An Alkyne Group with a Pair of Hydrogen Bonds: the Crystal Structure of 2,2′-Ethynylenedibenzeneboronic Acid at 122 K

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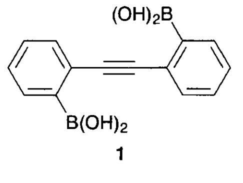
For each boronic acid group in **1** one hydrogen atom makes a hydrogen bond to an alkyne carbon atom as well as an intermolecular O–H···O bond; structural effects indicate the boronic acid group to be σ-electron releasing and π-electron withdrawing.

Attractive intermolecular contacts are of great importance in molecular recognition, for example in the selective binding of a hormone to a protein, or in the organisation of molecules in a crystal. Hydrogen bonding of the type X–H···Y where X and Y are both electronegative elements such as N or O play a leading role, but weaker types of hydrogen bonds have now been recognised which involve for example a C–H···O or C–H···N interaction where the hydrogen atom is not bonded to a notably electronegative element.[1,2] Conversely, the electron density of unsaturated linkages might be expected to be weak acceptors for a hydrogen bond. We now describe the molecular and crystal structure of the diboronic acid† **1** measured by X-ray diffraction at 122 K which shows short contacts between the alkyne bond and two hydrogen atoms, one from each boronic acid group.

This structure determination‡ is based on accurately measured low-temperature X-ray diffraction data, which provide an unambiguous determination of the positional parameters for the hydrogen atoms in the structure. In the crystal, the molecule is found on an inversion centre and consequently adopts a *trans* configuration. Fig. 1 shows the overall geometry and the atomic labelling. The molecule is built from two planar entities, phenyl and boronic acid groups, which make an interplanar angle of 28.43(7)°. The disposition of the hydrogen atoms in the boronic acid group is identical to those observed in other aryl boronic acids.[5–8] Both hydrogen atoms make intermolecular hydrogen bonds to oxygen atoms in other boronic acid groups: a linear one involving H(2) which gives rise to boronic acid dimers [H(2)···O(1)($1 - x$, $1 - y$, $-z$) 1.89(2) Å, O(2)–H(2)···O(1) 173°] and a bent one involving H(1) [H(1)···O(2)(x, $1 + y$, z) 2.06(2) Å, O(1)–H(1)···O(2) 147°] which connects the molecules into chains parallel to the *b*-axis (Fig. 2). However, the two H(1) atoms in each molecule are directed to the region above and below the triple bond so that they make 1,6 contacts to sp C atoms. The corresponding H···C (sp) distances are 2.51(2) Å, *ca.* 0.4 Å less than the sum of the traditional van der Waals radii for these elements. The H···C (sp) vectors lie almost perpendicular to the axis of the triple bond [H···C≡C angles 90.6(4)°]. The O–H···C (sp) angles are 115.8(1.1)° and the H(1)···C(7)–C(1)–C(2) torsion angles are 25.3°. The distances from the hydrogen atoms to the centre of the alkyne bond are 2.60(2) Å. The triple bond is bent slightly from linear at each sp C atom by 1.9°, and produces a slight *trans* distortion. These interactions can be considered to constitute hydrogen bonds to the electron density of the alkyne group.

Two small angular distortions have increased the length of each O–H···C (sp) interaction. The boronic acid and ethynyl groups are bent away from each other slightly in the plane of the benzene ring, leading to deviations from idealized geometry of *ca.* 3° at C(2) and 1.5° at C(1). The two C–B–O angles differ by *ca.* 6°, which causes the OH group closer to the triple bond to be deflected away from it. Similar distortions occur in the crystal structure of benzeneboronic acid **2**, increasing the *ortho*-H···H–O separation (H···H 2.22, 2.28 Å),[5] but not in the 2-nitro substituted analogue **3** where the boronic acid group lies perpendicular to the benzene ring.[8] The closest contact between the boronic acid group and an *ortho* hydrogen in **1** is of the order of the van der Waals distance [O(2)···H(3) 2.58 Å].

