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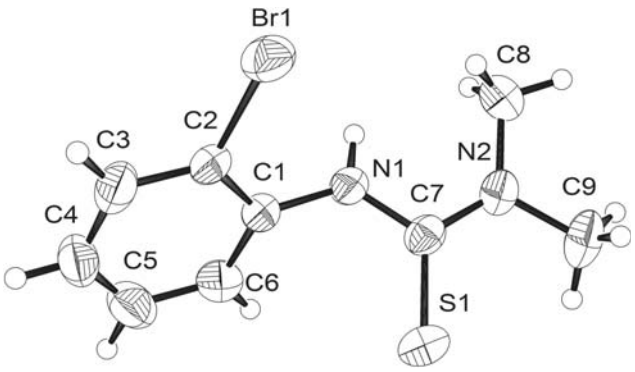
Crystal structure of 3-(2-bromophenyl)-1,1-dimethylthiourea, $C_9H_{11}BrN_2S$



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Abstract

$C_9H_{11}BrN_2S$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 7.5187(3)$ Å, $b = 8.0634(3)$ Å, $c = 17.5320(6)$ Å, $V = 1062.90(7)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0216$, $wR_{ref}(F^2) = 0.0536$, $T = 296(2)$ 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.

Source of material

3-(2-Bromophenyl)-1,1-dimethylthiourea was synthesized from the dropwise addition of a solution of dimethylamine (1.1 equivalents) in ethanol to a stirred solution of 2-bromophenyl isothiocyanate in anhydrous dioxane over 5 min. The

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Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	0.40 × 0.07 × 0.04 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	67.5 cm^{-1}
Diffractometer, scan mode:	SuperNova, ω
$2\theta_{max}$, completeness:	147°, >99% up to 125.3°
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	3493, 2052, 0.016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1969
$N(param)_{refined}$:	120
Programs:	CrysAlis^{PRO} [12], SHELX [13], WinGX [14]

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

Atom	x	y	z	U_{iso}*/U_{eq}
C1	−0.1300(4)	0.7897(4)	0.18698(16)	0.0385(6)
C2	−0.0864(4)	0.8683(4)	0.11919(15)	0.0397(6)
C3	−0.2084(6)	0.8842(5)	0.06025(18)	0.0516(9)
H3	−0.1772	0.9373	0.0151	0.062*
C4	−0.3767(6)	0.8197(5)	0.0699(2)	0.0580(10)
H4	−0.4603	0.8305	0.0312	0.070*
C5	−0.4225(5)	0.7389(6)	0.1369(3)	0.0606(10)
H5	−0.5360	0.6949	0.1427	0.073*
C6	−0.2998(5)	0.7239(5)	0.1949(2)	0.0513(8)
H6	−0.3310	0.6693	0.2397	0.062*
C7	−0.0060(4)	0.8368(4)	0.31579(16)	0.0383(6)
C8	0.3063(5)	0.7520(6)	0.3259(2)	0.0573(9)
H8A	0.2932	0.6364	0.3140	0.086*
H8B	0.4003	0.7659	0.3623	0.086*
H8C	0.3345	0.8123	0.2802	0.086*
C9	0.1465(7)	0.8677(6)	0.43742(19)	0.0663(11)
H9A	0.1900	0.9795	0.4402	0.100*
H9B	0.2242	0.7958	0.4656	0.100*
H9C	0.0291	0.8627	0.4588	0.100*
N1	0.0001(4)	0.7701(4)	0.24471(16)	0.0427(6)
H1	0.0914	0.7105	0.2337	0.051*
N2	0.1406(4)	0.8148(4)	0.35780(15)	0.0471(6)
S1	−0.18713(11)	0.94115(11)	0.34745(4)	0.0500(2)
Br1	0.14459(5)	0.95693(5)	0.10617(2)	0.05486(12)

mixture was stirred for 1 h at room temperature. The solid obtained after work-up was purified by crystallization from a mixture of ethyl acetate and hexane (4:1 by volume) to give the title compound (92%) as light yellowish crystals, Mp 143–144 °C (lit. 142–143 °C) [1].

Experimental details

H atoms were positioned geometrically and refined using a riding model. U_{iso}(H) for aromatic and N—H hydrogens were set to 1.2 times U_{eq} of the parent atom. The values for the methyl groups were 1.5 times U_{eq}(C) with free rotation about the C—C bond. Aromatic C—H bonds were fixed at 0.93 Å, methyl C—H at 0.96 Å and N—H at 0.86 Å. The Flack parameter refined to a value of −0.005(13) based on 790 quotients.

Discussion

Thiourea derivatives show various biological activities [2–5]. Therefore, the synthesis of such compounds is of general interest. The most common procedures for the synthesis of substituted thioureas involve reactions of amines with carbon disulfide in the presence of sodium or potassium hydroxide [6–8], of aliphatic amines with isocyanides in the presence of elemental sulfur [9] and of primary amines with isothiocyanates [10]. Thioureas can be used as precursors for the production of heterocycles, e.g. indigotin, *via* organolithium intermediates [1].

In the title structure the dimethylthiourea group is twisted from the plane of the bromophenyl moiety by 56.94(7)°. The amino groups are involved in intermolecular hydrogen bonds of the type N—H···S (with geometry: N···S = 3.410(3)Å, N—H···S = 141.5°) forming helical chains along [010]. The molecular conformation is similar to that found in the related 1-(2-bromo-4-chlorophenyl)-3,3-dimethylthiourea in which the intramolecular interplanar angle is 54.38(6)° and N—H···S hydrogen bonds also occur [11].

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