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Solid-state ¹¹B and ¹³C NMR, IR, and X-ray crystallographic characterization of selected arylboronic acids and their catechol cyclic esters

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Nine arylboronic acids, seven arylboronic catechol cyclic esters, and two trimeric arylboronic anhydrides (boroxines) are investigated using ¹¹B solid-state NMR spectroscopy at three different magnetic field strengths (9.4, 11.7, and 21.1 T). Through the analysis of spectra of static and magic-angle spinning samples, the ¹¹B electric field gradient and chemical shift tensors are determined. The effects of relaxation anisotropy and nutation field strength on the ¹¹B NMR line shapes are investigated. Infrared spectroscopy was also used to help identify peaks in the NMR spectra as being due to the anhydride form in some of the arylboronic acid samples. Seven new X-ray crystallographic structures are reported. Calculations of the ¹¹B NMR parameters are performed using cluster model and periodic gauge-including projector-augmented wave (GIPAW) density functional theory (DFT) approaches, and the results are compared with the experimental values. Carbon-13 solid-state NMR experiments and spectral simulations are applied to determine the chemical shifts of the *ipso* carbons of anylboronic acids and their catechol esters, as well as residual dipolar coupling, is discussed. Overall, this combined X-ray, NMR, IR, and computational study provides valuable new insights into the relationship between NMR parameters and the structure of boronic acids and esters. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: nuclear magnetic resonance; solid-state NMR; boron-11; carbon-13; boronic acids; boronate esters; relaxation anisotropy; isotope effects; quadrupolar coupling constant; chemical shift tensor

Introduction

As highlighted previously,^[1] boronic acids and boronate esters are particularly important classes of compounds that have a wide range of uses in organic synthesis and catalysis, as well as in biochemistry, pharmaceutical chemistry, industry, crystal engineering, and various other applications.^[2–5] Boronic acids are used extensively in organic chemistry as chemical building blocks^[6] and intermediates, and the most widely used example is the Suzuki–Miyaura coupling,^[7] which is a useful synthetic route to biaryl compounds. The diverse number of applications of boronic acids and esters means that an understanding of the structural and electronic properties of these compounds is imperative. Boron-11 solid-state nuclear magnetic resonance (SSNMR) spectroscopy can provide important information about such properties. Boron has two quadrupolar NMR-active nuclides, ¹⁰B (I = 3; n.a. = 19.9%; $\Xi \approx 10.744$ %) and ${}^{11}B$ (I = 3/2; n.a. = 80.1%; $\Xi \approx 32.084$ %). Both isotopes have small-to-moderate nuclear electric quadrupole moments, Q [Q $(^{10}B) = 8.459 \text{ fm}^2$; $Q(^{11}B) = 4.059 \text{ fm}^2$].^[8] The ¹¹B nucleus is more receptive to NMR spectroscopy because of its higher natural abundance, lower value of Q, and availability of a central transition (CT) (i.e. $m_1 = +1/2 \leftrightarrow -1/2$). Some interesting recent ¹¹B solid-state NMR studies have highlighted advanced methods for measuring dipolar and/or J coupling constants between pairs of ¹¹B spins in lithium diborate^[9] and bis(catecholato)diboron.^[10]

Ten boronic acids and ester derivatives were investigated in our previous study.^[1] In the present work, we report the experimental characterization and interpretation of ¹¹B chemical shift (CS) and electric field gradient (EFG) tensors in a novel series of solid arylboronic acids and their catechol cyclic esters (Scheme 1; Table 1), with an added focus on understanding the origins of spurious peaks in some of the spectra as being caused by impurities or the conditions used for spectral acquisition. The compound numbering scheme in Table 1 uses 'A' for acids, 'B' for esters, and 'C' for anhydrides. Boron-11 SSNMR experiments were performed under stationary and magic-angle spinning (MAS) conditions at magnetic field strengths (\mathbf{B}_0) of 9.40, 11.75, and 21.1 T. At 21.1 T, the influence of the chemical shift (CS) tensor on the observed SSNMR line shapes becomes

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Scheme 1. Samples studied in the present work (Table 1).

extremely important as its line shape contribution (in Hz) is proportional to \mathbf{B}_{0} .^[1,11]

Carbon-13 chemical shifts of the *ipso* carbon, which is attached to boron of arylboronic acids and their catechol cyclic esters have not been reported with high precision.^[12,13] This is due to residual dipolar and *J* coupling to the quadrupolar nuclei (^{10/11}B) attached to the carbon.^[14] The ¹³C NMR peak therefore exhibits fine structure because of the directly bonded quadrupolar nucleus. The fine structure may or may not be clearly resolved from other peaks in the ¹³C MAS NMR spectrum, depending on the compound. If the fine structure overlaps with other peaks, it is very difficult to determine the chemical shift of the *ipso* carbon. In the present work, we report accurate chemical shifts of the *ipso* carbons of arylboronic acids and their catechol cyclic esters, and one bond spin-spin coupling constants between ¹³C and ¹¹B in the same compounds.

