Gamal A. El-Hiti*, Keith Smith, Amany S. Hegazy, Mohammad Hayal Alotaibi and Benson M. Kariuki

Crystal structure of 3-(2-bromophenyl)-1,1-dimethylthiourea, C₉H₁₁BrN₂S

Table 1: Data collection and handling.

| Crystal: | Colourless needle |
| Size: | 0.40 × 0.07 × 0.04 mm |
| Wavelength: | Cu Kα radiation (1.54184 Å) |
| μ: | 67.5 cm⁻¹ |
| Diffractometer, scan mode: | SuperNova, ω |
| 2θmax, completeness: | 147°, >99% up to 125.3° |
| N(hkl)measured, N(hkl)unique, Rint: | 3493, 2052, 0.016 |
| Criterion for I(2σ(I)): I(2σ(I)) > 2 σ(I), 1969 |
| N(param)refined: | 120 |
| Programs: | CrystAlisPRO [12], SHELX [13], WinGX [14] |

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

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-0.1300(4)</td>
<td>0.7897(4)</td>
<td>0.1869(16)</td>
<td>0.0385(6)</td>
</tr>
<tr>
<td>C2</td>
<td>0.0864(4)</td>
<td>0.8683(4)</td>
<td>0.1191(15)</td>
<td>0.0397(6)</td>
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<tr>
<td>C3</td>
<td>0.2084(6)</td>
<td>0.8842(5)</td>
<td>0.06025(18)</td>
<td>0.0516(9)</td>
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<tr>
<td>H3</td>
<td>0.1772</td>
<td>0.9373</td>
<td>0.0151</td>
<td>0.062*</td>
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<tr>
<td>C4</td>
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<td>0.8197(5)</td>
<td>0.0699(2)</td>
<td>0.0580(10)</td>
</tr>
<tr>
<td>H4</td>
<td>0.4603</td>
<td>0.8305</td>
<td>0.0312</td>
<td>0.070*</td>
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<td>C5</td>
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<td>0.7389(6)</td>
<td>0.1369(3)</td>
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<tr>
<td>H5</td>
<td>0.5360</td>
<td>0.6949</td>
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<tr>
<td>C6</td>
<td>-0.2998(5)</td>
<td>0.7239(5)</td>
<td>0.1949(2)</td>
<td>0.0513(8)</td>
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<td>H6</td>
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<td>0.6693</td>
<td>0.2397</td>
<td>0.062*</td>
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<tr>
<td>C7</td>
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<td>0.8368(4)</td>
<td>0.31579(16)</td>
<td>0.0383(6)</td>
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<tr>
<td>C8</td>
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<td>0.7520(6)</td>
<td>0.3259(2)</td>
<td>0.0573(9)</td>
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<tr>
<td>H8A</td>
<td>0.2932</td>
<td>0.6364</td>
<td>0.3140</td>
<td>0.086*</td>
</tr>
<tr>
<td>H8B</td>
<td>0.4003</td>
<td>0.7659</td>
<td>0.3623</td>
<td>0.086*</td>
</tr>
<tr>
<td>H8C</td>
<td>0.3345</td>
<td>0.8123</td>
<td>0.2802</td>
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<tr>
<td>C9</td>
<td>0.1465(7)</td>
<td>0.8677(6)</td>
<td>0.43742(19)</td>
<td>0.0663(11)</td>
</tr>
<tr>
<td>H9A</td>
<td>0.1900</td>
<td>0.9795</td>
<td>0.4402</td>
<td>0.100*</td>
</tr>
<tr>
<td>H9B</td>
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<td>0.4588</td>
<td>0.100*</td>
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<tr>
<td>N1</td>
<td>0.0001(6)</td>
<td>0.7701(6)</td>
<td>0.24471(16)</td>
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<td>0.0914</td>
<td>0.7105</td>
<td>0.2337</td>
<td>0.051*</td>
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<td>N2</td>
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<td>0.8148(4)</td>
<td>0.35780(15)</td>
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<td>S1</td>
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<td>0.94115(11)</td>
<td>0.34745(4)</td>
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<td>Br1</td>
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<td>0.95693(5)</td>
<td>0.10617(2)</td>
<td>0.0548(6)</td>
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</table>

Abstract

C₉H₁₁BrN₂S, orthorhombic, P2₁2₁2₁ (no. 19), a = 7.5187(3) Å, b = 8.0634(3) Å, c = 17.5320(6) Å, V = 1062.90(7) Å³, Z = 4, R(F) = 0.0216, wR(F²) = 0.0536, T = 296(2) K.

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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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. $U_{eq}(H)$ 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 intramolecular 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].

Acknowledgements: The authors extend their appreciation to the College of Applied Medical Sciences Research Centre and the Deanship of Scientific Research at King Saud University for their funding of this research and to Cardiff University for continued support.

References