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1,3-Dihydro-1-hydroxy-3-morpholin-4-yl-2,1-benzoxaborole: product of the reaction of *o*-formylphenylboronic acid with morpholine

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***o*-Formylphenylboronic acid reacts with morpholine to form 1,3-dihydro-1-hydroxy-3-morpholin-4-yl-2,1-benzoxaborole. The typical hydrogen-bonded dimer motif with a planar benzoxaborole fragment has been obtained in the solid state. Copyright © 2005 John Wiley & Sons, Ltd.**

KEYWORDS: *o*-formylphenylboronic acid; morpholine; benzoxaborole; X-ray crystal structure

INTRODUCTION

Compounds possessing a boronic acid fragment connected by a spacer to an amine molecule are widely used as chemosensors for sugars.[1] Aminoboronic acids are also able to transport sugar molecules through liquid organic membranes.[2] From the point of view of their applications, the structures of these compounds have been investigated widely both in the solid state and in different solutions. The presence of a nitrogen atom gives the possibility of the formation of an intramolecular N–B bond, which enables complexation of the sugars at neutral pH.[3] Furthermore, the presence of hydroxy groups on the boron atom enables the formation of a strong intramolecular B–O–H···N hydrogen bond, which was observed in the solid state for several compounds.[4]

General methods for the synthesis of the above-mentioned compounds are shown in Scheme 1: the boronic group can be introduced to the amine molecule as shown in (a), or the *o*-formylphenylboronic acid can be transformed to the Schiff and finally the Mannich base as shown in (b).

On the other hand, arylboronic acid reacts with aliphatic amines to form complexes of their anhydrides with the amine molecule $(ArBO)_3 \cdot$ amine.[5] The structure presented in this paper is an unexpected product of the condensation reaction between *o*-formylphenylboronic acid and morpholine.

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EXPERIMENTAL

Synthesis

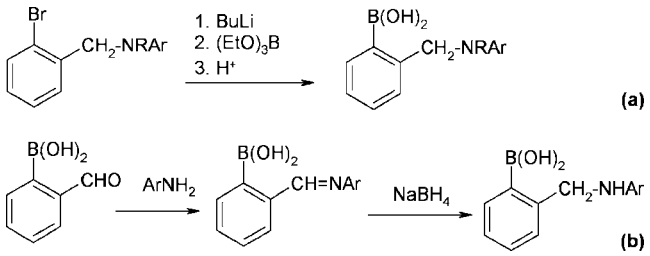
Morpholine (2.0 mmol) was added to a solution of *o*-formylphenylboronic acid (6.0 mmol) in ether (30 ml) and stirred for 1 h at room temperature. The reaction mixture was left for about 1 week for slow evaporation of the solvent; after this time, colourless crystals of compound **1** were filtered and dried in air; m.p. ca. 132 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 [4H, m, C_6H_4], 5.89 [1H, s, CH], 3.73 [4H, s, $(CH_2)_2O$], 2.71 ppm [4H, s, $(CH_2)_2N$]. ^{11}B NMR (64.1 MHz, $CDCl_3$) δ: 31.3 ppm. Analysis calculated for $C_{11}H_{14}BNO_3$: C 60.32, H 6.44, N 6.40; found: C 60.22, H 6.28, N 6.12.

Analyses

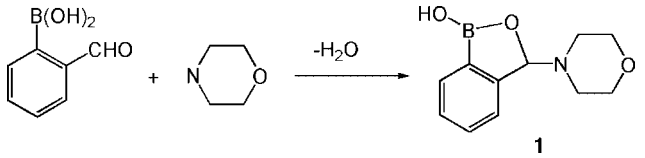
The NMR spectra were recorded on a Varian Mercury 400 BB spectrometer operating at 400 and 128.3 MHz for ^{1}H and ^{11}B, respectively. Elemental analysis was performed using a Perkin-Elmer 2400 apparatus.

X-ray diffraction

Data were collected at 100(2) K on a KUMA CCD *k*-axis diffractometer with graphite-monochromated Mo Kα radiation. $C_{11}H_{14}BNO_3$, $M = 219.04$, triclinic, P^-1, $a = 5.991(1)$, $b = 8.487(2)$, $c = 11.334(3)$ Å, $\alpha = 69.27(3)$, $\beta = 83.80(2)$, $\gamma = 86.90(2)°$, $V = 535.8(2)$ Å^3, $Z = 2$, R (1405 data with $I > 2\sigma(I)$; $\theta_{max} = 25.0°$) $= 0.039$, wR (all 1873 data) $= 0.092$. Programs used: CrysAlis CCD,[6] CrysAlis RED,[6] SHELXL,[7] DIAMOND.[8] CCDC deposition number: 277161.



