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2,3-Dimethoxy-10-oxostrychnidinium 3-carboxybenzoate trihydrate: the 1:1 proton-transfer compound of brucine with isophthalic acid

Graham Smith, Urs D. Wermuth, David J. Young and Jonathan M. White
2,3-Dimethoxy-10-oxostyrchnidinium 3-carboxybenzoate trihydrate: the 1:1 proton-transfer compound of brucine with isophthalic acid

The structure of the title compound, 

\[ \text{C}_{23}\text{H}_{27}\text{N}_{2}\text{O}_{4}^+ \cdot \text{C}_{6}\text{H}_{5}\text{O}_{4}^- \cdot 3\text{H}_{2}\text{O}, \]

has been determined at 130 K. The hydrogen isophthalate anions and the water molecules (one of which is disordered over two approximately equal sites) associate through extensive hydrogen-bonded interactions, including those with the common undulating brucinium cation layer substructures, forming a three-dimensional framework structure.

Comment

The Strychnos alkaloids strychnine and brucine have mostly been used to resolve enantiomorphic mixtures of chiral compounds, and the number of crystal structures of both salts and adducts of strychnine and brucine with such compounds reflects this. However, these alkaloids form salts equally well with achiral acids, but as with the chiral compounds, formation of good crystalline products is largely a hit-or-miss process. Oshikawa et al. (2002) observed the selectivity of brucine for meta-substituted benzoic acids, so we have continued that investigative theme, preparing and characterizing a number of brucine compounds with substituted benzoic acid analogues. Structurally characterized examples include the brucinium salts with 3-nitrophthalic acid (Smith, Wermuth et al., 2005), and 5-nitrosalicylic acid, 3,5-dinitrosalicylic acid and 5-sulfosalicylic acid (Smith et al., 2006a). Strychnine demonstrated a lesser tendency to form crystalline salts with this same acid series but did give good crystals with 5-nitrosalicylic acid and 3,5-dinitrosalicylic acid (Smith, Wermuth & White, 2005).

We also reacted isophthalic acid (1,3-benzenedicarboxylic acid) in a 1:1 stoichiometric ratio with both brucine and strychnine in 80% propan-2-ol–water, this solvent being employed instead of the 80% ethanol–water used in our normal preparative procedure. This was also done to test the observation by Sada et al. (1998) that the use of propan-2-ol promotes the crystallization of brucinium carboxylate compounds, often with incorporation of propan-2-ol solvent.

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molecules. However, the product from our reaction of isophthalic acid with brucine was a hydrate, (I), and its structure is reported here. The parallel reaction employing strychnine gave no crystalline product.

In compound (I), protonation occurs, as expected, at N19 of the brucine cage (Fig. 1). Setting the absolute configuration for the brucine cage (Fig. 1) according to that determined for the parent strychnine gave no crystalline product.

Crystal data

\[ \text{C}_{14} \text{H}_{14} \text{N}_{2} \text{O}_4 \cdot \text{C}_{12} \text{H}_{12} \text{O}_4 \cdot 3 \text{H}_2 \text{O} \]

\[ Z = 4 \]

\[ D_r = 1.395 \text{ Mg m}^{-3} \]

Orthorhombic, \( P2_12_12_1 \)

\[ a = 12.4560 \text{ Å} \]

\[ b = 29.3559 \text{ Å} \]

\[ c = 8.0020 (5) \text{ Å} \]

\[ V = 2926.0 (3) \text{ Å}^3 \]

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\[ a = 12.4560 \text{ Å} \]

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\[ c = 8.0020 (5) \text{ Å} \]

\[ V = 2926.0 (3) \text{ Å}^3 \]

Data collection

Bruker SMART CCD area-detector diffractometer

3815 independent reflections

2474 reflections with \( I > 2 \sigma(I) \)

Refinement

Refinement on \( F^2 \)

\( R(F^2) = 0.054 \)

\( wR(F^2) = 0.095 \)

\( S = 0.85 \)

3815 reflections

410 parameters

\( \Delta R_{	ext{max}} = 0.26 \text{ e Å}^{-3} \)

\( \Delta R_{	ext{free}} = -0.22 \text{ e Å}^{-3} \)

Table 1

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D−H···A</th>
<th>D−H</th>
<th>H···A</th>
<th>D···A</th>
<th>D−H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N19−H19···O11i</td>
<td>0.91 (3)</td>
<td>1.73 (3)</td>
<td>2.629 (3)</td>
<td>173 (4)</td>
</tr>
<tr>
<td>N19−H19···O121ii</td>
<td>0.91 (3)</td>
<td>2.57 (4)</td>
<td>3.217 (3)</td>
<td>129 (3)</td>
</tr>
<tr>
<td>O321−H321···O1W</td>
<td>0.89 (4)</td>
<td>2.646 (3)</td>
<td>178 (7)</td>
<td></td>
</tr>
<tr>
<td>O1W−H11W···O22ii</td>
<td>0.90 (3)</td>
<td>1.95 (3)</td>
<td>2.818 (3)</td>
<td>162 (4)</td>
</tr>
<tr>
<td>O1W−H12W···O12ii</td>
<td>0.90 (3)</td>
<td>1.95 (3)</td>
<td>2.841 (3)</td>
<td>179 (4)</td>
</tr>
<tr>
<td>O2W−H21W···O31i</td>
<td>0.85 (5)</td>
<td>2.19 (5)</td>
<td>2.780 (4)</td>
<td>126 (4)</td>
</tr>
<tr>
<td>O2W−H22W···O2W</td>
<td>0.85 (6)</td>
<td>2.42 (6)</td>
<td>2.815 (3)</td>
<td>110 (5)</td>
</tr>
<tr>
<td>O3WA−H31W···O12i</td>
<td>0.91 (6)</td>
<td>1.96 (6)</td>
<td>2.822 (10)</td>
<td>178 (8)</td>
</tr>
<tr>
<td>O3WA−H32W···O22ii</td>
<td>0.90 (7)</td>
<td>1.85 (7)</td>
<td>2.705 (7)</td>
<td>157 (6)</td>
</tr>
<tr>
<td>O3WB−H33W···O12i</td>
<td>0.90 (7)</td>
<td>1.77 (7)</td>
<td>2.667 (10)</td>
<td>179 (5)</td>
</tr>
<tr>
<td>O3WB−H34W···O2W</td>
<td>0.89 (7)</td>
<td>1.86 (7)</td>
<td>2.752 (11)</td>
<td>179 (5)</td>
</tr>
</tbody>
</table>

Symmetry codes:

(i) \( x + \frac{1}{2}, y - \frac{1}{2}, z + 1 \);

(ii) \( x - 1, y, z - 1 \);

(iii) \( x + 1, y, z \);

(iv) \( -x + 1, -y + 2, z \);

(v) \( -x, -y + 1, z \);

(vi) \( x - \frac{1}{2}, y + \frac{1}{2}, z + 1 \).
H atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions, with C—H(aromatic) = 0.95 Å and C—H(aliphatic) = 0.98–1.00 Å, and treated using a riding model, with $U_{	ext{iso}}(H) = 1.2U_{eq}(C)$. The atom-numbering scheme employed for the brucinium cation cage in (I) follows the original Robinson convention for strychnine (Holmes, 1952). The absolute configuration determined for the parent strychnine (Peerdeman, 1956) was invoked.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997) in WinGX (Farrugia, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997) in WinGX; molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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References