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Structure of 4-Carboxy-2-nitrobenzeneboronic Acid

BY S. SOUNDARARAJAN

Enzon, Inc., 40 *Cragwood Road, S. Plainfield, NJ* 07080, *USA*

E. N. DUESLER

Department of Chemistry, University of New Mexico, Albuquerque, NM 87131, *USA*

AND J. H. HAGEMAN*

Department of Chemistry, Box 3*C, New Mexico State University, Las Cruces, NM* 88003, *USA*

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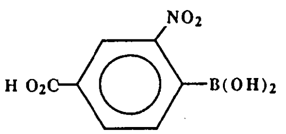
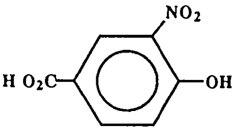
Abstract. 4-(Dihydroxyboryl)-3-nitrobenzoic acid, $C_7H_6BNO_6$, $M_r = 210.94$, monoclinic, $P2_1/n$, $a = 10.542$ (2), $b = 6.411$ (1), $c = 13.105$ (4) Å, $\beta = 106.47$ (2)°, $V = 849.3$ (4) Å^3, $Z = 4$, $D_m = 1.65$ (flotation in CCl_4/1,2-dibromoethane), $D_x = 1.649$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.135$ mm^{-1}, $F(000) = 432$, $T = 293$ K, $R = 0.0530$ for 1328 observed reflections with $F > 2\sigma(F)$. The molecule is flat [the carboxy and nitro groups are rotated 5.8 (4) and 1.9 (4)°, respectively, out of the plane] with the boronic acid group almost normal to the plane of the benzene ring, 92.4 (3)°. The B atom and one O atom of the nitro group are separated by only 2.457 (4) Å implying an interaction that is consistent with observed chemical behavior.

Introduction. Benzeneboronic acids form stable complexes with *cis*-diols (Ferrier, 1978). The efficiency of boronate–diol complex formation and the utilization of this property in affinity chromatography for the isolation of biomolecules depend on the ionization constant of the benzeneboronic acid (Maestas, Prieto, Kuehn & Hageman, 1980; Hageman & Kuehn, 1992). Ionization constants and boronate–diol complex formation constants of several potentially useful benzeneboronic acids were determined by a sensitive spectral difference method (Soundararajan, Badawi, Kohlrust & Hageman, 1989). Among the benzeneboronic acids studied, the values obtained for 4-carboxy-2-nitrobenzeneboronic acid (I) by the spectral method were quite different from those obtained by a potentiometric method. In addition, aqueous solutions (pH = 9.0) of (I) were observed (Soundararajan, 1984) to undergo ultraviolet and visible spectral changes with time, which suggested the formation of (II).

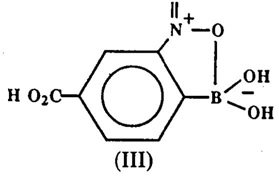
Furthermore, after several hours at pH 9.0, solutions of (I) could be resolved into four different species by thin-layer chromatography, which led to the suggestion that the *ortho*-nitro group might form the cyclized product (III) through intramolecular bonding at boron. These observations have prompted us to undertake the X-ray crystal structure analysis of (I) to determine the atomic arrangement in the solid state, a consideration of potential importance in the synthetic design of other boronic acids.



(I)



(II)



(III)

Experimental. Crude samples of (I) were obtained by nitration of 4-carboxybenzeneboronic acid (Torssell, 1957; Soundararajan *et al.*, 1989) and recrystallized

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* Author to whom correspondence should be addressed.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	−22 (2)	8794 (3)	3502 (2)	24 (1)
C(2)	26 (3)	10606 (3)	2930 (2)	25 (1)
C(3)	1089 (2)	11910 (3)	3294 (2)	24 (1)
C(4)	2124 (3)	11581 (3)	4212 (2)	25 (1)
C(5)	2037 (3)	9755 (3)	4770 (2)	30 (1)
C(6)	989 (3)	8376 (3)	4421 (2)	29 (1)
C(7)	−1165 (3)	7365 (3)	3093 (2)	27 (1)
N(1)	1153 (2)	13774 (3)	2657 (2)	31 (1)
O(1)	−1056 (2)	5601 (2)	3633 (1)	39 (1)
O(2)	−2094 (2)	7735 (2)	2328 (1)	40 (1)
O(3)	250 (2)	14121 (3)	1856 (1)	51 (1)
O(4)	2109 (2)	14925 (3)	2961 (1)	46 (1)
O(5)	3307 (2)	14658 (3)	5274 (1)	35 (1)
O(6)	4492 (2)	12742 (3)	4323 (1)	40 (1)
B(1)	3351 (3)	13113 (4)	4590 (2)	28 (1)

