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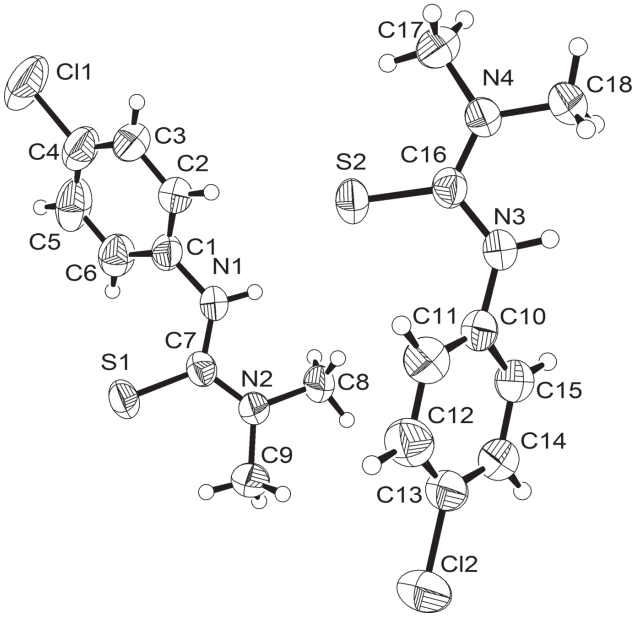
Gamal A. El-Hiti*, Keith Smith, Mohammed B. Alshammari, Amany S. Hegazy and Benson M. Kariuki

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 × 0.12 × 0.08 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	46.6 cm^{-1}
Diffractometer, scan mode:	SuperNova, ω
$2\theta_{max}$, completeness:	148.2°, >98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6796, 2624, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2459
$N(param)_{refined}$:	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, $\beta = 99.733(2)°$, $V = 1063.10(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0399$, $wR_{ref}(F^2) = 0.1099$, $T = 296(2)$ K.

CCDC no.: 1508746

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

Atom	x	y	z	U_{iso}*/U_{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)

***Corresponding author: Gamal A. El-Hiti,** Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, P.O. Box 10219, Riyadh 11433, Saudi Arabia, e-mail: gelhiti@ksu.edu.sa
Keith Smith, Amany S. Hegazy and Benson M. Kariuki: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK
Mohammed B. Alshammari: Chemistry Department, College of Sciences and Humanities, Prince Sattam bin Abdulaziz University, P.O. Box 83, Al-Kharij 11942, Saudi Arabia

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 $C_9H_{11}ClN_2S$. 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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