] and Et [13]. While not isostructural, the three structures exhibit the same trends in geometric parameters and in their respective crystals, the formation of eight-membered $\{\cdots HNCS\}_2$ synthons mediated by thioamide-*N*—*H*···*S*(thione) hydrogen bonds.

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