three times from an ethanol–water mixture at room temperature. A clear crystal of dimensions 0.092 × 0.161 × 0.440 mm was used for data collection. X-ray intensity data were measured with a Nicolet *P3/F* automated four-circle diffractometer equipped with a graphite monochromator using Mo $K\alpha$ radiation at ambient temperature. Preliminary examination showed monoclinic symmetry. Cell constants were obtained from a least-squares fit to the centered settings of 25 reflections ($12 < 2\theta < 42°$). The θ–2θ scan data for $2 < 2\theta < 60°$ were measured for the quadrants $h, -k, -l$ and $h, -k, +l$. The scan range was 2.5 plus $K\alpha_1 - K\alpha_2$ separation, scan speed 3–30° $\min^{-1}$, total background scan time/total scan time set to 0.5. Three standards were monitored every 141 reflections. These showed no sign of crystal deterioration (variation of standard intensities $< \pm 3\%$). A small empirical absorption correction based on azimuthal scans was applied (max. and min. transmission factors were 0.942 and 0.928, respectively). All crystallographic computing and plots were performed with the *SHELXTL-Plus* program package (Siemens Analytical X-ray Instruments, 1990). The data were scaled on the standard reflections and corrected for Lorentz and polarization effects. Redundant data were averaged (R_{int} = 1.17%). 5728 reflections were collected, 2077 unique, of which 1328 were observed with $F > 2\sigma(F)$, where $\sigma(F) = \sigma(I)/2\ F\text{Lp}T$. $F = (I/\text{Lp}T)^{1/2}$, where I = intensity, Lp is Lorentz and polarization factor and T is the transmission factor. The weights have the form $1/[\sigma(F) + 0.000504F^2]$. Full-matrix least-squares refinement, minimizing $\sum(w|F_o - F_c|^2)$, employed anomalous-dispersion corrections for atoms with atomic numbers greater than two. Neutral-atom scattering form factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) were used. The structure was solved by direct methods. The best E map gave positions for all non-H atoms. Isotropic refinement converged to 13%. Anisotropic refinement converged to 7.6%. A difference map at this point clearly showed all H-atom positions. For the final refinement, the aromatic ring H atoms were included in idealized positions (riding model) with fixed isotropic U's set to $1.25U_{eq}$ of the parent atoms. The acidic H atoms could vary in position but had fixed isotropic U's set to $1.45U_{eq}$ of the parent atom. For 145 variables and 1328 reflections, the final agreement factors are: $R(F) = 0.053$, $wR(F) = 0.050$, $S = 1.34$, $(\Delta/\sigma)_{max} = 0.003$, $(\Delta\rho)_{min} = -0.27$ e $Å^{-3}$, $(\Delta\rho)_{max} = 0.28$ e $Å^{-3}$.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1.392 (3)	C(1)—C(6)	1.389 (3)
C(1)—C(7)	1.488 (3)	C(2)—H(2)	0.960
C(2)—C(3)	1.371 (3)	C(3)—C(4)	1.392 (3)
C(3)—N(1)	1.470 (3)	C(4)—C(5)	1.398 (3)
C(4)—B(1)	1.588 (4)	C(5)—H(5*A*)	0.960
C(5)—C(6)	1.387 (3)	C(6)—H(6*A*)	0.960
C(7)—O(1)	1.322 (3)	C(7)—O(2)	1.209 (3)
N(1)—O(3)	1.221 (3)	N(1)—O(4)	1.221 (3)
O(1)—H(1)	0.876 (30)	O(5)—H(5)	0.828 (29)
O(5)—B(1)	1.346 (3)	O(6)—H(6)	0.813 (30)
O(6)—B(1)	1.365 (4)		
C(2)—C(1)—C(6)	119.5 (2)	C(2)—C(1)—C(7)	118.0 (2)
C(6)—C(1)—C(7)	122.6 (2)	C(1)—C(2)—H(2)	120.9 (1)
C(1)—C(2)—C(3)	118.2 (2)	H(2)—C(2)—C(3)	120.9 (1)
C(2)—C(3)—C(4)	124.9 (2)	C(2)—C(3)—N(1)	117.6 (2)
C(4)—C(3)—N(1)	117.6 (2)	C(3)—C(4)—C(5)	115.3 (2)
C(3)—C(4)—B(1)	123.1 (2)	C(5)—C(4)—B(1)	121.6 (2)
C(4)—C(5)—H(5*A*)	119.2 (1)	C(4)—C(5)—C(6)	121.7 (2)
H(5*A*)—C(5)—C(6)	119.2 (1)	C(1)—C(6)—C(5)	120.4 (2)
C(1)—C(6)—H(6*A*)	119.8 (1)	C(5)—C(6)—H(6*A*)	119.8 (1)
C(1)—C(7)—O(1)	113.3 (2)	C(1)—C(7)—O(2)	124.1 (2)
O(1)—C(7)—O(2)	122.6 (2)	C(3)—N(1)—O(3)	119.1 (2)
C(3)—N(1)—O(4)	118.2 (2)	O(3)—N(1)—O(4)	122.7 (2)
C(7)—O(1)—H(1)	108.4 (19)	H(5)—O(5)—B(1)	111.4 (22)
H(6)—O(6)—B(1)	113.4 (23)	C(4)—B(1)—O(5)	119.0 (3)
C(4)—B(1)—O(6)	120.7 (2)	O(5)—B(1)—O(6)	119.9 (2)

