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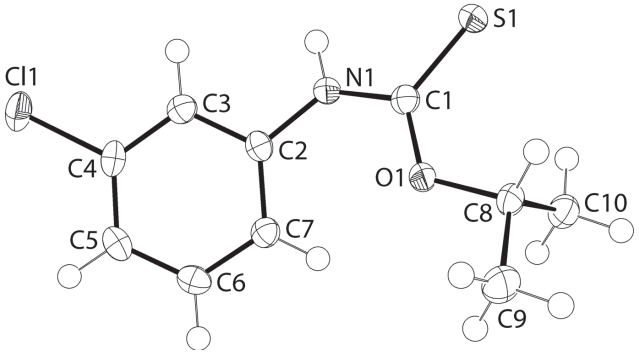
Crystal structure of *N*-(3-chlorophenyl)(propan-2-yloxy)carbothioamide, $C_{10}H_{12}ClNOS$



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Abstract

$C_{10}H_{12}ClNOS$, monoclinic, $P2_1/n$ (no. 14), $a = 13.2003(12)$ Å, $b = 6.0448(6)$ Å, $c = 13.9403(13)$ Å, $\beta = 101.9180(10)°$, $V = 1088.36(18)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0291$, $wR_{ref}(F^2) = 0.0807$, $T = 100(2)$ K.

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

Source of materials

3-Chlorophenyl isothiocyanate (Sigma Aldrich; 2.5 mmol, 0.33 mL) was added to NaOH (Merck; 2.5 mmol, 0.10 g) in iPrOH (Merck; 5 mL) and the mixture was left for stirring at room temperature for 2 h. This was 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 crystals after 5 weeks. M.p. (Krüss KSP1N): 347–349 K. IR (Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR; cm^{-1}): 3220 (s) ν(N—H), 1478 (s) ν(C—N), 1203 (s) ν(C=S), 1095 (s) ν(C—O). Elem. Anal. (Perkin Elmer PE 2400 CHN): Calc. for $C_{10}H_{12}ClNOS$: C, 52.04; H, 5.14; N, 6.33%. Found: 52.28; H, 5.27; N, 6.10%.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.25 × 0.09 × 0.06 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.1 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX, ω scans
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12986, 2497, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2196
$N(param)_{refined}$:	132
Programs:	Bruker programs [1, 2], SHELX [3, 4], ORTEP [5]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cl1	0.45970(3)	0.03216(7)	0.10488(3)	0.02439(11)
S1	0.38771(3)	0.47645(6)	0.59269(3)	0.01761(11)
O1	0.29120(7)	0.10134(17)	0.52802(7)	0.0161(2)
N1	0.40998(9)	0.2174(2)	0.44643(8)	0.0154(2)
H1N	0.4559(11)	0.318(2)	0.4410(12)	0.018*
C1	0.36131(11)	0.2534(2)	0.52058(10)	0.0143(3)
C2	0.39332(10)	0.0544(2)	0.37143(10)	0.0139(3)
C3	0.42858(10)	0.1094(2)	0.28661(10)	0.0155(3)
H3	0.4605	0.2485	0.2814	0.019*
C4	0.41646(11)	−0.0411(2)	0.21042(10)	0.0165(3)
C5	0.36997(11)	−0.2446(2)	0.21476(10)	0.0174(3)
H5	0.3616	−0.3452	0.1614	0.021*
C6	0.33581(11)	−0.2972(2)	0.29969(10)	0.0172(3)
H6	0.3040	−0.4367	0.3043	0.021*
C7	0.34692(10)	−0.1511(2)	0.37813(10)	0.0151(3)
H7	0.3232	−0.1906	0.4357	0.018*
C8	0.23245(11)	0.1151(2)	0.60690(10)	0.0161(3)
H8	0.2111	0.2715	0.6149	0.019*
C9	0.13810(12)	−0.0270(3)	0.57210(12)	0.0254(3)
H9A	0.0989	0.0304	0.5096	0.038*
H9B	0.0944	−0.0245	0.6210	0.038*
H9C	0.1597	−0.1794	0.5631	0.038*
C10	0.29920(12)	0.0325(2)	0.70175(11)	0.0194(3)
H10A	0.3590	0.1306	0.7213	0.029*
H10B	0.3232	−0.1177	0.6922	0.029*
H10C	0.2585	0.0312	0.7531	0.029*

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Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5 U_{eq}(C)$. 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 1.2 $U_{eq}(N)$. Owing to poor agreement, a reflection, i.e. (10 0 8), was omitted from the final cycles of refinement.

Comment

The motivation for the preparation of the title compound was the observation that alkoxythiocarbamides, i.e. ROC(=S)N(H)R′ for R/R′ = alkyl/aryl, when complexed to phosphanegold(I), generate bioactive compounds in the context of both cancer [6] and bacterial infection [7], and the structure determination follows on-going systematic structural investigations in this area [8, 9].

The molecular structure of iPrOC(=S)N(H)$C_6H_4Cl_3$ is shown in the Figure (70% displacement ellipsoids) and comprises a planar CNOS core [r.m.s. deviation = 0.0052 Å] which forms a dihedral angle of 20.50(8)° with the N-bound 3-chlorophenyl group, there being a twist about the N1—C2 bond; the C1—N1—C2—C3 torsion angle is 156.74(14)°. The thioamide-N—H and thione-S atoms are syn, and to a first approximation, the chlorine atom lies to the same side of the molecule as does the thione-S atom.

In the molecular packing, the syn-disposition of the thioamide-N—H and thione-S atoms facilitates the formation of thioamide-N—H···S(thione) hydrogen bonds and eight-membered $\{\cdots HNCS\}_2$ synthons [N1—H1n···$S1^{i}$: 2.535(14) Å and 164.6(12)° for symmetry operation i: $1-x$, $1-y$, $1-z$]. Interestingly, weak Cl···Cl halogen bonding is also apparent [Cl1···$Cl1^{ii}$ = 3.3345(7) Å for symmetry operation ii: $-x$, $-y$, $1-z$]. These serve to link the dimeric aggregates into supramolecular chains parallel to [$\bar{1}$ 1 5].

While there are no direct precedents for the title compound in the crystallographic literature [8, 9], the structure of the ethoxy derivative has been reported recently [10]. In the latter, the same syn disposition of the thioamide-N—H and thione-S atoms in the molecular structure and supramolecular $\{\cdots HNCS\}_2$ synthon in the molecular packing are observed. The key difference in structures is found in the relative dispositions of the thione-S and chloro atoms which lie to opposite sides in the molecule of the ethoxy derivative as opposed to the conformation observed in the title compound.

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