

4-2011


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Simmons, Scott; Fratini, Albert; and Benin, Vladimir, "A Sodium Salt of the Dimer of Boronoterephthalic Acid Anhydride" (2011). *Chemistry Faculty Publications*. Paper 17.
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A sodium salt of the dimer of boronoterephthalic acid anhydride

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Received 7 January 2011

Accepted 3 March 2011

Online 12 April 2011

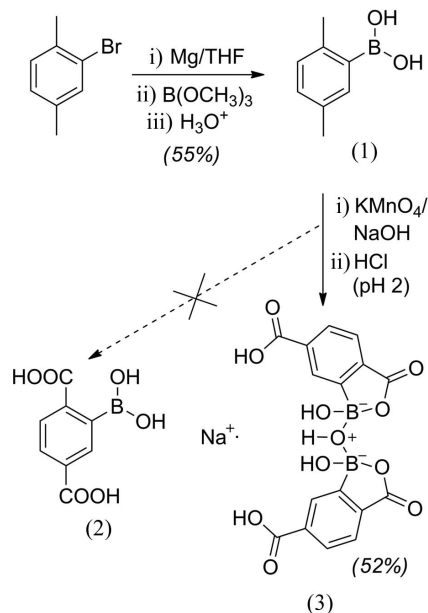
The title compound, sodium bis(6-carboxy-1-hydroxy-3-oxo-1,3-dihydro-2,1-benzoxaborol-1-yl)oxidanium, $\text{Na}^+ \cdot \text{C}_{16}\text{H}_{15}\text{B}_2\text{O}_{13}^-$, was prepared in two steps from 2-bromo-*p*-xylene. Its crystal structure was determined at 140 K and has triclinic ($P\bar{1}$) 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 KMnO_4 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 $\text{B2}-\text{O1}-\text{B1}-\text{O3}$ and $\text{B1}-\text{O1}-\text{B2}-\text{O8}$, both close to 180° (Table 1). The dimer is highly symmetric with respect to the central O1 atom, with $\text{B1}-\text{O1} = 1.559$ (2) Å and $\text{B2}-\text{O1} = 1.549$ (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 π -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

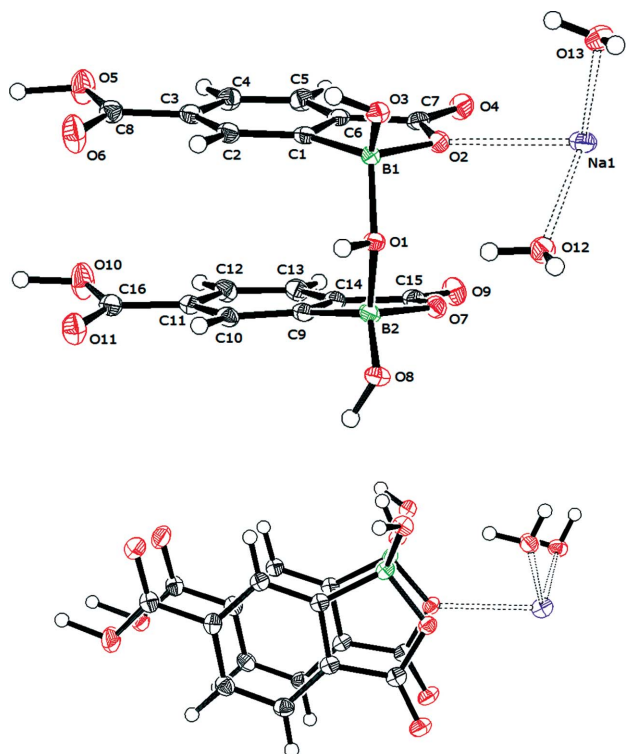


Figure 1
Two views of the crystal structure of compound (3). Displacement ellipsoids are drawn at the 50% probability level.

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

¹H and ¹³C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, and referenced to the solvent [CDCl₃ 7.27 p.p.m.; DMSO-*d*₆ 2.49 p.p.m.; CD₃OD 3.32 (¹H) and 49.0 p.p.m. (¹³C); D₂O 4.76 p.p.m.]. 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. KMnO₄ (6.55 g, 41.40 mmol) in H₂O (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.

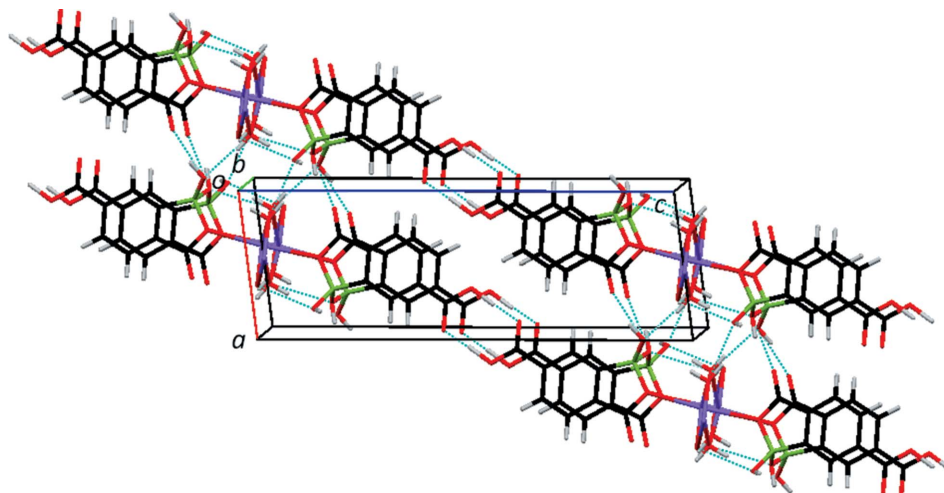


Figure 2
A crystal packing plot of (3), including the hydrogen bonds (dotted lines), viewed along the *b* axis.

