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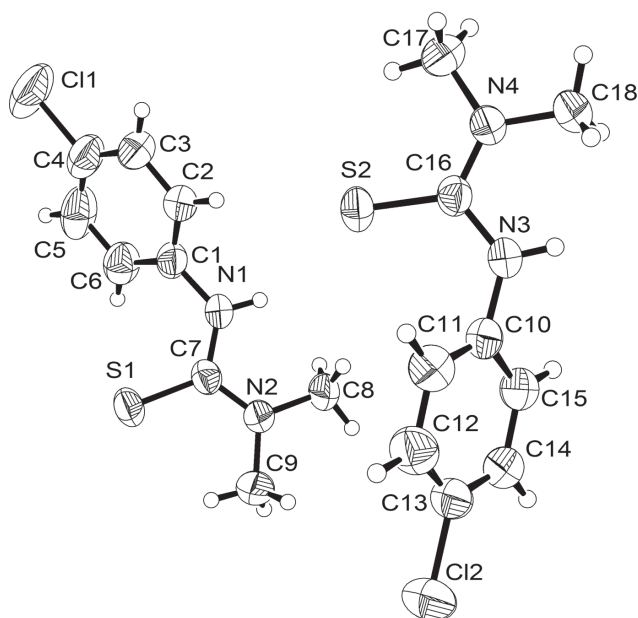
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Crystal structure of 3-(4-chlorophenyl)-1,1-dimethylthiourea, $C_9H_{11}ClN_2S$



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 plate
Size:	$0.40 \times 0.12 \times 0.08$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	46.6 cm^{-1}
Diffractometer, scan mode:	SuperNova, ω
$2\theta_{\text{max}}$, completeness:	148.2° , $>98\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6796, 2624, 0.024
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2459
$N(\text{param})_{\text{refined}}$:	239
Programs:	CrysAlis ^{PRO} [20], SHELX [21], ORTEP [22], WinGX [22], CHEMDRAW [23]

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Abstract

$C_9H_{11}ClN_2S$, monoclinic, Pc (no. 7), $a = 14.8440(4)$ Å, $b = 7.2002(2)$ Å, $c = 10.0920(2)$ Å, $\beta = 99.733(2)^\circ$, $V = 1063.10(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0399$, $wR_{\text{ref}}(F^2) = 0.1099$, $T = 296(2)$ K.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3472(3)	0.5692(6)	0.5499(4)	0.0567(9)
C2	0.3470(4)	0.7518(7)	0.5039(5)	0.0683(12)
H2	0.3841	0.7853	0.4423	0.082*
C3	0.2915(4)	0.8835(8)	0.5499(5)	0.0796(15)
H3	0.2906	1.0051	0.5185	0.096*
C4	0.2380(4)	0.8326(9)	0.6421(6)	0.0788(16)
C5	0.2370(4)	0.6512(11)	0.6874(7)	0.0873(19)
H5	0.1999	0.6185	0.7494	0.105*
C6	0.2910(3)	0.5191(8)	0.6403(5)	0.0700(12)
H6	0.2896	0.3966	0.6692	0.084*
C7	0.4626(3)	0.3173(5)	0.5665(4)	0.0470(8)
C8	0.4746(5)	0.1813(6)	0.3474(5)	0.0721(14)
H8A	0.4092	0.1721	0.3253	0.108*
H8B	0.5018	0.0723	0.3164	0.108*
H8C	0.4948	0.2891	0.3047	0.108*
C9	0.5743(4)	0.0710(7)	0.5525(5)	0.0688(12)
H9A	0.5915	0.0984	0.6465	0.103*
H9B	0.6263	0.0863	0.5084	0.103*
H9C	0.5528	-0.0548	0.5417	0.103*
C10	0.8885(3)	0.9278(6)	0.1826(4)	0.0539(9)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C11	0.9454(3)	0.9755(6)	0.3009(5)	0.0595(10)
H11	0.9479	1.0977	0.3310	0.071*
C12	0.9989(3)	0.8400(7)	0.3744(6)	0.0680(12)
H12	1.0369	0.8707	0.4544	0.082*
C13	0.9950(3)	0.6572(7)	0.3270(5)	0.0619(11)
C14	0.9412(4)	0.6117(7)	0.2098(5)	0.0685(12)
H14	0.9405	0.4905	0.1778	0.082*
C15	0.8872(4)	0.7461(6)	0.1374(4)	0.0628(10)
H15	0.8495	0.7140	0.0574	0.075*
C16	0.7738(3)	1.1821(4)	0.1435(4)	0.0451(8)
C17	0.6630(4)	1.4272(7)	0.0756(5)	0.0661(11)
H17A	0.6418	1.3906	0.1565	0.099*
H17B	0.6133	1.4214	0.0013	0.099*
H17C	0.6860	1.5520	0.0853	0.099*
C18	0.7619(4)	1.3199(6)	-0.0812(5)	0.0686(13)
H18A	0.8272	1.3293	-0.0714	0.103*
H18B	0.7344	1.4293	-0.1250	0.103*
H18C	0.7414	1.2126	-0.1343	0.103*
N1	0.4026(3)	0.4389(5)	0.4958(3)	0.0609(9)
H1	0.3979	0.4363	0.4097	0.073*
N2	0.5016(3)	0.1974(4)	0.4929(4)	0.0531(8)
N3	0.8341(3)	1.0604(5)	0.1022(3)	0.0583(8)
H3A	0.8395	1.0649	0.0187	0.070*
N4	0.7356(3)	1.3025(4)	0.0511(3)	0.0514(7)
S1	0.48905(8)	0.32265(14)	0.73619(9)	0.0591(3)
S2	0.74814(8)	1.17450(14)	0.30027(9)	0.0570(3)
Cl1	0.16859(13)	0.9989(3)	0.6997(2)	0.1229(8)
Cl2	1.06072(11)	0.4871(2)	0.42090(16)	0.0923(5)

