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1,1'-((1,4-Butanediyl)bis(tetrahydrofuranium)) trifluoromethanesulfonate

The title compound, C_{12}H_{26}O_{2}^{2+}·2CF_{3}O_{4}S^{−}, is the first bisoxonium salt for which a crystal structure is reported. The cation is located on an inversion centre and it features a nonplanar C_{3}O^{+} oxonium unit where the O atom is displaced by 0.375 (2) Å from the plane of its substituents.

Comment

It is well known that organosilyl trifluoromethanesulfonates (OTIs), such as Me_{3}SiOTf, are potent initiators for the cationic polymerization of tetrahydrofuran (THF) (Hirakach & Marynowski, 1995). The title compound, (I), obtained accidentally from a THF solution of i-Bu_{3}SiOTf (Uhlig & Tschach, 1989) as colourless hygroscopic crystals, can be regarded as an oligomeric intermediate of the THF polymerization. The same bisoxonium salt has been reported previously from the reaction of triflic acid anhydride with THF but was not characterized by X-ray crystallography at that time (Smith et al., 1977).

The molecular structure of (I) is shown in Fig. 1. The cation is centrosymmetric and features a nonplanar C_{3}O^{+} oxonium unit, where the O atom is displaced by 0.375 (2) Å from the plane of its substituents. The shortest oxonium-to-trifluoromethanesulfonate O···O distance of 3.200 (4) Å is slightly longer than the sum of the van der Waals radii (3.04 Å; Bondi, 1964). The cations and anions are arranged into homoionic columns running along the crystallographic c axis.

Experimental

Crystals of (I) suitable for structure analysis were obtained directly from a THF solution of i-Bu_{3}SiOTf prepared according to the literature procedure (Uhlig & Tschach, 1989).

Crystal data

\[
\begin{align*}
\text{C}_{12}\text{H}_{26}\text{O}_{2}^{2+}·2\text{CF}_{3}\text{O}_{4}\text{S}^{−} & \\
M_r & = 498.45 \\
\text{Monoclinic, } P2_1/c & \\
a & = 6.5708 (14) \text{ Å} & \\
b & = 12.542 (3) \text{ Å} & \\
c & = 13.334 (3) \text{ Å} & \\
\beta & = 102.765 (5)^{\circ} & \\
V & = 1039.1 (4) \text{ Å}^3 & \\
\end{align*}
\]

Z = 2

D_{c} = 1.593 \text{ Mg m}^{-3}

Mo Kα radiation

\(\mu = 0.35 \text{ mm}^{-1}\)

Plate, colourless

0.50 \times 0.15 \times 0.06 \text{ mm}
Data collection
Bruker SMART CCD area-detector diffractometer
y and ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2000)
Tmin = 0.760, Tmax = 0.979
8862 measured reflections
2249 independent reflections
1708 reflections with I > 2σ(I)
Rint = 0.077
θmax = 27.0°

Refinement
Refinement on F²
wR(F²) = 0.133
S = 1.13
2249 reflections
146 parameters
H-atom parameters constrained

w = 1/[σ²(F⁰²) + (0.07P)²]
where P = (F² + 2F̃²)/3
(Δ/σ)max < 0.001
Δρmax = 0.58 e Å⁻³
Δρmin = -0.32 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-O1</td>
<td>1.492 (3)</td>
</tr>
<tr>
<td>C4-O1-C5</td>
<td>108.62 (15)</td>
</tr>
<tr>
<td>C4-O1-C5</td>
<td>117.84 (16)</td>
</tr>
<tr>
<td>O1-C5-C6-C7</td>
<td>-59.6 (3)</td>
</tr>
<tr>
<td>C3-C4-O1-C5</td>
<td>-167.5 (3)</td>
</tr>
<tr>
<td>C3-C4-O1-C5</td>
<td>154.3 (2)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) −x, −y, z + 2, −z + 1.

One of the C atoms of the tetrahydrofuran ring is disordered over two positions, C3 and C3′, with occupancy factors of 0.73 (2) and 0.27 (2), respectively. All H atoms were introduced at calculated positions and constrained to ride on their parent atoms with C-H distances of 0.99 Å and Ueq(H) = 1.2Ueq(C).

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Bergerhoff et al., 1996); software used to prepare material for publication: SHELXL97.

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References