Single-crystal X-ray crystal structures of seven arylboronic acids are also presented to assist in our understanding of the NMR data. Gauge-including atomic orbital (GIAO) cluster model and gauge-including projector-augmented wave (GIPAW) DFT calculations of the NMR parameters of the samples studied are performed using the atomic coordinates and cell parameters available from refinements of the X-ray crystallographic data.

Conventions

The ¹¹B SSNMR spectra presented here are affected by nuclear magnetic shielding (σ) and by the quadrupolar interaction between the nuclear quadrupole moment (Q) and the EFG at the nucleus. The relevant theory for interpreting the ¹¹B NMR spectra reported in this work has been summarized recently by Weiss and Bryce.^[1] We present here only the conventions used for reporting tensor data. Magnetic shielding may be represented by a second-rank tensor, σ . Diagonalization of the symmetric portion of σ provides the orientation of its principal axis system (PAS) relative to a reference axis system. In its PAS, the three principal components of σ are ordered as follows: $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$. The three principal components of the CS tensor are ordered as follows: $\delta_{11} \ge \delta_{22} \ge \delta_{33}$. For both the σ and CS tensors, the isotropic value is the average of the three principal components. The Maryland convention is used for describing the σ and CS tensor parameters.^[15] The span (Ω) is defined as^[15]

$$\Omega = \sigma_{33} - \sigma_{11} \approx \delta_{11} - \delta_{33} \tag{1}$$

The skew (κ) is defined as^[15]

$$\kappa = \frac{3(\sigma_{iso} - \sigma_{22})}{\Omega} = \frac{3(\delta_{22} - \delta_{iso})}{\Omega}.$$
 (2)

The EFG tensor may be diagonalized to provide its principal components and the orientation of its PAS. The principal components of the EFG tensor are defined as follows: $|V_{33}| \ge |V_{22}| \ge |V_{11}|$. The nuclear quadrupolar coupling constant (C_Q) is given by

Table 1.	Samples studied in the present work (Scheme 1)				
Arylboron	ic acids	W	х	У	z
A1	Phenylboronic acid	н	Н	н	Н
A2	4-Methoxyphenylboronic acid	Н	Н	OCH ₃	Н
A3	3,4-Dimethoxyphenylboronic acid	Н	OCH ₃	OCH ₃	Н
A4	4-Methylphenylboronic acid	Н	Н	CH ₃	Н
A5	2-Methylphenylboronic acid	CH ₃	Н	Н	Н
A6	4-Fluorophenylboronic acid	Н	Н	F	Н
A7	4-Chlorophenylboronic acid	Н	Н	Cl	Н
A8	2-Chloro-5-(trifluoromethyl)phenylboronic acid	Cl	Н	Н	CF ₃
A9	4-(Methylthio)phenylboronic acid	Н	Н	SCH ₃	Н
Arylboron	ic acid catechol cyclic esters	W	х	У	z
B1	Phenylboronic acid catechol cyclic ester	н	Н	н	Н
B2	4-Methoxyphenylboronic acid catechol cyclic ester	Н	Н	OCH ₃	Н
B3	3,4-Dimethoxyphenylboronic acid catechol cyclic ester	Н	OCH ₃	OCH ₃	Н
B4	4-Methylphenylboronic acid catechol cyclic ester	Н	Н	CH₃	Н
B5	2-Methylphenylboronic acid catechol cyclic ester	CH ₃	Н	Н	Н
B6	4-Fluorophenylboronic acid catechol cyclic ester	Н	Н	F	Н
B7	4-Chlorophenylboronic acid catechol cyclic ester	Н	Н	Cl	Н
2,4,6-triary	lboroxines (anhydrides)			У	
C1	2,4,6-Triphenylboroxine			н	
C2	2,4,6-Tris(4-fluorophenyl)boroxine			F	

$$C_{\rm Q} = \frac{eV_{33}Q}{h},\tag{3}$$

where e is the fundamental charge, and h is the Planck constant. The asymmetry parameter of the EFG tensor is defined as