Source of material

3-(4-Chlorophenyl)-1,1-dimethylthiourea was synthesized from reaction of 4-chlorophenyl isothiocyanate and dimethylamine (1.1 equivalents) in anhydrous dioxane at low temperature for 1 h. After work-up, the crude product obtained was purified by crystallization from hexane to give the title compound (95%) as colourless crystals, Mp 151–152 °C (lit. 149–151 °C [1], 151 °C [2], 150–151.5 °C [3], 152 °C [4]).

Experimental details

All hydrogen atoms were placed in calculated positions and refined using a riding model. Methyl C–H bonds were fixed at 0.96 Å and the groups were allowed to spin about the C–C bond with displacement parameters 1.5 times $U_{eq}(C)$. Aromatic C–H distances were set to 0.93 Å and N–H set to 0.86 Å with U_{iso} set to 1.2 times the U_{eq} for the parent atoms. The absolute structure was established by a refinement of the Flack parameter (0.09(2)) using 423 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$.

Discussion

Thioureas can be synthesized using various procedures and have been used as intermediates in organic syntheses [5–11].

Some derivatives show interesting applications as biologically active compounds [12–17].

In the crystal structure of the title compound, the asymmetric unit comprises two crystallographically independent molecules of C₉H₁₁ClN₂S. In the two molecules, the dimethylthiourea groups are planar (apart from the methyl H atoms). A twist between the chlorophenyl and dimethylthiourea groups is observed in the molecules, in a manner similar to 3-(4-chlorophenyl)-1,1-dimethylurea [18] and 1,1-dimethyl-3-phenylthiourea [19]. The angles between the least-squares planes through the chlorophenyl and dimethylthiourea groups are 55.89(15) and 58.01(12)°, respectively. N–H···S interactions occur, forming chains along [001] with geometry: N1···S1 = 3.549(4) Å, N1–H1···S1 = 128.3° and N3···S2 = 3.530(4) Å, N3–H3a···S2 = 127.1°

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