Scheme 1. Synthesis of amino-substituted phenylboronic acids.



1

Scheme 2. Synthesis of the title compound **1**.

RESULTS AND DISCUSSION

o-Formylphenylboronic acid reacts under mild conditions with morpholine to form the cyclic condensation product **1** (Scheme 2), which is stable in air.

The crystal structure of the title compound (Fig. 1) consists of the hydrogen-bonded dimer motif, which is very similar to that observed in two other benzoxaborole derivatives, namely 1-hydroxy-1,3-dihydro-2,1-benzoxaborole[9] and its 5,7-dimethoxy derivative.[10] In all cases the dimer is centrosymmetric and the interactions are relatively strong, with O···O distances of 2.75–2.80 Å. The latter value refers to the current system and the lengthening may be attributed (at least partly) to the steric effect of the morpholine fragment. In fact, two bulky substituents at this position preclude dimer formation, as observed in the third benzoxaborole derivative for which a crystal structure is known, i.e. 3-ethyl-1-hydroxy-3-(4-hydroxybenzoyl)-1,3-dihydro-2,1-benzoxaborole.[11] Similar to the other benzoxaborole derivatives,[9–11] the present structure shows that the boron centre is completely planar and the B–O bonds are quite distinct, i.e. 1.353(2) Å and 1.393(2) Å for B–O(H) and B–O(C), respectively.

A closer inspection of the borole fragment reveals that the electronic structure of boron is extremely sensitive to the structural modifications arising from substitution. The C–B, B–O and C–O bond lengths in the aforementioned structures vary in very broad ranges: 1.50–1.57, 1.37–1.41 and 1.44–1.49 Å, respectively; the longest C–B and C–O distances are observed in the present system. In addition, the B–O(H) distances range from 1.34 to 1.37 Å. Importantly, these differences are not only the consequence of the electronic structure of the substituent but are also due to the intermolecular interactions in the crystal structure. For instance, the C–B bond varies over 0.4 Å in two independent molecules of 1-hydroxy-1,3-dihydro-2,1-benzoxaborole.[9] Unfortunately, the lack of structural characterization of other benzoxaborole derivatives precludes a systematic study of this point.

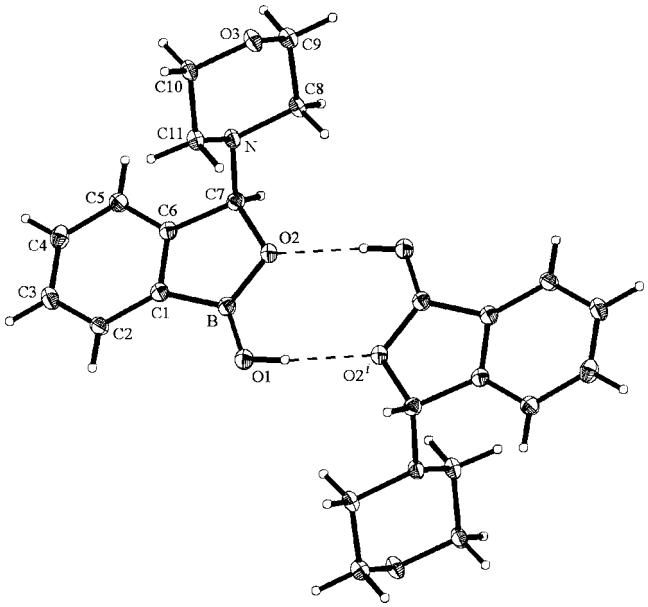


Figure 1. Centrosymmetric dimer in compound **1**. Selected bond lengths (Å): B–C1, 1.565(3); B1–O1, 1.353(2); B–O2, 1.393(2); O2–C7, 1.488(2). Hydrogen bond parameters: O1–H···O2^{i}, 1.94 Å; O1···O2^{i}, 2.797(2) Å. Angle at H is 172° for *i*: 1 − *x*, 2 − *y*, −*z*.

Systematic work on the synthesis and characterization of the products of reactions with other amines is in progress.

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