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Synthesis and structure of 3,4,5,6-tetrahydro-8-hydroxy-1H,6H-naphtho-[1,2-h]pyrrolo[2,1-e][1,3,6,2]dioxazaboronin-6-one dimer

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Abstract

A highly diastereoselective synthesis (>99%) of a novel chiral dimer obtained from 3,4,5,6-tetrahydro-8-hydroxy-1H,6H-naphtho[1,2-h]pyrrolo[2,1-e][1,3,6,2]dioxaza-boronin-6-one is described and details of the dimer crystal structure are presented.

Keywords: β-Naphthol; L-Proline; Boron; Diastereoselectivity; Crystal structure

Boronorganic compounds play at present a significant role in organic chemistry [1]. They are often used as catalysts in asymmetric synthesis, for example, in reduction of carbonyl derivatives [2] or Diels–Alder synthesis [3]. Formation of strong coordination bond to nitrogen atom by boron derivatives is applied in design and synthesis of new hetero- and macrocyclic compounds [4]. A number of examples of such derivatives with biologically active compounds are described in review paper by Contreras [5].

In our previous work [6], we described synthesis of 3,4,5,6-tetrahydro-8-hydroxy-1H,6H-naphtho[1,2-h]pyrrolo-[2,1-e][1,3,6,2]dioxazaboronin-6-one (**2**), which can be made by reaction of 1-[(2-hydroxy-1-naphthyl)-methyl]proline (**1**) with borium acid. By heating **2** in acetonitrile for a few hours, a dimer (**3**) is formed by taking away one water molecule (Scheme 1).

Interestingly, this reaction is characterized by an unusually high diastereoselectivity, of dimer **3** with d.e. >99% [7]. The dimer **3** was purified using column chromatography with the ethyl ester applied as eluent. After a few hours some well defined monocrystals of the dimer appear. The X-ray structure of the dimer **3** is shown in Fig. 1 [8]. In the solid state, the dimer **3** crystallises in the orthorhombic $P2_12_12_1$ space symmetry group with one molecule of the dimer and one co-crystallising diethyl ester moiety in the independent part of the unit cell. Although the dimer, in principle, could possibly be symmetric and crystallise in a special position, the ester molecule is asymmetric and is also located in an asymmetric manner relative to the aromatic fused rings of the dimer. There is also no disorder in the crystal. In consequence, one is obtaining a non-centrosymmetric space group. Unfortunately, we were unable to establish the absolute structure due to poor quality of data collected. The oxygen–boron bonds are quite flexible and their lengths are in the range from 1.381(3) Å for B(1)–O(1) through 1.384(3) Å for B(2)–O(1), 1.439(3) Å for B(1)–O(2), 1.444(3) Å for B(2)–O(5), 1.493(3) Å for B(2)–O(6) up to 1.508(4) Å for B(1)–O(3). It is interesting that although the valence angle B(1)–O(1)–B(2) opens up to 131.1(2)°, the bond lengths to the central oxygen O(1) are relatively short, shorter

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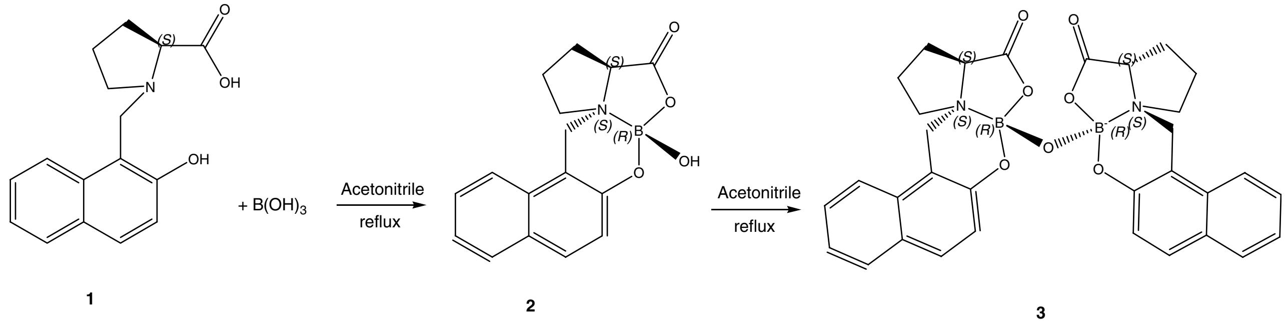

Scheme 1. Reaction leading to the dimer studied.

