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A Sodium Salt of the Dimer of Boronoterephthalic Acid Anhydride

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A sodium salt of the dimer of boronoterephthalic acid anhydride

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The title compound, sodium bis(6-carboxy-1-hydroxy-3-oxo-1,3-dihydro-2,1-benzoxaborol-1-yl)oxidanium, Na⁺/C₁₆H₁₅B₂O₁₅, was prepared in two steps from 2-bromo-p-xylene. Its crystal structure was determined at 140 K and has triclinic (P₁) symmetry. The compound presents a unique structural motif, including two units of the cyclic anhydride of boronoterephthalic acid, joined by a protonated, and thereby trivalent, oxonium center. Association in the crystal is realized by complementary hydrogen bonding of the carboxyl groups, as well as by coordination of the sodium cations to the oxygen centers on the five-membered rings.

Comment

Flame retardants are widely used in polymeric and composite materials, and their share of the overall polymer additive market has grown to nearly 30%. While almost half of the materials in use are halogenated structures, increased government scrutiny and environmental and toxicology problems have played an important role in the recent surge of research work and commercial activity related to the discovery and implementation of new nonhalogenated flame retardants. The latter are frequently phosphorus- or nitrogen-based, but there has also been increasing interest in boron-containing compounds (Pitts, 1973; Troitzsch, 1998; Morgan et al., 2000). Borates and boric acid have been shown to act as synergists and are often used in combination with other flame-retardant substances, such as halogenated materials (Wu et al., 2007). Recent years have also seen developments in the area of boron-containing reactive flame retardants (Armitage et al., 1996).

In our ongoing effort to design and prepare novel boron-based reactive flame retardants, we recently endeavored to prepare boronoterephthalic acid, (2), which led to an unexpected synthetic outcome, illustrated in the Scheme. The starting material, 2-bromo-p-xylene, was converted to a Grignard reagent under standard conditions, followed by reaction of the latter with trimethyl borate and subsequent acidification, to generate 2,5-dimethylphenylboronic acid, (1) (Chen et al., 2003). Oxidation of the methyl groups with KMnO₄ under basic conditions (Tao et al., 2002), followed by acidification to pH 2, resulted in the formation of a white solid material, which was anticipated to be the target structure, (2). Instead, X-ray crystallographic analysis demonstrated that it was in fact sodium bis(6-carboxy-1-hydroxy-3-oxo-1,3-dihydro-2,1-benzoxaborol-1-yl)oxidanium, (3), a novel type of structure, containing two units of cyclic boronic carboxylic anhydride connected via a formally positively charged oxygen bridge.

The asymmetric unit of (3) exhibits an almost perfect stacking of the two aromatic rings (Fig. 1), as evidenced by the torsion angles B₂—O₁—B₁—O₃ and B₁—O₁—B₂—O₈, both close to 180° (Table 1). The dimer is highly symmetric with respect to the central O₁ atom, with B₁—O₁ = 1.559 (2) Å and B₂—O₁ = 1.549 (3) Å. The B centers are each part of a five-membered ring, properly described as a cyclic mixed carboxylic–boronic acid anhydride ring, with a hydroxy group attached to the B atom. The B—OH distances [1.428 (3) and 1.435 (3) Å] are virtually identical, and considerably elongated compared with typical distances for B—O(H) bonds in related arylboronic acids, such as 4-carboxyphenylboronic acid [1.275 (3) Å; SeethaLekshmi & Pedireddi, 2007] or 4-carboxy-2-nitrobenzeneboronic acid [1.346 (3) and 1.365 (4) Å; Soundararajan et al., 1993]. The B—O distances in the five-membered rings of (3) are even longer, at 1.509 (3) and 1.524 (3) Å. Two plausible reasons may be advanced to account for the differences. First, the degree of B—O—conjugation, which is greater when boron is in a trigonal-planar environment, results in shorter B—O distances. Thus, an increase of about 0.1 Å is observed for the B—O distance upon transition from phenylboronic acid [tricoordinated boron, B—O = 1.371 (7) Å] to its diethanolamine adduct [tetracoordinated boron, B—O = 1.469 (3) and 1.457 (3) Å; Rettig & Trotter, 1975, 1977] or the 2,6-dimethanolpyridine adduct [B—O = 1.479 (6) and 1.459 (6) Å; Vargas et al., 2005]. A second factor could be the steric crowding, which is greater...
at a tetrahedral (compared with a trigonal-planar) B center, leading to elongation of the B—O distances and thereby minimizing van der Waals interactions.

The carboxyl groups, as expected, are nearly coplanar with the aromatic rings, due to stabilizing conjugation. The C=O and C—O bond lengths differ from their typical values. The former are longer than typical [1.248 (3) and 1.253 (3) Å], while the latter are shorter [1.287 (3) and 1.283 (3) Å]. Such bond-length alteration has been observed in the crystal structures of other carboxylic acids (Etter et al., 1988), although it is not a general phenomenon. The bond difference can vary from less than 0.01 Å in 2,3-dimethoxybenzoic acid (Gopalakrishna & Cartz, 1972) to about 0.17 Å in 2-ethoxybenzoic acid (Bryan & White, 1982). The difference in lengths is similar in 4-carboxyphenylboronic acid hydrate [1.237 (2) and 1.295 (2) Å; SeethaLekshmi & Pedireddi, 2007], but it is somewhat greater in 4-carboxy-2-nitrophenylboronic acid [1.209 (3) and 1.322 (3) Å; Soundararajan et al., 1993].