$$\eta_{\rm Q} = \frac{V_{11} - V_{22}}{V_{33}}.\tag{4}$$

Experimental and Computational Details

Sample preparation

As shown in Scheme 1 and Table 1, nine arylboronic acids, which have different aryl substituents were purchased from Aldrich. All arylboronic acids except A6 were recrystallized from hot water in the air, filtered and dried at room temperature, and then stored in a refrigerator at 5 °C. A6 converted to its trimeric anhydride (C2) when it was recrystallized from hot water, isopropanol, or tetrahydrofuran in the air. It is well known that most arylboronic acids may be converted easily to their trimeric anhydride forms when they are heated (Scheme 2).^[2,16–18] Seven arylboronic acid cyclic catechol esters were synthesized by combining the corresponding boronic acids with catechol in toluene and heating at reflux with a Dean Stark trap. After 3 h, the reaction mixture was cooled to room temperature and concentrated to dryness. The resulting boronate esters were used without further purification or purified by recrystallization from hexanes as needed. These esters were stored in a dry place at room temperature and were maintained at room temperature during the NMR experiments.

Instrumentation and measurements

4.7 T NMR experiments

Carbon-13 NMR experiments were conducted using a Bruker Avance III 200 NMR spectrometer ($\mathbf{B}_0 = 4.7 \text{ T}$, $v_L(^{13}\text{C}) = 50.31 \text{ MHz}$) at room temperature. Spectra were acquired using Bruker TopSpin 2.1 software. A Bruker 7.0 mm HXY triple-resonance MAS probe was used for all experiments. Experimental referencing, calibration, and setup were done using glycine. The carbon-13 chemical shifts were referenced with respect to tetramethylsilane (TMS) by setting the carboxylic carbon peak of external solid glycine to 176.40 ppm. Cross polarization (CP), total suppression of spinning sidebands (TOSS),^[19] and dipolar dephasing (DD) pulse sequences^[20] were used to obtain the chemical shifts of the *ipso* carbons of the samples under investigation. A dephasing delay of 40 µs and a MAS frequency of 4.5 kHz were used.

9.4 T NMR experiments

Boron-11 and carbon-13 NMR experiments were conducted using a Bruker Avance III 400 NMR spectrometer ($\mathbf{B}_0 = 9.4$ T, v_L



Scheme 2. Interconversion of phenylboronic acid and its anhydride.

 ${}^{(11}B) = 128.38 \text{ MHz}, v_1 {}^{(13}C) = 100.62 \text{ MHz}$) at room temperature. Spectra were acquired using TopSpin 2.1 software. All experiments were performed using a Bruker 4.0 mm HXY triple-resonance MAS probe. For the ¹¹B NMR experiments, experimental referencing, calibration, and setup were done using solid powdered sodium borohydride (NaBH₄), which has a chemical shift of -42.06 ppm relative to the primary standard, liquid $F_3B \cdot O(C_2H_5)_2$ (where $\delta(^{11}B) =$ 0.00 ppm).^[21] For both MAS and stationary samples, the Hahn echo $(\pi/2 - \tau_1 - \pi - \tau_2 - ACQ)$ pulse sequence^[22,23] was used with high power proton decoupling. Echo delays ranged from approximately 40 to $80\,\mu s$ for experiments on all spectrometers and probes. The MAS frequency was 10 kHz. The typical ¹¹B $\pi/2$ pulse length for solid NaBH₄ was 24.0 μ s. For all samples in this study, the 'solid $\pi/2'$ pulse was used (e.g., 24.0 μ s/(l + 1/2) = 12.0 μ s, where l = 3/2 for ¹¹B). Recycle delays of 10–90 s were employed. The probe exhibited a small but manageable background ¹¹B signal as a result of boron nitride in the stator. The Hahn echo pulse sequence was generally found to be effective at suppressing this background signal. For ¹³C NMR experiments, the referencing, calibration, and setup procedures were identical to those performed on the 4.7 T NMR spectrometer. CP and DD pulse sequences were used to measure the chemical shifts of the ipso carbons of the samples under investigation.

11.75 T NMR experiments

Boron-11 NMR experiments were conducted using a Bruker Avance 500 NMR spectrometer ($\mathbf{B}_0 = 11.75 \text{ T}$, $v_L(^{11}\text{B}) = 160.46 \text{ MHz}$) at room temperature. Spectra were acquired using TopSpin 1.3 software. A Bruker 4 mm HXY MAS probe was used. The referencing, calibration, and setup procedures were identical to those performed on the 9.4 T NMR spectrometer. For both MAS and stationary samples, the Hahn echo pulse sequence was used. The MAS frequency was 10 kHz. Typical $\pi/2$ pulse lengths and recycle delays were the same as those at 9.4 T.

