DE GRUYTER Z. Kristallogr. NCS 2018; 233(3): 511–512

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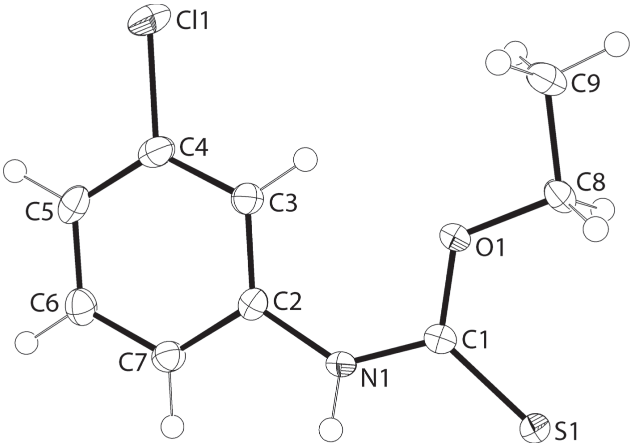
Crystal structure of *N*-(3-chlorophenyl)ethoxycarbothioamide, $C_9H_{10}ClNOS$



https://doi.org/10.1515/ncrs-2017-0403
Received December 12, 2017; accepted March 18, 2018; available online March 30, 2018

Abstract

$C_9H_{10}ClNOS$, monoclinic, $C2/c$ (no. 15), $a = 18.8783(6)$ Å, $b = 4.5518(2)$ Å, $c = 23.6739(8)$ Å, $\beta = 91.501(4)°$, $V = 2033.61(13)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.082$, $T = 100(2)$ K.

CCDC no.: 1830621

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.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.30 \times 0.22 \times 0.05$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.4 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX, ω scans
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9015, 2327, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2015
$N(param)_{refined}$:	122
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	0.39796(3)	0.55128(12)	0.24380(2)	0.03764(15)
S1	0.36135(2)	−0.36422(9)	−0.00973(2)	0.01921(12)
O1	0.42262(6)	−0.0977(2)	0.07864(5)	0.0194(2)
N1	0.30855(7)	0.0069(3)	0.06370(6)	0.0163(3)
H1N	0.2704(7)	−0.028(4)	0.0438(7)	0.020*
C1	0.36499(8)	−0.1440(3)	0.04656(6)	0.0157(3)
C2	0.30022(8)	0.2121(3)	0.10787(6)	0.0163(3)
C3	0.35058(8)	0.2705(4)	0.15030(7)	0.0199(3)
H3	0.3948	0.1711	0.1513	0.024*
C4	0.33465(9)	0.4769(4)	0.19103(7)	0.0218(4)
C5	0.27084(9)	0.6245(4)	0.19176(7)	0.0220(3)
H5	0.2614	0.7648	0.2203	0.026*
C6	0.22107(9)	0.5617(4)	0.14962(7)	0.0223(4)
H6	0.1765	0.6586	0.1494	0.027*
C7	0.23542(8)	0.3593(3)	0.10777(7)	0.0200(3)
H7	0.2009	0.3206	0.0788	0.024*
C8	0.48604(8)	−0.2722(4)	0.06945(7)	0.0223(4)
H2A	0.5083	−0.2145	0.0337	0.027*
H2B	0.4742	−0.4839	0.0676	0.027*
C9	0.53472(9)	−0.2092(5)	0.11901(8)	0.0339(5)
H3A	0.5780	−0.3261	0.1159	0.051*
H3B	0.5111	−0.2605	0.1540	0.051*

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 EtOH (Merck; 3 mL) and the mixture was stirred 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; 15 mL) and left for evaporation at room temperature, yielding colourless crystals after 2 weeks. M.p. (Krüss KSP1N): 349–350 K. IR (Perkin Elmer Spectrum 400 F T Mid-IR/Far-IR; cm^{-1}): 3248 (*s*) ν(N—H), 1476 (*s*) ν(C—N), 1199 (*s*) ν(C=S), 1040 (*s*) ν(C—O). Elem. Anal. (Perkin Elmer PE 2400 CHN):

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Calc. for $C_9H_{10}ClNOS$: C, 50.11; H, 4.67; N, 6.49%. Found: C, 50.21; H, 4.55; N, 6.69%.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95−0.99 Å) and refined as riding with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2{-}1.5\ U_{\mathrm{eq}}(\mathrm{C})$. The N-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint of N—H = 0.88 ± 0.01 Å, and with $U_{\mathrm{iso}}(\mathrm{H})$ set to 1.2 $U_{\mathrm{eq}}(\mathrm{N})$. Owing to poor agreement, two reflections, i.e. (2 0 0) and (0 0 2), were omitted from the final cycles of refinement, presumably owing to interference from the beam-stop.

Comment

The structural landscape of molecules of the general formula ROC(=S)N(H)*R′*, for *R*, *R′* = alkyl/aryl, has been summarized recently [6]. The overwhelming majority of structures, including a more recently reported derivative [7], share common features such as a *syn*-disposition of the thioamide-N—H and thione-S atoms [6, 7] with the exceptions, i.e. with anti-dispositions of these atoms, arising owing to the dictates of thioamide-N—H···O, N hydrogen bonding, as the O– and/or N-bound substituents carry good oxygen or nitrogen hydrogen bond acceptors [6]. In continuation of these studies, the title compound EtOC(=S)N(H)(3-ClPh) was investigated by X-ray crystallography.

The molecular structure is shown in the Figure (50% displacement ellipsoids) and this features the anticipated *syn*-disposition of the thioamide-N—H and thione-S atoms. The central CNOS chromophore is planar and forms a dihedral angle of 7.94(9)° with the N-bound 3-chlorophenyl ring. The whole molecule is practically planar with the r.m.s. for the 13 fitted non-hydrogen atoms being 0.0594 Å with maximum deviations of 0.1186(12) and 0.0973(12) Å for the O1 and N1 atoms, respectively. Overall, the molecule has a U-shape as the ethoxy and phenyl-chloro groups lie to the same side of the molecule.

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 between centrosymmetrically related molecules and therefore, eight-membered thioamide synthons $\{\cdots\mathrm{HNCS}\}_2$; N1—H1n···$\mathrm{S1^i}$: 2.641(14) Å and 164.7(14)° for symmetry operation i: $1/2 - x$, $-1/2 - y$, $-z$. Globally, in the crystal, dimeric aggregates stack in columns parallel to the *b* axis.

Acknowledgements: The University of Malaya's X-ray laboratory is thanked for the data collection. Sunway University is thanked for support of biological and crystal engineering studies of metal alkoxycarbothioamides.

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