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 (D_2O): δ 7.60 (*d*, J = 6.90 Hz, 1H), 7.88 (*d*, J = 9.00 Hz, 1H), 8.01 (*s*, 1H); ^1H NMR ($\text{DMSO}-d_6$): δ 6.92 (*s*, 1H), 7.53 (*d*, J = 7.78 Hz, 1H), 7.75 (*dd*, J_1 = 1.22 Hz, J_2 = 7.81 Hz, 1H), 7.89 (*d*, J = 8.08 Hz, 1H), 8.03 (*dd*, J_1 = 1.69 Hz, J_2 = 8.12 Hz, 1H), 8.22 (*s*, 1H), 8.39 (*d*, J = 1.49 Hz, 1H); ^1H NMR (CD_3OD): δ 7.85 (*d*, J = 7.58 Hz, 1H), 8.01 (*dd*, J_1 = 1.37 Hz, J_2 = 7.97 Hz, 1H), 8.13 (*d*, J = 0.88 Hz, 1H); ^{13}C NMR (CD_3OD): δ 126.76, 130.51, 131.88, 134.99, 140.74, 169.96, 174.21. Analysis calculated for $\text{C}_{16}\text{H}_{11}\text{B}_2\text{NaO}_{11}\cdot 2\text{H}_2\text{O}$: C 41.79, H 3.29%; found: C 41.94, H 3.35%.

Crystal data

$\text{Na}^+\cdot\text{C}_{16}\text{H}_{15}\text{B}_2\text{O}_{13}^-$ γ = 83.040 (6) $^\circ$
 M_r = 459.89 V = 893.83 (10) \AA^3
 Triclinic, $P\bar{1}$ Z = 2
 a = 6.7195 (5) \AA Cu $K\alpha$ radiation
 b = 7.1118 (4) \AA μ = 1.48 mm^{-1}
 c = 19.2802 (12) \AA T = 140 K
 α = 80.061 (5) $^\circ$ 0.40 \times 0.13 \times 0.02 mm
 β = 81.798 (6) $^\circ$

Data collection

Oxford Xcalibur Sapphire3 diffractometer Reid (1995)
 T_{\min} = 0.729, T_{\max} = 0.974
 Absorption correction: analytical [CrysAlis PRO (Oxford Diffraction, 2010), based on expressions derived by Clark & Reid (1995)]
 8576 measured reflections
 3521 independent reflections
 2825 reflections with $I > 2\sigma(I)$
 R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046 349 parameters
 $wR(F^2)$ = 0.111 All H-atom parameters refined
 S = 1.06 $\Delta\rho_{\text{max}}$ = 0.27 e \AA^{-3}
 3521 reflections $\Delta\rho_{\text{min}}$ = -0.32 e \AA^{-3}

All H atoms were initially located in difference Fourier maps and freely refined (coordinates and isotropic displacement parameters); C—H = 0.96 (3)–1.00 (3) \AA and O—H = 0.82 (3)–0.92 (4) \AA , except for carboxyl O—H = 1.18 (6)–1.22 (6) \AA .

Data collection: CrysAlis PRO (Oxford Diffraction, 2010); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

X-ray crystallographic measurements were conducted at the NEST Center of the University of Dayton. SS thanks the University of Dayton Research Council for summer financial support.

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.

Table 1

Selected geometric parameters (\AA , $^\circ$).

Na1—O2	2.5953 (17)	B2—O8	1.428 (3)
O1—B2	1.549 (3)	B2—O7	1.524 (3)
O1—B1	1.559 (2)	O5—C8	1.287 (3)
C1—B1	1.604 (3)	O6—C8	1.248 (3)
B1—O3	1.435 (3)	O10—C16	1.283 (3)
B1—O2	1.509 (3)	O11—C16	1.253 (3)
B2—O1—B1	131.96 (16)	C7—O2—B1	110.98 (16)
O3—B1—O1	105.20 (16)	O8—B2—O1	103.39 (16)
O2—B1—C1	102.31 (16)	O7—B2—C9	101.58 (16)
B2—O1—B1—O3	179.34 (17)	C4—C3—C8—O5	-8.2 (3)
B1—O1—B2—O8	179.56 (17)	C12—C11—C16—O11	169.1 (2)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O9 ⁱ	0.89 (3)	1.77 (3)	2.621 (2)	160 (3)
O3—H3 \cdots O4 ⁱ	0.87 (4)	1.88 (4)	2.708 (2)	161 (3)
O5—H5A \cdots O11 ⁱⁱ	1.22 (6)	1.39 (6)	2.610 (2)	173 (5)
O8—H8A \cdots O3 ⁱⁱⁱ	0.92 (4)	1.84 (4)	2.721 (2)	160 (3)
O10—H10A \cdots O6 ⁱⁱ	1.18 (6)	1.43 (6)	2.608 (2)	177 (5)
O12—H12A \cdots O1	0.91 (3)	2.07 (3)	2.950 (2)	163 (3)
O12—H12B \cdots O3 ^{iv}	0.82 (3)	2.00 (3)	2.814 (2)	167 (3)
O13—H13A \cdots O8 ^v	0.85 (4)	1.89 (4)	2.731 (2)	169 (3)
O13—H13B \cdots O8 ^{iv}	0.91 (4)	1.99 (4)	2.849 (2)	156 (3)

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) $x, y + 1, z$.

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