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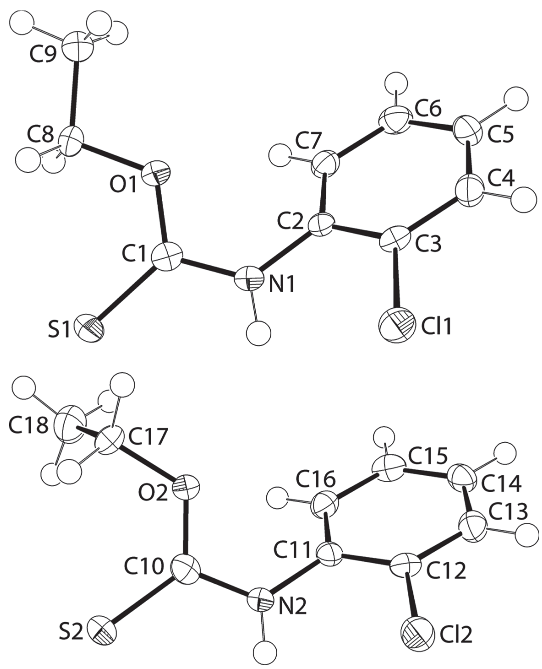
Crystal structure and molecular packing of *O*-ethyl (2-chlorophenyl)carbamothioate, $C_9H_{10}ClNOS$



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Abstract

$C_9H_{10}ClNOS$, triclinic, $P\bar{1}$ (no. 2), $a = 7.2277(3)$ Å, $b = 9.9791(3)$ Å, $c = 14.7725(7)$ Å, $\alpha = 81.007(3)°$, $\beta = 82.268(4)°$, $\gamma = 73.210(3)°$, $V = 1003.01(7)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0364$, $wR_{ref}(F^2) = 0.0828$, $T = 100(2)$ 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.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.25 \times 0.20 \times 0.15$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.5 cm^{-1}
Diffractometer, scan mode:	SuperNova Dual, ω scans
$2\theta_{max}$, completeness:	55.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14831, 4637, 0.041
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3653
$N(param)_{refined}$:	243
Programs:	Agilent programs [1], SHELX [2, 3], ORTEP [4]

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 −4 °C, yielding colourless crystals after 8 weeks. Crystals melted once taken out of the mother liquor and hence, the only characterisation was done by X-ray crystallography.

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 $U_{eq}(N)$.

Comment

In connection with the exciting biological potential exhibited by O-alkylthiocarbamates, i.e. $R_3PAu[SC(OR')=NR'']$, e.g. as anti-cancer [5] and anti-microbial [6] agents, and the dependence of biological activity upon the nature of R, R′ and R″ (=alkyl and/or aryl), considerable effort has been made to prepare the alkoxycarbothioamide precursor molecules of the general formula R′OC(=S)N(H)R″. These molecules, while biologically inert, exhibit interesting structural chemistry in terms of crystal engineering endeavours,

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cl1	0.23116(7)	0.89133(5)	0.55038(4)	0.01979(12)
S1	0.72551(7)	0.49578(5)	0.39208(4)	0.01832(12)
O1	0.88124(18)	0.69256(13)	0.42503(9)	0.0160(3)
N1	0.6098(2)	0.68018(16)	0.51302(12)	0.0158(4)
H1N	0.516(2)	0.6395(19)	0.5275(14)	0.019*
C1	0.7412(3)	0.62787(18)	0.44502(13)	0.0142(4)
C2	0.6172(3)	0.78160(18)	0.56952(13)	0.0131(4)
C3	0.4465(3)	0.88320(18)	0.59369(13)	0.0132(4)
C4	0.4447(3)	0.97812(19)	0.65309(14)	0.0174(4)
H4	0.3277	1.0472	0.6686	0.021*
C5	0.6130(3)	0.9722(2)	0.68978(14)	0.0187(4)
H5	0.6123	1.0371	0.7306	0.022*
C6	0.7832(3)	0.8711(2)	0.66676(14)	0.0186(4)
H6	0.8988	0.8663	0.6925	0.022*
C7	0.7861(3)	0.77709(19)	0.60657(13)	0.0151(4)
H7	0.9039	0.7092	0.5905	0.018*
C8	1.0369(3)	0.64433(19)	0.35395(14)	0.0162(4)
H8A	0.9828	0.6474	0.2953	0.019*
H8B	1.1125	0.5463	0.3728	0.019*
C9	1.1636(3)	0.7427(2)	0.34278(15)	0.0214(5)
H9A	1.0855	0.8397	0.3268	0.032*
H9B	1.2679	0.7168	0.2937	0.032*
H9C	1.2200	0.7358	0.4006	0.032*
Cl2	1.28896(7)	0.21559(5)	0.84908(4)	0.02177(13)
S2	0.75835(7)	0.65221(5)	0.92706(4)	0.01836(12)
O2	0.66577(19)	0.47596(13)	0.83298(9)	0.0165(3)
N2	0.8997(2)	0.37710(16)	0.92427(11)	0.0153(3)
H2N	0.984(2)	0.388(2)	0.9574(13)	0.018*
C10	0.7728(3)	0.49736(19)	0.89268(13)	0.0147(4)
C11	0.9090(3)	0.23908(18)	0.90591(13)	0.0141(4)
C12	1.0862(3)	0.15144(19)	0.87418(13)	0.0145(4)
C13	1.1029(3)	0.01333(19)	0.86231(14)	0.0177(4)
H13	1.2249	−0.0461	0.8419	0.021*
C14	0.9424(3)	−0.03740(19)	0.88013(14)	0.0183(4)
H14	0.9533	−0.1318	0.8715	0.022*
C15	0.7639(3)	0.04928(19)	0.91076(14)	0.0180(4)
H15	0.6529	0.0142	0.9224	0.022*
C16	0.7480(3)	0.18672(19)	0.92426(13)	0.0161(4)
H16	0.6265	0.2452	0.9461	0.019*
C17	0.5246(3)	0.59411(19)	0.78729(14)	0.0173(4)
H17A	0.5179	0.5757	0.7240	0.021*
H17B	0.5669	0.6810	0.7829	0.021*
C18	0.3270(3)	0.6155(2)	0.83930(16)	0.0255(5)
H18A	0.2911	0.5264	0.8496	0.038*
H18B	0.2318	0.6873	0.8035	0.038*
H18C	0.3292	0.6467	0.8987	0.038*