Discussion. The fractional coordinates of non-H atoms and their isotropic equivalent temperature factors are given in Table 1,* bond lengths and angles are listed in Table 2. Fig. 1 is a thermal-ellipsoid plot of the molecule drawn using *SHELXTL-Plus*, Fig. 2 shows the hydrogen-bonding network and Fig. 3 shows a packing diagram of the unit cell. Bond lengths and angles of (I) are comparable to those found in other boron compounds with a few exceptions. The O(6)—B(1) length of 1.365 (4) Å compares well to 1.360 Å in 4-bromobenzeneboronic acid (Zvonkova & Glushkova, 1958), to the average bond distance of 1.3615 Å reported for benzeneboronic acid (Rettig & Trotter, 1977) and to the average bond distance of

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55734 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0552]

1.367 Å in mannitol tris(benzeneboronic) ester (Gupta, Kirfel, Will & Wulff, 1977). In contrast, the O(5)—B(1) bond distance of 1.346 (3) Å is only similar to one of the B—O bond distances, 1.348 Å in the mannitol boronic ester (Gupta *et al.*, 1977). On the other hand, the 1.588 (4) Å C(4)—B(1) length is significantly longer than the corresponding distances of 1.54 Å in 4-bromobenzeneboronic acid and 1.562 Å in benzeneboronic acid. The average N—O bond distance of 1.221 (3) Å compares well to the 1.226 Å bond length in 3-nitrobenzoic acid (Dhaneswar, Tavale & Pant, 1974).

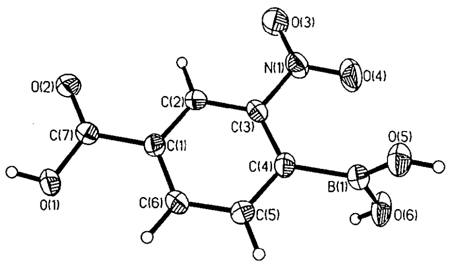

Fig. 1. Drawing of a single unit of the title compound showing thermal ellipsoids at the 50% probability level for non-H atoms and the atom-numbering scheme. H atoms have been set arbitrarily to a radius of 0.2 Å.

