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Crystal structure of 1-[(Z)-[4-(4-methoxyphenyl)butan-2-ylidene]amino]-3-phenylurea, C\textsubscript{18}H\textsubscript{21}N\textsubscript{3}O\textsubscript{2}

Abstract

C\textsubscript{18}H\textsubscript{21}N\textsubscript{3}O\textsubscript{2}, triclinic, P\textbar\textbar\textsubscript{1} (no. 2), a = 8.5155(4) Å, b = 10.6415(4) Å, c = 19.0732(10) Å, β = 89.689(4)°, γ = 80.666(4)°, V = 1683.74(14) Å\textsuperscript{3}, Z = 4, R\textsubscript{gt}(F) = 0.055, wR\textsubscript{ref}(F\textsuperscript{2}) = 0.133, T = 100 K.

CCDC no.: 1830404

Table 1: Data collection and handling.

<table>
<thead>
<tr>
<th>Crystal:</th>
<th>Colourless prism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size:</td>
<td>0.44 × 0.29 × 0.10 mm</td>
</tr>
<tr>
<td>Wavelength:</td>
<td>Mo Kα radiation (0.71073 Å)</td>
</tr>
<tr>
<td>µ:</td>
<td>0.8 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>Diffractometer, scan mode:</td>
<td>SuperNova Dual, ω scans</td>
</tr>
<tr>
<td>2θ\textsubscript{max}, completeness:</td>
<td>55°, &gt;99%</td>
</tr>
<tr>
<td>N(hkl)\textsubscript{measured}, N(hkl)\textsubscript{unique}, R\textsubscript{int}:</td>
<td>15637, 7710, 0.040</td>
</tr>
<tr>
<td>Criterion for I\textsubscript{obs}, N(hkl)\textsubscript{gt}:</td>
<td>I\textsubscript{obs} &gt; 2 σ(I\textsubscript{obs}), 4964</td>
</tr>
<tr>
<td>N(param)\textsubscript{refined}:</td>
<td>431</td>
</tr>
<tr>
<td>Programs:</td>
<td>Agilent [1], SHELX [2, 3], ORTEP [4]</td>
</tr>
</tbody>
</table>

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 materials

To a solution of 4-phenylsemicarbazide (0.151 g, 1 mmol) in heated absolute ethanol (20 mL) was added slowly a heated ethanol solution (20 mL) of 4-methoxy-2-butanone (0.102 g, 1 mmol) while stirring for 20 min. The white precipitate was filtered, washed with cold ethanol and dried in vacuo. Single crystals were grown at room temperature from slow evaporation of a mixture of ethanol and acetonitrile (1:1 v/v). IR (cm\textsuperscript{-1}): 3338 (N—H), 1665 (C=O), 1597 (C=N), 1239 (C—N), 1025 (C=S). MS: m/z 311.25 [M]+.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with U\textsubscript{iso}(H) = 1.2–1.5 U\textsubscript{eq}(C). The N-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint of N—H = 0.88 ± 0.01 Å, and with U\textsubscript{iso}(H) set to 1.2 U\textsubscript{eq}(N).

Comment

It is well known that the condensation of semicarbazides with aldehydes/ketones gives rise to a class of potential Schiff base ligands. These molecules attract interest in...
terms of potential biological activity, most notably in the context of their anti-convulsant properties with the 4-(4-fluorophenoxo)benzaldehyde semicarbazone being the subject of considerable investigations in this regard [5]. In connection with on-going studies of the biological activity of transition metal thiosemicarbazone complexes [6], recently the synthesis and characterization of a new Schiff base ligand, derived from the reaction of aryl semicarbazide and vanillylacetone, was described [7]. In continuation of these studies, the title Schiff base molecule was characterized.

Two independent molecules comprise the asymmetric unit of the title compound. As seen from the Figure (70% displacement ellipsoids), the molecules present many similarities but, with the obvious difference related to the relative disposition of the methoxyphenyl residues. The molecule comprises a di-substituted urea residue. At one end, there is a phenyl ring while at the other, an imine (Z-configuration) group connects the urea residue to the 4-methoxyphenyl ring
via an ethane link. The four atoms of the urea core are strictly planar with a r.m.s. deviation of 0.0004 Å for the fitted atoms [0.0014 Å for the O3-molecule]. The amine-N—H and imine-N atoms are syn, a disposition that enables the formation of intramolecular amine-N—H···N(amine) hydrogen bonds [N1—H1n···N3: 2.111(16) Å and 113.8(14)°; N4—H4n···N6: 2.125(16) Å and 113.7(13)°]. The dihedral angle between the CN2O plane and the adjacent phenyl ring is 3.85(13)° [7.54(12)°], consistent with a co-planar relationship. The dihedral angles between the outer phenyl rings are 37.56(8) and 66.56(5)° for the O1- and O3-molecules, respectively.

The most prominent feature of the molecular packing is the formation of an eight-membered {···HNCO}2 amide synthon formed between the two independent molecules comprising the asymmetric unit [N2—H2n···O3: 2.001(14) Å and 171.0(18)°; N5—H5n···O1: 1.956(14) Å and 172.8(17)°].

There is a sole literature precedent for molecules of this type as discussed recently [7]. The structure of this molecule, derived from the reaction of semicarbazide and vanillinacetone, presents very similar features to that described above.

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**References**