Redetermination of the crystal structure of endo-2-carboxy-bicyclo[2.2.1]-heptane, C₈H₁₂O₂

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Abstract

C₈H₁₂O₂, triclinic, P₁̅n̅ (no. 2), a = 5.8945(4) Å, b = 6.0522(3) Å, c = 10.7643(7) Å, α = 101.219(2)°, β = 90.581(2)°, γ = 95.445(2)°, V = 374.8 Å³, Z = 2, Rₑ(f) = 0.0417, wRₑ(f) = 0.1105, T = 200 K.

Table 1. Data collection and handling.

<table>
<thead>
<tr>
<th>Crystal: colourless blocks,</th>
<th>structure factor amplitudes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength: Mo Kα radiation (0.71073 Å)</td>
<td>µ = 0.88 cm⁻¹</td>
</tr>
<tr>
<td>Diffractionometer, scan mode: Bruker APEX-II CCD, ϕ and θ</td>
<td>2θ_max: 56.54°</td>
</tr>
<tr>
<td>N(hkl)min, N(hkl)max:</td>
<td>8121, 1827</td>
</tr>
<tr>
<td>Criterion for I_min, I_max:</td>
<td>I_max &gt; 2 σ(I_max), 1574</td>
</tr>
<tr>
<td>N zijlstra(WINGX)</td>
<td>92</td>
</tr>
<tr>
<td>Programs: SHEXL, WinGX, MERCURY, PLATON [11–14]</td>
<td></td>
</tr>
</tbody>
</table>

Source of material

The compound was obtained commercially (Frinton Laboratories). Crystals suitable for the diffraction study were obtained upon sublimation of the product at room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.99 Å for methylene groups and C–H 1.00 Å for methine groups) and were included in the refinement in the riding model approximation, with U(eq) set to 1.2U(eq)(C). The H atom of the carboxyl group was allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [11]), with U(eq)(H) set to 1.5U(eq)(O). Due to very low residual electron densities after refinement of given structural model, no disorder model could be set up.

Discussion

The bicycloheptane scaffold has been a focus of research in organic chemistry for many decades. Especially questions centered around classical and non-classical carbocations focused on this key structure and only very recently the existence of penta-coordinate carbon could be proven experimentally on grounds of diffractometer experiments based on single crystals [1, 2]. The latter finding motivated us to include bicycloheptane-derived ligands into our research efforts in synthesizing novel coordination compounds of transition metals. As a convenient starting point for our studies, the title compound was chosen as it is commercially available. The molecular and crystal structure of endo-norbornane-2-carboxylic acid have been mentioned in the literature once, however, no 3D coordinates have been provided [3]. As the structures of envisioned target molecules shall be elucidated by means of diffraction experiments on single crystals, the structure of the title compound was redetermined. The title compound is the endo-configured carboxylic acid of norbornane. A puckering analysis according to Cremer & Pople [4] showed the five-membered rings in the norbornane scaffold to adopt an E₁ and an E₅ conformation, respectively [5]. The flap atom in both cases is carbon atom C7. For the six-membered ring, a B₃₁₅ (B₁₅,C₇₅) conformation was found [6]. The C–O bond lengths were measured at 1.2130(14) Å and 1.3206(14) Å for the double-bonded and the single-bonded oxygen atom. The latter two values are in good agreement with other values reported for carboxylic acids whose metrical parameters have been deposited with the Cambridge Structural Database [7]. In the crystal, classical hydrogen bonds of the O–H···O type are predominant. There are C–H···O contacts whose range falls below the sum of van-der-Waals radii of the atoms participating in them. While the hydrogen bonds give rise to the formation of centrosymmetric dimers as often observed for carboxylic acids [8], the C–H···O contacts extend these dimeric units to strands along the crystallographic a axis. The latter contacts are supported by one of the hydrogen atoms at a bridge-head position of the norbornane scaffold and employ the carboxylic oxygen atom as acceptor thus giving rise to two anti-dromic C–H···O contact chains. In terms of graph-set analysis [9, 10], the descriptor for the classical hydrogen bonds is R²(8) on the unary level while the C–H···O contacts necessitate a C₁(5) descriptor on the same level.

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References