The crystal structure of **1** contains an accurately measured pair of intramolecular hydrogen bonds to an alkyne. Several examples of intermolecular O–H···C (sp) hydrogen bonding in crystals have been recognised recently,[9,10] where the steric bulk of local substituents prevents the strong O–H···O interaction. Thus, such interactions link half of the molecules of crystalline **4**[11] into dimers [H···C (sp) 2.25, 2.35 Å, O–H···C (sp) *ca.* 161°] and form part of the hydrogen bonding network in **5**[9] [H···C (sp)



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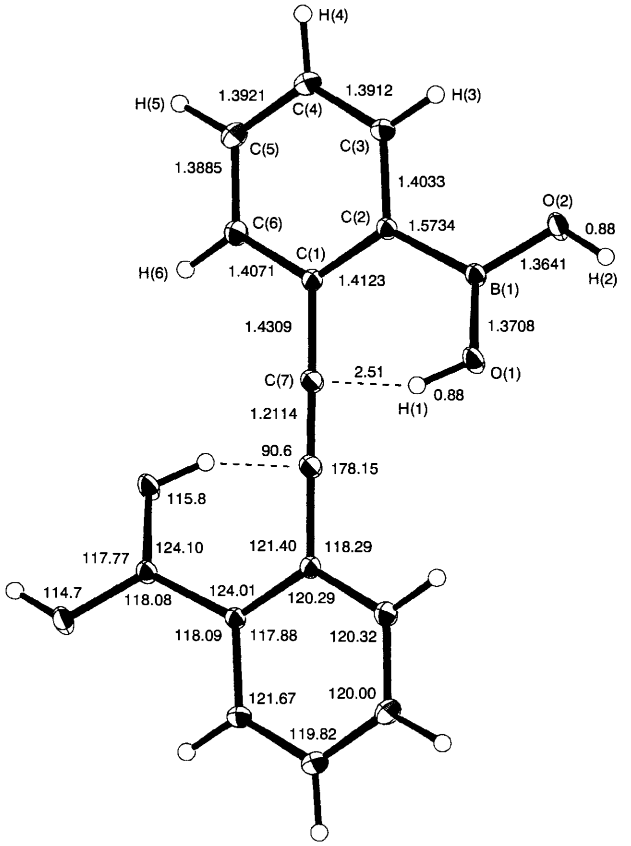


Fig. 1 Molecular structure and geometry of **1**. Anisotropic displacement parameters for non-H atoms drawn at the 50% level, H atoms drawn as spheres with fixed radius. Half the molecule crystallographically unique, interatomic distances (upper half of diagram, in Å) with e.s.d.s 0.0008–0.0009 Å except for C(7)–C(7′) (0.0011 Å) and distances involving one H atom (0.02 Å), and angles (lower half, in °) with e.s.d.s 0.05° except for C(1)–C(7)≡C(7′) (0.08°), H(1)···C(7)≡C(7′) (0.04°) and H–O–B angles (1.1°).

2.45 Å, O–H···C (sp) 144°]. Semi-empirical calculations at the AM1 and PM3 level on O–H···C (sp) hydrogen bonding predict H···C (sp) distances of 2.5–2.8 Å.[10] In **1**, the H···C (sp) distance is longer than in **4** or **5** since the hydrogen is also involved in an intermolecular hydrogen bond to oxygen. Hydrogen bonds to the electron density of an alkene[12] and a phenyl ring[13] have been reported.

The solid-state structure of the diboronic acid **1** contrasts sharply with that of the dicarboxylic acid analogue **6**[14] which has a *cis* conformation, short C=O···C (sp) interactions, and the carboxylic acid groups closer to planarity with the phenyl ring planes. It is particularly noteworthy that an alkyne will form short interactions with either electron-rich or electron-poor atoms.

Analysis of the angular deviations from 120° in substituted benzene rings has led to the assignment of a characteristic set of deviations for a given substituent, $\Delta\alpha - \Delta\delta$ (Fig. 3).[15] The values of the deviations at α and γ correlate with Taft's substituent parameters, σ_I and σ_R, respectively. Subtracting the contributions of the arylethynyl group§ from the angular deviations in **1** the following values for the boronic acid group can be estimated: $\Delta\alpha = -2.2$, $\Delta\beta = +1.2$, $\Delta\gamma = +0.1$ and $\Delta\delta = +0.3°$. This unique combination is quite different from that for the carboxylic acid group and corresponds to strong σ electron-releasing and π-withdrawing effects.

