Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,4-Phenylenediboronic acid

Patricia Rodríguez-Cuamatzi,[a] Gabriela Vargas-Díaz,[a] Thierry Maris,[b] James D. Wuest[b] and Herbert Höpfl[a]*

[a]Centro de Inverstigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, CP 62210 Cuernavaca, Mexico, and [b]Université de Montréal, Département de Chimie, Montréal, Québec, Canada H3C 3J7

Correspondence e-mail: hhopfl@buzon.uaem.mx

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.050
wR factor = 0.135
Data-to-parameter ratio = 11.9

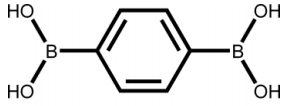
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 22 June 2004
Accepted 1 July 2004
Online 9 July 2004

In the crystal structure of the title compound, $C_6H_8B_2O_4$, centrosymmetric 1,4-phenylenediboronic acid molecules are linked by characteristic hydrogen bonding of $B(OH)_2$ groups. Primary association involves the formation of centrosymmetric cyclic dimers which leads to the formation of linear chains; these, in turn, associate by secondary hydrogen bonding, *via* unit-cell translations in the *a* axis direction, to form sheets.

Comment

Boronic acids possess a $B(OH)_2$ group as functional moiety and have applications in organic synthesis (Miyaura *et al.*, 1981; Corey & Helal, 1998), the molecular recognition of biochemically active molecules (Nozaki *et al.*, 1995; Shinkai *et al.*, 2001; Reetz *et al.*, 1991), as well as in medicine as antibiotics (Dunitz *et al.*, 1971; Nakumura *et al.*, 1977), inhibitors (Shenvi, 1986) and for the treatment of tumors (Soloway *et al.*, 1998). As a continuation of our recent interest in the structural elucidation of boronic acid derivatives (Fournier *et al.*, 2003; Rodríguez-Cuamatzi *et al.*, 2004), we present here the crystal structure of 1,4-phenylenediboronic acid, (I), which reveals interesting features, demonstrating the intriguing hydrogen-bonding patterns of boronic acid structures.



(I)

The crystal structure of (I) (Fig. 1) contains a two-dimensional arrangement of 1,4-phenylenediboronic acid molecules in the form of a layer, as shown in Fig. 2. Within these layers, two hydrogen-bonding motifs, *A* and *B*, can be distinguished, which are both centrosymmetric. Each $B(OH)_2$ group has a *syn–anti* conformation (with respect to the H atoms) and participates in a total of four O—H···O hydrogen bonds. The

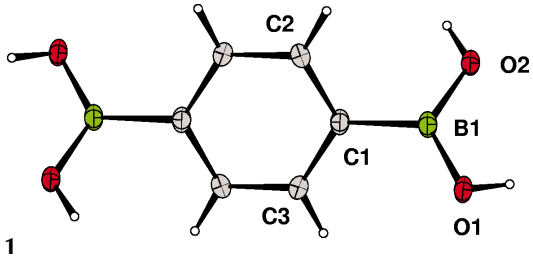


Figure 1
View of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Unlabeled atoms are related by the symmetry code $(1-x, -y, 2-z)$.

hydrogen-bonding pattern in motif A (Fig. 2 and first line of Table 1) is comparable to the one found generally in the dimeric units formed between carboxylic acids and has apparently similar stability, since it is found in most of the phenylboronic acid derivatives characterized so far by X-ray crystallography (Rettig & Trotter, 1977; Soundararajan *et al.*, 1993; Scouten *et al.*, 1994; Pilkington *et al.*, 1995; Gainsford *et al.*, 1995; Bradley *et al.*, 1996; Akita & Kobayashi, 1997; Schilling *et al.*, 1997; Norrild & Sotofte, 2001; Fournier *et al.*, 2003; Braga *et al.*, 2003; Bresner *et al.*, 2004; Rodríguez-Cuamatzi *et al.*, 2004). Through these interactions one-dimensional linear chains are formed, which are aligned parallel to each other and interconnected through additional O—H···O bonds (motif B, second line of Table 1). The cyclic hydrogen-bonded motifs B are $(OH)_4$ units, which are frequently observed in the crystal structures of diols (Hawkins *et al.*, 1990).