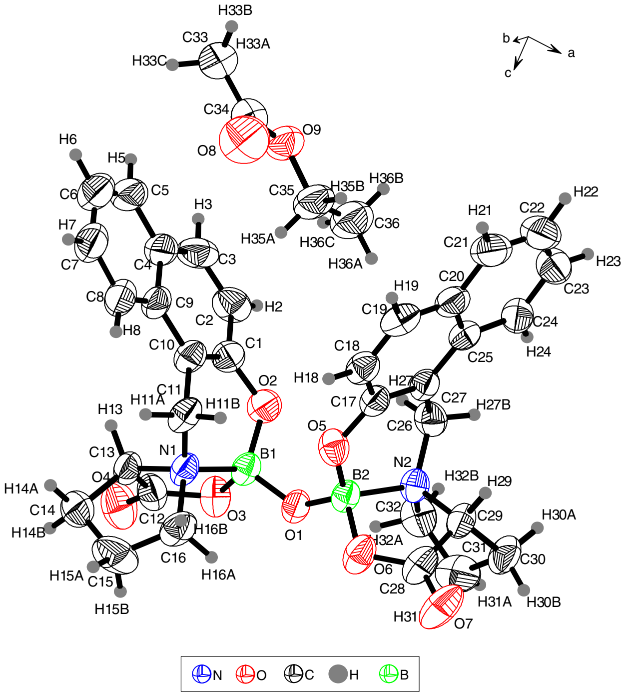

Fig. 1. Atomic labels and thermal ellipsoids (illustration of the atomic displacement parameters) for one molecule of the dimer **3** co-crystalised with one molecule of diethyl ether.

than the other B–O bonds. The B(1) and B(2) atoms have tetrahedral hybridisation with most of the valence angles close to 109°. The N–B bond lengths are equal to: 1.637(3) Å for N(1)–B(1) and 1.646(3) Å for N(2)–B(2). Comparing to the B–O bonds these bonds seems to be long but their bond lengths are similar to that of the other derivatives of this type [4,5,8]. The selected bond lengths and valence angles are listed in Table 2.

The molecule of the ester is located in an asymmetric manner between two naphthalene fragments which form an opening void defined by the O(2)...O(5) distance equal to 3.027(3) Å and the separation between the aromatic C(6) and C(22) atoms of 9.365(4) Å. The ester moiety interacts with the aromatic rings via C–H...π electron interactions of the the alkyl groups with the π-electrons of the aromatic rings. For example, the C(36)–H(36C) bond dipole interacts with the π-electron density of atoms C(2) and C(3), whereas C(36)–H(36A) interacts with aromatic carbons C(20) and C(25) (for numerical details of these close contacts, see Table 1). These last two intermolecular contacts are well below the van der Waals limit (0.15 and 0.23 Å, respectively). The other end of the diethyl ester is closed by a second molecule of the dimer; C(33)–H(33B)...O(1) [$1/2-x, -y, -1/2+z$] (see Fig. 2). Also the ester carbonyl

Table 1
Geometry of the shortest intermolecular contacts

D–H...A	Symmetry	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
C(36)–H(36C)...C(2)		0.96	2.86	3.650(5)	140
C(36)–H(36C)...C(3)		0.96	2.84	3.662(5)	144
C(36)–H(36A)...C(20)		0.96	2.75	3.479(5)	133
C(36)–H(36A)...C(25)		0.96	2.67	3.567(4)	156
C(24)–H(24)...O(8)	$1-X, -1/2+Y, 1.5-Z$	0.93	2.55	3.337(4)	143
C(33)–H(33B)...O(1)	$1/2-X$, −Y, $-1/2+Z$	0.96	2.65	3.385(4)	134
C(5)–H(5)...C(25)	$X-1, Y, Z$	0.93	2.89	3.531(4)	128
C(13)–H(13)...O(7)	$X-1, Y, Z$	0.98	2.39	3.149(4)	134
C(15)–H(15B)...C(7)	X − 1/2, $1/2-Y, 2-Z$	0.97	2.86	3.419(5)	118
C(31)–H(31A)...O(2)	$X-1/2, 1/2-Y, 2-Z$	0.97	2.61	3.566(4)	168
C(31)–H(31A)...O(3)	$X-1/2, 1/2-Y, 2-Z$	0.97	2.63	3.313(4)	128
C(31)–H(31)...B(1)	$X-1/2, 1/2-Y, 2-Z$	0.97	3.07	3.979(4)	157
C(23)–H(23)...C(8)	$1-X, Y-1/2, 3/2-Z$	0.93	2.83	3.567(4)	136