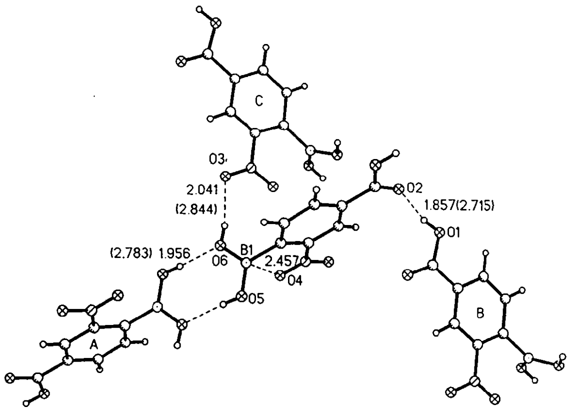

Fig. 2. Hydrogen-bonding network seen for a unit of 4-carboxy-2-nitrobenzeneboronic acid. Values of hydrogen-bond distances (Å), given as H···O (O···O), are reported in the text and shown in the figure. E.s.d. values for H···O and O···O bond lengths are 0.030 and 0.003 Å, respectively. Symmetry operators are $1-x$, $3-y$, $1-z$ (for *A*); $-0.5-x$, $0.5+y$, $0.5-z$ (for *B*) and $0.5-x$, $-0.5+y$, $0.5-z$ (for *C*).

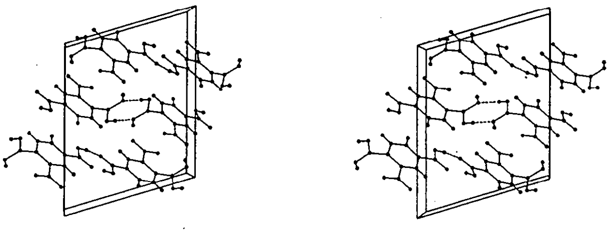

Fig. 3. A stereoscopic drawing of the molecular packing of the unit cell of 4-carboxy-2-nitrobenzeneboronic acid. The *a* axis is perpendicular to the plane of the paper, the *b* and *c* axes are horizontal and vertical, respectively.

In (I), the bond angles C(4)—B(1)—O(5), O(5)—B(1)—O(6) and C(4)—B(1)—O(6) are 119.0 (3), 119.9 (2) and 120.7 (2)°, which differs significantly from the corresponding angles of 118.2, 116.3 and 125.0° of benzeneboronic acid (Rettig & Trotter, 1977); the hydrogen bonding in (I) may account for this difference. Indications of interactions between the boronic acid group and the 2-nitro group in (I) are seen in comparing its structure to that of 2-nitrobenzoic acid (Sakore, Tavale & Pant, 1967). The C(4)—C(3)—N(1) and C(2)—C(3)—N(1) bond angles in (I) are equal at 117.6 (2)° whereas the corresponding angles in 2-nitrobenzoic acid are 119.1 and 116.7°, respectively. In addition, the C(5)—C(4)—B(1) and C(3)—C(4)—B(1) angles of (I) are almost equal at 121.6 (2) and 123.1 (3)° whereas the corresponding angles at the carboxylic C atom in 2-nitrobenzoic acid are very different at 118.4 and 125.4°. It appears that the nitro group of 2-nitrobenzoic acid, which is roughly orthogonal to the aromatic ring, is repelling the carboxyl group, in contrast to the situation in (I).

All three substituents of the benzene ring are involved in one or more hydrogen bonds between molecules of the unit cell (Fig. 2). The bonds are (1) O(5)—H···O(6)($1-x$, $3-y$, $1-z$); (2) O(6)—H···O(3)($0.5-x$, $0.5+y$, $0.5-z$); and (3) O(2)···H—O(1)($-0.5-x$, $0.5+y$, $0.5-z$), with H···O and O···O distances of 1.956 (30) and 2.783 (3) Å for (1), 2.041 (30) and 2.844 (2) Å for (2) and 1.857 (30) and 2.715 (2) Å for (3). If O(5) forms a hydrogen bond with O(1) it must be very weak since the O···O distance is significantly larger than that for the others (< 3 Å).