Interestingly, the $B(OH)_2$ groups are twisted out of the mean plane of the phenylene group by approximately 35°, apparently as a result of these hydrogen-bonding requirements. In 1,4-phenylenediboronic acid tetrahydrate, in which linear chains of hydrogen-bonded boronic acid molecules were located between two-dimensional layers of water molecules (Rodríguez-Cuamatzi *et al.*, 2004), the twists of the $B(OH)_2$ groups had values of only 2 and 7°. The resulting overall conformation of the two-dimensional layer is shown in Fig. 3.

Experimental

1,4-Phenylenediboronic acid, (I), was synthesized by reaction of the Grignard reagent prepared from 1,4-dibromobenzene with tri-*n*-methyl borate, followed by hydrolysis (Coutts *et al.*, 1970). Crystals were grown from water.

Crystal data

$C_6H_8B_2O_4$
M_r = 165.74
Triclinic, $P\overline{1}$
a = 4.989 (3) Å
b = 5.305 (3) Å
c = 7.368 (4) Å
α = 104.429 (10)°
β = 97.886 (9)°
γ = 93.797 (10)°
V = 186.05 (19) Å^3
Z = 1
D_x = 1.479 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1056 reflections
θ = 4.0–27.3°
μ = 0.12 mm^{-1}
T = 293 (2) K
Block, colorless
0.45 × 0.39 × 0.21 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: none
1948 measured reflections
728 independent reflections
678 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 26.0°
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 6$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.135
S = 1.21
728 reflections
61 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.0474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.015
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

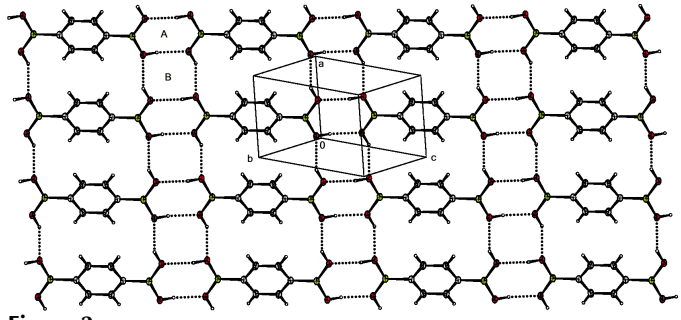


Figure 2
The packing arrangement of the two-dimensional layers in the unit cell, showing the hydrogen-bonding interactions as dashed lines.

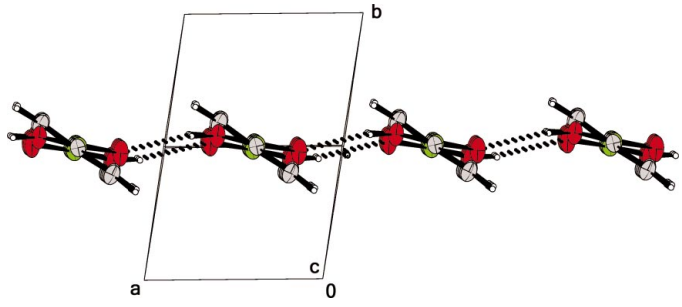


Figure 3
View of the unit cell along the *c* axis. Hydrogen bonds are shown as dashed lines.

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H10···O2^{i}	0.84 (2)	1.93 (2)	2.761 (2)	172 (3)
O2—H20···O1^{ii}	0.841 (17)	2.036 (14)	2.781 (2)	148 (2)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-1, y, z$.

