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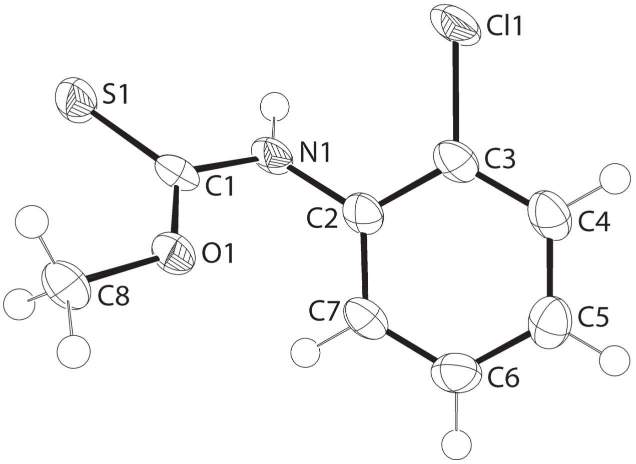
Crystal structure of *N*-(2-chlorophenyl)methoxycarbothioamide, C_8H_8ClNOS



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Abstract

C_8H_8ClNOS, triclinic, $P\bar{1}$ (no. 2), $a = 6.7658(5)$ Å, $b = 8.0344(10)$ Å, $c = 9.6285(12)$ Å, $\alpha = 66.279(12)°$, $\beta = 72.245(9)°$, $\gamma = 87.699(8)°$, $V = 454.31(10)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.056$, $wR_{ref}(F^2) = 0.158$, $T = 100$ 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

2-Chlorophenyl isothiocyanate (Sigma Aldrich; 2.5 mmol, 0.33 mL) was added to NaOH (Merck; 2.5 mmol, 0.10 g) in MeOH (Merck; 3 mL) and the mixture was stirred 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; 15 mL) and left for evaporation at room temperature, yielding colourless crystals after 2 weeks. **M.p.:** 343 K. **Elem. Anal.** Calc. for C_8H_8ClNOS: C, 47.64; H, 4.00; N, 6.95%. Found: C, 47.44; H, 3.67; N, 6.96%. **IR** (cm^{-1}): 3223 (s) ν(N—H); 1440 (s) ν(C—N); 1213 (s) ν(C=S); 1055 (s) ν(C—O).

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.25 \times 0.20 \times 0.15$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	6.0 cm^{-1}
Diffractometer, scan mode:	SuperNova Dual, ω scans
$2\theta_{max}$, completeness:	50.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	3419, 1612, 0.044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1412
$N(param)_{refined}$:	113
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], ORTEP [4]

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

Atom	*x*	*y*	*z*	$U_{iso}*/U_{eq}$
Cl1	0.74319(9)	0.15138(8)	0.31896(8)	0.0279(3)
S1	0.20199(10)	0.36917(9)	0.67712(7)	0.0257(3)
O1	0.0511(3)	0.2195(2)	0.52448(19)	0.0214(5)
N1	0.3755(3)	0.3487(3)	0.3994(2)	0.0206(5)
H1N	0.482(3)	0.408(3)	0.399(3)	0.025*
C1	0.2063(4)	0.3101(3)	0.5286(3)	0.0187(6)
C2	0.3925(4)	0.3038(3)	0.2674(3)	0.0190(6)
C3	0.5623(4)	0.2137(3)	0.2164(3)	0.0204(6)
C4	0.5892(4)	0.1769(3)	0.0841(3)	0.0243(6)
H4	0.7059	0.1172	0.0497	0.029*
C5	0.4467(4)	0.2268(3)	0.0020(3)	0.0248(6)
H5	0.4644	0.2010	−0.0889	0.030*
C6	0.2763(4)	0.3155(3)	0.0527(3)	0.0252(6)
H6	0.1769	0.3488	−0.0030	0.030*
C7	0.2518(4)	0.3548(3)	0.1830(3)	0.0222(6)
H7	0.1370	0.4176	0.2153	0.027*
C8	−0.1426(4)	0.1699(4)	0.6562(3)	0.0270(6)
H8A	−0.2418	0.1017	0.6381	0.040*
H8B	−0.2012	0.2808	0.6633	0.040*
H8C	−0.1155	0.0938	0.7563	0.040*

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Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 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, one reflection, i.e. (1 3 5), was omitted from the final cycles of refinement.

Discussion

Structural mimicry is an interesting concept in crystal engineering whereby the chemical exchange of substituents/residues does not impact upon the global molecular packing [5]. This implies the pair/set of substituents/residues either engage in comparable intermolecular interactions or do not engage in directional intermolecular interactions at all. In order to explore such phenomena, systematic crystallographic studies of closely related molecules are required. In this context, herein the X-ray crystal structure of MeOC(=S)N(H)(2-ClPh) is described and compared with its o-tolyl congenor [6].

The molecular structure is shown in the Figure (70% displacement elliposids) and features the anticipated syn-disposition of the thione-S and thioamide-N—H atoms. The central residue is strictly planar with the r.m.s. deviation for the S1,O1,N1,C1 atoms from their least-squares plane being 0.0040 Å. The molecule is twisted about the the N1—C2 bond with the C1—N1—C2—C7 torsion angle being 54.3(3)°. This results in a dihedral angle between the best planes through the SONC and phenyl rings of 53.06(8)°. 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, thioamide-N—H···S(thione) hydrogen bonds are formed between centrosymmetrically-related molecules resulting in eight-membered thioamide synthons $\{\cdots HNCS\}_2$; N1–H1n···$S1^i$: 2.57(2) Å and 165(2)° for symmetry operation i: $1-x,\ 1-y,\ 1-z$. The dimeric aggregates are connected into supramolecular layers parallel to $[1\ \bar{1}\ 0]$ via a combination of π–π stacking interactions between the tolyl rings [inter-ring centroid separation = 3.5864(16) Å for symmetry operation ii: $1-x$, $1-y, -z$] and weak C8–H8a···π(tolyl) contacts [H8a···ring centroid separation = 2.90 Å and angle at H8a = 122° for symmetry operation iii: $x, y, 1-z$]. The chlorine atoms project to either side of the layer with possibly the most important interlayer contact being a weak Cl···O halogen bond, i.e. Cl1···O1 of 3.228(2) Å [symmetry operation iv: $1-x, y, 1-z$].

The observed molecular conformation in the title compound is in accord with previous studies [7, 8] and with the structure of the o-tolyl derivative [6]. The latter also crystallises in a triclinic crystal system with very similar unit cell dimensions ($V = 461.38(19)$ Å^3) and a single independent molecule in the asymmetric unit which is also twisted; the dihedral angle between the SONC and phenyl planes is 51.89(5)°. In the molecular packing of the o-tolyl derivative, supramolecular layers parallel to $[0\ 1\ \bar{1}]$ are formed via thioamide-N—H···S(thione) hydrogen bonds, leading to dimers, and π–π stacking interactions. The connections between layers are of the type tolyl-methyl-C—H···π(tolyl). Thus, it is possible to conclude that there are relatively similar and important roles for each of the chlorine atom and tolyl-methyl substituent in their respective molecular packing.

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