in particular the adoption or otherwise of a *syn*-disposition of the thioamide-N—H and thione-S atoms, and the propensity to form thioamide-N—H···S(thione) hydrogen bonds in their crystals [7, 8]. As a continuation of these studies, the crystal and molecular structures of the title compound, $EtOC(=S)N(H)C_6H_4Cl$-2, have been investigated.

The molecular structures are shown in the Figure (70% displacement ellipsoids) and features the anticipated [7, 8] *syn*-disposition of the thione-S and thioamide-N—H atoms in each of the two independent molecules comprising the asymmetric unit. 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 0.0011 Å [0.0000 Å for the S2-containing molecule]. Each molecule is twisted about the N1—C2 [N2—C11] bond with the C1—N1—C2—C3 torsion angle being 141.49(19)°; the S2-molecule is even more twisted with C10—N2—C11—C12 being 129.3(2)°. The dihedral angles between the planes through the SONC and phenyl rings are 46.21(7) and 56.86(6)° for the S1- and S2-molecules, respectively. The other notable conformational difference in the molecules is seen in the relative orientations of the ethoxy groups which best quantified in terms of the C1—O1—C8—C9 and C10—O2—C17—C18 torsion angles of 176.33(16) and −93.4(2)°, respectively, indicating + anti-periplanar and − anti-clinal conformations, respectively.

In the molecular packing, each independent molecule self-associates *via* thioamide-N—H···S(thione) hydrogen bonds with centrosymmetrically-related mates resulting in eight-membered thioamide synthons $\{\cdots HNCS\}_2$ [N1—H1n···S1^{i}: 2.566(17) Å and 166.1(17)°, and N2—H2n···S2^{ii}: 2.598(17) Å and 164.1(17)° for symmetry operations i: $1-x, 1-y, 1-z$ and ii: $2-x, 1-y, 2-z$]. Globally, the crystal comprises columns of dimeric aggregates parallel to the *a*-axis. Columns assemble into alternating rows of columns stacked along the *c*-axis. The interactions connecting the columns are as follows. Specific connections between columns comprising S1-molecules are of the type phenyl-C3—Cl1···Cg(C2—C7)^{iii} of 3.5249(10) Å with angle at Cl1 of 83.88(7)° for symmetry operation iii: $1-x, 2-y, 1-z$. Similarly, the interactions specific to rows of S2-molecules are phenyl-C14—H···S2^{iv} of 2.86 Å and 141°, and π(C11—C16)—π(C11—C16)^{iii} of 3.5880(11) Å for symmetry operation iv: $x, -1+y, z$. The connections between rows are of the type phenyl-C17—H17b···Cg(C2—C7) of 2.80 Å and 130°.

Such a detailed description of the molecular packing is made as it is observed that the crystals of the title compound and the 2-tolyl derivative [9] are isostructural, i.e. a case of structural mimicry whereby the chemical exchange of substituents/residues such as chloro/methyl does not influence the global molecular packing [10]. In the molecular packing of $EtOC(=S)N(H)C_6H_4Me$-2, the global arrangement of molecules mimics that for the 2-Cl derivative and the interactions between columns identified for 2-Cl derivative persist in the packing of the 2-Me structure with one exception, namely the C—Cl···π contact. However, in the 2-Me structure, this putative interaction is directly replaced by a C—H···π interaction. Hence, in the isostructural crystals, the C—Cl···π and C—H···π interactions are interchangeable.

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