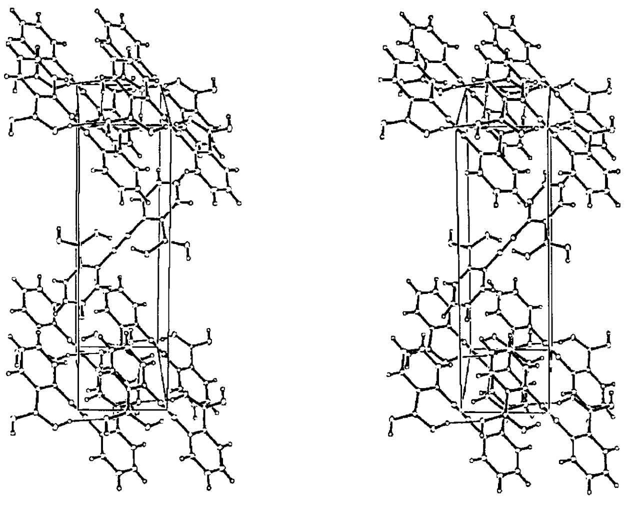
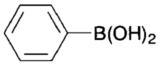


Fig. 2 Stereoview of the crystal packing arrangement for **1** viewed down the *a* axis and with the O–H···O hydrogen bonds shown as thin lines



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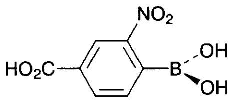

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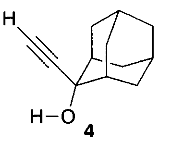

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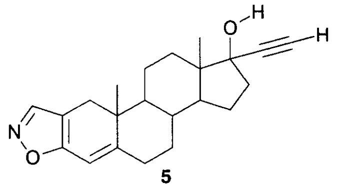

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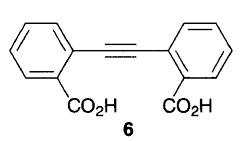

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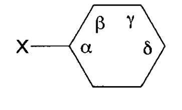

Fig. 3 Labels designating angles in a monosubstituted benzene ring

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Footnotes

† 2,2′-Ethynylenedibenzeneboronic acid, prepared from 2,2′-dibromoethynylenedibenzene[3] as described,[4] mp 212–223 °C, δ_H (270 MHz, CD_3CN): 7.81 (dd, *J* 7.1, 1.4 Hz, 3-H), 7.59 (dm, *J* 8.2 Hz, 6-H), 7.46 (dt, *J* 7.4, 1.6 Hz) and 7.41 (dt, *J* 7.4, 1.5) (4-, 5-H) and 6.39 (s, 2 × OH); *m/z* (CI, NH_3): 222 ($[M - BO_2H]^+$, 25), 195 ($[M - 2BO_2H + NH_3]^+$, 100) and 178 ($[M - 2BO_2H]^+$, 10%); ν_{max} (evaporated film): 3470, 3338, 2964, 2860, 1592, 1452, 1376, 1341, 1144, 1044, 1018, 758 and 640 cm^{-1}.

‡ *Crystal data* for 2: $C_{14}H_{12}B_2O_4$ $M_r = 265.8$, monoclinic, space group $P2_1/n$, $a = 7.794(2)$, $b = 5.0790(11)$, $c = 16.458(4)$ Å, $\beta = 103.39(2)°$, $U = 633.8(3)$ Å^3, $T = 122 \pm 1$ K, $Z = 2$, $D_c = 1.39$ g cm^{-3}, μ(Mo-Kα) = 0.10 mm^{-1}, 3694 reflections with $I > 2\sigma(I)$, max. $\sin\theta/\lambda = 0.995$ Å^{-1}, final $R = 0.0413$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ $\Delta\alpha = -0.6$, $\Delta\beta = +0.1$, $\Delta\gamma = +0.3$ and $\Delta\delta = -0.1°$ calculated from the monosubstituted rings in diphenylethyne[16] and 2-(dimethylamino)diphenylethyne.[17]

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