As seen in Fig. 1, (I) consists of four planar groups, namely the nitro, carboxylic acid, boronic acid and benzene ring moieties. Planes calculations give the dihedral angles from these planes to the benzene ring as: carboxylic acid 5.8 (4)°, nitro 1.9 (4)° and boronic acid 92.4 (3)°. The boronic acid group is nearly perpendicular to the rest of the molecule. The distance between B(1) and O(4) is relatively short at 2.457 (4) Å; in contrast, the closest approach of the carboxylic O atom to the N atom in 2-nitrobenzoic acid is 2.81 (4) Å. Also, the B(1) atom lies 0.052 (4) Å out of the C(4), O(5), O(6) plane and is displaced towards O(4). Together these results indicate that some considerable degree of interaction between the boronic acid and nitro group can occur, consistent with observations of (I) in solution (Soundararajan *et al.*, 1989).

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Structure of 4(5)-Nitroimidazole at 100 K

By Hendrik L. De Bondt,* E. Ragia, N. M. Blaton, O. M. Peeters and C. J. De Ranter†

Laboratorium voor Analytische Chemie en Medicinale Fysicochemie, Instituut voor Farmaceutische Wetenschappen, Katholieke Universiteit Leuven, Van Evenstraat 4, *B*-3000 *Leuven, Belgium*

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Abstract. 4(5)-Nitroimidazole, $C_3H_3N_3O_2$, $M_r = 113.08$, monoclinic, $P2_1/n$, $a = 6.9559\ (4)$, $b = 9.9130\ (6)$, $c = 7.3045\ (4)$ Å, $\beta = 119.41\ (4)^\circ$, $V = 438.8\ (4)$ Å^3, $Z = 4$, $D_m(293\ \mathrm{K}) = 1.64$, $D_x = 1.7117$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 0.1367$ mm^{-1}, $F(000) = 232$, $T = 100$ K. Final $R = 0.024$ for 633 unique observed [$F \geq 4\sigma(F)$] reflections. The molecules are planar and are stacked in planes almost parallel to the *bc* plane. These molecular layers are built up by three hydrogen bonds. 4–5-tautomerism is discussed.

Introduction. Nitroimidazoles are generally known as antiprotozoic and antibiotic drugs (Edwards, 1981). The investigation of 4(5)-nitroimidazole is part of an extensive structure–activity study which includes conformational analysis on low-temperature data as well as charge density analysis on high-resolution low-temperature data sets.

Experimental. The title compound was supplied by Aldrich–Europe (Beerse, Belgium). Colourless crystals were obtained from a standard 2:1 dimethyl sulfoxide/methanol solution and were used for density measurements by flotation in $CCl_4/CHBr_3$. A prismatic crystal, with approximate dimensions 0.25 × 0.26 × 0.2 mm, was mounted for X-ray diffraction data collection on a Stoe STADI-4 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ (reflection 200) radiation. The space group, $P2_1/n$, was determined from observed symmetry and systematic absences $h0l$ ($h + l = 2n + 1$), $0k0$ ($k = 2n + 1$). Unit-cell dimensions were obtained by least-squares refinement of accurately determined 2θ values of 28 reflections with $20 \leq 2\theta \leq 50^\circ$. X-ray intensities were collected in the $\omega/2\theta$ scan mode up to maximal $(\sin\theta)/\lambda = 0.65$ Å^{-1} ($2\theta_{\max} = 55^\circ$) and for $-8 \leq h \leq 7$, $-11 \leq k \leq 11$, $0 \leq l \leq 8$. For all reflections, peak profiles of 96 steps were stored. Intensities of three standard reflections ($\bar{2}22$, 301 and $\bar{1}03$), monitored every hour of radiation, showed an average decrease in intensity of 3.2% in 66 h radiation. The reflection intensities were rescaled using a cubic regression curve. A total of 1657 reflections were measured. Symmetry-related reflections were averaged to give 828 unique reflections of which 633 were considered observed with $F \geq 4\sigma(F)$. $R_{\mathrm{int,\ observed},\ F}$ is 0.015. Data reduction with the peak profile analysis program *DREAM* (Blessing, 1987). Lorentz and polarization corrections were applied. Structure factors were calculated with scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B) and contracted hydrogen form factors from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were performed for all non-H atoms (Ibers &

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* Present address: Department of Chemistry and Lawrence Berkeley Laboratory, University of California at Berkeley, CA 94720, USA.

† Author to whom correspondence should be addressed.

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