A plot of the crystal packing of (3) is shown in Fig. 2. Association in the crystal is realised in two different ways: (i) by coordination of O-atom centers from the five-membered rings to Na+ cations, and (ii) by complementary hydrogen bonding of the carboxyl groups, forming an eight-membered ring structure with two hydrogen bonds, in a fashion typical for carboxylic acids in general (Gavezzotti, 2008). The carboxyl hydrogen-bond H···O distances (Table 2) are significantly shorter than those observed in the crystal structures of closely related compounds, such as 4-carboxy-2-nitrophenylboronic acid [H—O = 1.86 (3) Å and O···O = 2.715 (3) Å; Soundararajan et al., 1993] or 4-carboxyphenylboronic acid quarter-hydrate (SeethaLekshmi & Pedireddi, 2007). The nearly equal C—O distances and shortened hydrogen bonds (Table 2) should be attributed to strong interactions within the hydrogen-bonded dimer.

**Experimental**

$^1$H and $^{13}$C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, and referenced to the solvent [CDCl$_3$, 7.27 p.p.m.; DMSO-$d_6$, 2.49 p.p.m.; CD$_3$OD, 3.32 (H) and 49.0 p.p.m. ($^{13}$C)]. Elemental analysis was provided by Atlantic Microlab, Norcross, Georgia, USA. 2,5-Dimethylphenylboronic acid, (1), was prepared from 2-bromo-p-xylene according to the literature procedure of Chen et al. (2003).

For the preparation of (3), 2,5-dimethylphenylboronic acid (1.35 g, 9.01 mmol) was dissolved in NaOH (9.0 ml, 50% wt. solution) and water (18.0 ml) and heated to 323 K. KMnO$_4$ (6.55 g, 41.40 mmol) in H$_2$O (70 ml) was added dropwise over a period of 1 h. The solution was kept at 323 K for 3 h, and then cooled to 273 K. The pH was adjusted to 8, using concentrated HCl, and the mixture was filtered.

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**Figure 1**
Two views of the crystal structure of compound (3). Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**
A crystal packing plot of (3), including the hydrogen bonds (dotted lines), viewed along the b axis.
The filtrate was further acidified to pH 2 at 273 K. The solvent was removed under reduced pressure and the resultant white solid was recrystallized from water to yield colorless crystals (yield 1.01 g, 52%). The product did not melt below 623 K. 1H NMR (D2O): 6.76 (d, J = 6.90 Hz, 1H), 7.88 (d, J = 6.90 Hz, 1H), 8.01 (s, 1H); 13C NMR (DMSO-6d6): δ 6.92 (s, 1H), 7.53 (d, J = 7.78 Hz, 1H), 7.75 (dd, J1 = 1.22 Hz, J2 = 7.81 Hz, 1H), 7.89 (d, J = 8.08 Hz, 1H), 8.03 (dd, J1 = 1.69 Hz, J2 = 8.12 Hz, 1H), 8.22 (s, 1H), 8.39 (d, J = 1.49 Hz, 1H); 1H NMR (CD3OD): 6.90 (d, J = 9.00 Hz, 1H), 7.88 (d, J = 9.00 Hz, 1H), 8.01 (s, 1H); 13C NMR (CD3OD): δ 7.81 Hz, 1H), 7.89 (d, J = 8.08 Hz, 1H), 8.03 (dd, J1 = 1.69 Hz, J2 = 8.12 Hz, 1H), 8.22 (s, 1H), 8.39 (d, J = 1.49 Hz, 1H).

Crystal data
Na+·C16H11B2O13·H2O: C 41.79, H 3.29%; found: C 41.94, H 3.35%.

Table 1
Selected geometric parameters (Å, °).

<table>
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<tr>
<th>Formula</th>
<th>d(H–A) · · · A' (Å)</th>
<th>d(H–A) · · · A' (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–H1</td>
<td>0.96 (3)–1.00 (3)</td>
<td>C1–H1</td>
</tr>
<tr>
<td>O–H1</td>
<td>0.82 (3)–0.92 (4)</td>
<td>O–H1</td>
</tr>
</tbody>
</table>

Table 2
Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D–H–A</th>
<th>D–H–A</th>
<th>D–H–A</th>
<th>D–H–A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1–H1A–O9a</td>
<td>0.89 (3)</td>
<td>O3–H3A–O4'</td>
<td>0.87 (4)</td>
</tr>
<tr>
<td>O5–H5A–O11b</td>
<td>1.22 (6)</td>
<td>O8–H8A–O3''</td>
<td>0.92 (4)</td>
</tr>
<tr>
<td>O10–H10A–O6ii</td>
<td>1.18 (6)</td>
<td>O12–H12A–O1</td>
<td>0.91 (3)</td>
</tr>
<tr>
<td>O12–H12B–O3''</td>
<td>0.82 (3)</td>
<td>O13–H13A–O5'</td>
<td>0.85 (4)</td>
</tr>
<tr>
<td>O13–H13B–O8''</td>
<td>0.91 (4)</td>
<td>O12–H12B–O3''</td>
<td>0.82 (3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x + 1, y, z; (ii) −x + 2, −y, −z + 1; (iii) x, y − 1, z; (iv) −x + 2, −y + 1, −z; (v) x, y, z.

References
SHELXTL (Sheldrick, 2008; software used to solve structure: SHELX97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3076). Services for accessing these data are described at the back of the journal.

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