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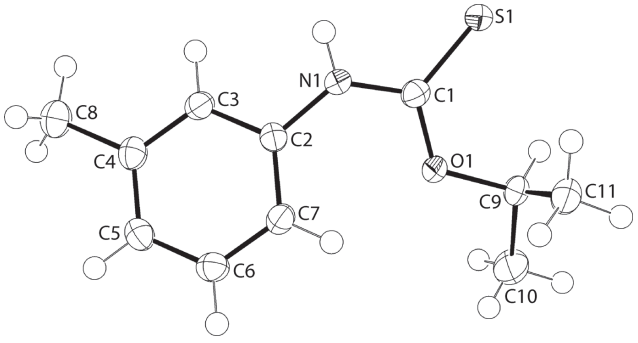
Crystal structure of *N*-(3-methylphenyl)(propan-2-yloxy)carbothioamide, $C_{11}H_{15}NOS$



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Abstract

$C_{11}H_{15}NOS$, monoclinic, $C2/c$ (no. 15), $a = 21.0452(12)$ Å, $b = 6.1447(4)$ Å, $c = 17.1892(10)$ Å, $\beta = 93.3520(10)°$, $V = 2219.0(2)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0291$, $wR_{ref}(F^2) = 0.0854$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals and solvents were used as purchased without purification. The reaction was 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.

Preparation of the title compound: *m*-Tolyl isothiocyanate (Merck; 2.5 mmol, 0.34 mL) was added to NaOH

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.20 × 0.11 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.26 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX, ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13386, 2545, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2283
$N(param)_{refined}$:	133
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.35255(2)	−0.21699(5)	0.00951(2)	0.01905(10)
O1	0.36789(4)	0.15300(15)	0.08977(5)	0.01890(19)
N1	0.26773(5)	0.03575(17)	0.07219(6)	0.0165(2)
H1N	0.2418(6)	−0.063(2)	0.0530(8)	0.020*
C1	0.32909(5)	0.00139(19)	0.05886(6)	0.0157(2)
C2	0.23881(5)	0.19710(19)	0.11801(6)	0.0148(2)
C3	0.18019(5)	0.1410(2)	0.14645(7)	0.0171(2)
H3	0.1625	0.0017	0.1348	0.021*
C4	0.14727(6)	0.2859(2)	0.19151(7)	0.0186(2)
C5	0.17389(6)	0.4890(2)	0.20825(7)	0.0188(2)
H5	0.1523	0.5892	0.2395	0.023*
C6	0.23190(6)	0.5457(2)	0.17949(7)	0.0188(2)
H6	0.2495	0.6852	0.1911	0.023*
C7	0.26468(6)	0.40209(19)	0.13412(7)	0.0170(2)
H7	0.3042	0.4429	0.1143	0.020*
C8	0.08445(7)	0.2229(2)	0.22276(9)	0.0296(3)
H8A	0.0848	0.2582	0.2784	0.044*
H8B	0.0776	0.0663	0.2156	0.044*
H8C	0.0500	0.3032	0.1946	0.044*
C9	0.43606(5)	0.1434(2)	0.07709(7)	0.0195(3)
H9	0.4510	−0.0111	0.0796	0.023*
C10	0.46806(7)	0.2724(3)	0.14296(9)	0.0334(3)
H10A	0.4568	0.2105	0.1929	0.050*
H10B	0.4538	0.4241	0.1395	0.050*
H10C	0.5143	0.2665	0.1393	0.050*
C11	0.44799(6)	0.2392(2)	−0.00183(8)	0.0236(3)
H11A	0.4280	0.1470	−0.0428	0.035*
H11B	0.4939	0.2468	−0.0081	0.035*
H11C	0.4298	0.3858	−0.0057	0.035*

(Merck; 2.5 mmol, 0.10 g) in *i*-PrOH (Merck; 5 mL) and the mixture was left for stirring at room temperature for 2 h, followed by the addition of excess 5 *M* HCl solution. The resulting mixture was stirred for a further 1.5 h. The final product was extracted with chloroform (Merck; 20 mL) and left for evaporation at room temperature, yielding brown crystals after 3 weeks. *M*.pt: 323–325 K. IR (cm^{-1}): 3220 (*s*) ν(N—H), 1491 (*s*) ν(C—N), 1207 (*s*) ν(C—O), 1091 (*s*) ν(C=S).