H atoms of the benzene ring were placed in idealized positions and treated as riding, with C—H = 0.93 Å, while the H atoms bonded to O atoms were located in a difference Fourier map and refined with restraints on distances [0.84 (1) Å]. Isotropic displacement parameters of the H atoms were set at $U_{iso} = 1.2U_{eq}$(C) or $1.5U_{eq}$ (O).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

References

Akita, T. & Kobayashi, K. (1997). *Adv. Mater.* **9**, 346–349.
Bradley, D. C., Harding, I. S., Keefe, A. D., Motevalli, M. & Zheng, D. H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3931–3936.
Braga, D., Polito, M., Bracaccini, M., Addario, D., Tagliavini, E., Sturba, L. & Grepioni, F. (2003). *Organometallics*, **22**, 2142–2150.
Bresner, C., Aldridge, S., Fallis, I. A. & Ooi, L.-L. (2004). *Acta Cryst.* E**60**, m441–m443.
Bruker (2000). *SHELXTL* (Release 6.10) and *SMART* (Release 5.618). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT*. Release 6.04. Bruker AXS Inc., Madison, Wisconsin, USA.
Corey, E. J. & Helal, C. J. (1998). *Angew. Chem. Int. Ed.* **37**, 1986–2012.

Coutts, I. G. C., Goldschmid, H. R. & Musgrave, O. C. (1970). *J. Chem. Soc.* pp. 488–493.
Dunitz, J. D., Hawley, D. M., Miklos, D., White, D. N. J., *Berlin*, Y., Marusic, R. & Prelog, V. (1971). *Helv. Chim. Acta*, **54**, 1709–1713.
Fournier, J.-H., Maris, T., Wuest, J. D., Guo, W. & Galoppini, E. (2003), *J. Am. Chem. Soc.* **125**, 1002–1006.
Gainsford, G. J., Meinhold, R. H. & Woolhouse, A. D. (1995). *Acta Cryst.* C**51**, 2694–2696.
Hawkins, S. C., Scudder, M. L., Craig, D. C., Rae, A. D., Raof, R. B. A., Bishop, R. & Dance, I. G. (1990). *J. Chem. Soc. Perkin Trans.* 2, pp. 855–870.
Miyaura, N., Yangi, T. & Suzuki, A. (1981). *Synth. Commun.* **11**, 513–519.
Nakumura, H., Iitacaka, Y., Kitahara, T., Okasaki, T. & Okami, Y. (1977). *J. Antibiot.* **30**, 714–719.
Norrild, J. C. & Sotofte, I. (2001). *J. Chem. Soc. Perkin Trans.* 2, pp. 727–732.
Nozaki, K., Tsutsumi, T. & Takaya, H. (1995). *J. Org. Chem.* **60**, 6668–6669.
Pilkington, M., Wallis, J. D. & Larsen, S. (1995). *Chem. Commun.* pp. 1499–1500.
Reetz, M. T., Niemeyer, C. M. & Harms, K. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 1474–1476.
Rettig, S. J. & Trotter, J. (1977). *Can. J. Chem.* **55**, 3071–3075.
Rodríguez-Cuamatzi, P., Vargas-Díaz, G. & Höpfl, H. (2004). *Angew. Chem. Int. Ed.* **43**, 3041–3044.
Schilling, B., Kaiser, V. & Kaufmann, D. E. (1997). *Chem. Ber.* **130**, 923–932.
Scouten, W. H., Liu, X.-C., Khangin, N., Mullica, D. F. & Sappenfield, E. L. (1994). *J. Chem. Crystallogr.* **24**, 621–626.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Shenvi, A. B. (1986). *Biochemistry*, **25**, 1286–1291.
Shinkai, S., Ikeda, M., Sugasaki, A. & Takeuchi, M. (2001). *Acc. Chem. Res.* **34**, 494–503.
Soloway, A. H., Tjarks, W., Barnum, R.-A., Rong, F.-G., Barth, R. F., Codogni, I. M. & Wilson, J. G. (1998). *Chem. Rev.* **98**, 1515–1562.
Soundararajan, S., Duesler, E. N. & Hageman, J. H. (1993). *Acta Cryst.* C**49**, 690–693.
Watkin, D. J., Prout, C. K., Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.