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 was refined with a distance restraint of N—H = 0.88±0.01 Å, and with $U_{iso}(H)$ set to $1.2U_{equiv}(N)$. Owing to poor agreement, the $(\bar{9}\,1\,1)$ reflection was omitted from the final cycles of refinement.

Comment

A recent overview of the known crystal structures for molecules of the general formula, ROC(=S)N(H)*R*″ (*R*/*R*″ = alkyl and/or aryl), *i.e.* the alkoxycarbothioamides, showed a high degree of concordance in their structural features [6]. Most notable was the universal adoption of a thioamide tautomer. The majority of structures featured a *syn*-disposition of the thione-S and thioamide-N—H atoms. The exceptions occur when an anti-disposition of the thione-S and thioamide-N—H atoms is found as, for example, in the structure where *R* = Me and *R*″ = 4-C(= *O*)Me-phenyl [7], allowing for the formation of intermolecular N—H···O hydrogen bonding, and where *R* = 4-pyridylphenyl and *R*″ = phenyl [8], allowing for intermolecular N—H···N hydrogen bonding. Herein, as a continuation of structural studies of this class of compound [6, 7, 9], the crystal and molecular structures of the compound with *R* = ^{i}Pr and *R*″ = 3-Me-phenyl are described.

The molecular structure is shown in the figure (70% displacement ellipsoids) and features the normally observed [6] *syn*-disposition of the thione-S and thioamide-N—H atoms. In accord with expectation, the central C1, N1, O1, S1 residue is planar with the r.m.s. deviation being 0.0044 Å. The dihedral angle between the central plane and appended 3-tolyl group is 23.06(5)°. Evidence for the thioamide tautomer is found in the magnitude of the C1=S1 [1.6772(12) Å] and C1—N1 [1.3412(15) Å] bond lengths, and in the location of the thioamide-N—H atom in the crystallographic refinement. The angles subtended at the quaternary-C1 atom follow the expected trends with S1—C1—O1 [124.81(9)°] being wider than S1—C1—N1 [121.82(9)°] and each of these being wider than O1—C1—N1 [113.36(10)°].

The *syn*-disposition of the thione-S1 and thioamide-N—H atoms allows for the formation of thioamide-*N*—*H*···*S*(thione) hydrogen bonds in the molecular packing [N1–H1n···S1^{i}: H1n···S1^{i} = 2.584(13) Å, N1···S1^{i} = 3.4352(11) Å with angle at H1n = 167.0(11)° for symmetry operation i: $1/2-x, -1/2-y, -z$]. As these occur between centrosymmetrically related molecules, eight-membered $\{\cdots HNCS\}_2$ synthons ensue. Intermolecular points of contact of the type tolyl-C—H···π [C6—H6···*Cg*(C2–C7)^{ii}: H6···*Cg*(C2–C7)^{ii} = 2.80 Å, C6···*Cg*(C2–C7)^{ii} = 3.4597(13) Å and angle at H6 = 127° for ii: $1/2-x, 1/2+y, 1/2-z$] and parallel C=S···π [C1—S1···*Cg*(C2–C7)^{iii}: S1···*Cg*(C2–C7)^{iii} = 3.8929(6) Å, C1···*Cg*(C2–C7)^{iii} = 3.9582(12) Å and angle at S1 = 79.85(4)° for iii: $1/2-x, 1/2-y, -z$], each involving the 3-tolyl ring, serve to link molecules into a supramolecular layer in the *bc*-plane. Layers stack along the *a* axis direction without directional interactions between them.

The most closely related structures in the literature are the polymorphic structures EtOC(= *S*)*N*(*H*)(3-Me-phenyl) [6, 10], *i.e.* where ^{i}Pr is substituted with Et; both polymorphs are monoclinic. In the $P2_1/c$ form [6], there are two independent molecules in the asymmetric unit whereas in the $C2/c$ form [10], one molecule comprises the asymmetric unit. Not unexpectedly, similar trends in conformation and geometric parameters are evident, along with supramolecular association *via* $\{\cdots HNCS\}_2$ synthons, as described above.

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