21.1 T NMR experiments

Boron-11 NMR experiments were conducted using a Bruker Avance II 900 NMR spectrometer ($\mathbf{B}_0 = 21.1 \text{ T}$, $v_L(^{11}\text{B}) = 288.80 \text{ MHz}$) at room temperature. Spectra were acquired using TopSpin 1.3 software at the National Ultrahigh-Field NMR Facility for Solids in Ottawa (www.nmr900.ca). A Bruker 4 mm HXY MAS probe was used. The referencing, calibration, and setup procedures were identical to those performed at 9.4 T. For both MAS and stationary samples, the solid echo ($\pi/2 - \tau_1 - \pi/2 - \tau_2$ -ACQ) pulse sequence was used. The MAS frequency was 10 kHz. All solid $\pi/2$ pulse lengths were 5.0 µs, and pulse delays were 10 s.

FT-IR ATR experiments

All IR spectra were recorded using a Varian 640 Fourier transform infrared (FT-IR) spectrometer with PIKE MIRacleTM ATR (attenuated total reflectance) accessories having a single reflection ZnSe ATR crystal fixed at an incident angle of 60° with a resolution of 4 cm^{-1} in the spectral region of $4000-600 \text{ cm}^{-1}$. The ATR accessories were fitted with a high pressure clamp, providing contact between the sample and the ATR crystal. Varian Resolutions Pro (ver. 5.1.0.829) has been installed on the spectrometer. FT-IR ATR data for each sample were collected with 64 scans at room temperature. Background signal was obtained for every sample with 64 scans. Atmospheric contributions from carbon

dioxide and water vapor were not accounted for beyond a simple background subtraction.

Single crystal X-ray diffraction

Crystal structures were collected at the University of Ottawa in the X-ray Diffraction Laboratory. The crystals were mounted on thin glass fibres using paraffin oil. Data for **A5**, **A9**, and **B7** were collected at 296.15 K. Crystals of the other four compounds were cooled to 200.15 K prior to data collection. Data were collected on a Bruker AXS SMART single crystal diffractometer equipped with a sealed Mo tube source (wavelength = 0.71073 Å) and an APEX II CCD detector. Raw data collection and processing were performed with the APEX II software package from Bruker AXS.^[24] All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being $6.12.33.^{[25]}$ Crystallographic data and selected data collection parameters are reported in Table 2.

Compounds **A5**, **A8**, **B7**, and **C2** consistently formed very small crystals, and the results presented here are the best from a series of collection attempts for each compound. In addition to small sample size, crystals of compound **C2** demonstrated non-merohedral twinning. Separate two-component orientation matrices for non-merohedral twinning were found by analyzing positions of reflections in reciprocal space using the RLATT software package and were confirmed by CELL-NOW software data analysis.^[25] The structure was solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2 . Twinning was accounted for by refining the final structural model against split reflections and intensity data with the twinning parameter refined to 11.5% for the smaller component.

Spectral simulation and computation

Spectral processing and simulation

Data were processed using TopSpin 1.3. FIDs were left-shifted to the echo maxima when necessary, apodized using a Gaussian function of 50 Hz for MAS samples and 100 Hz for stationary samples, and then Fourier transformed. Stack plots were produced with DMFit.^[26] All spectral simulations were performed using the WSolids1 program,^[27] which incorporates the space-tiling algorithm of Alderman *et al.*^[28]

Magnetic Resonance in

Quantum chemical calculations

Single crystal X-ray data for all compounds studied in this work except B2, B3, and B5 were used for NMR calculations. The geometries of those three compounds are not known experimentally and, instead, were generated using standard bond lengths in Gaussview 3.0 and, then, fully optimized using a hybrid DFT functional (B3LYP)^[29] and the 6-311 + G* basis set for all atoms using Gaussian 09.^[30] All compounds for which experimental structures are known were subjected to geometry optimization of the hydrogen positions only (B3LYP/6-311 + G*). The optimized structures were subjected to further magnetic shielding, EFG, and spin-spin coupling constant calculations. Conformational effects on the boron NMR parameters were investigated by varying the C-C-B-O dihedral angle (ϕ_{CCBO}). EFG and magnetic shielding tensors were also calculated using the GIPAW DFT approach, after optimization of hydrogen atom positions, as implemented in the CASTEP code, using Materials Studio (ver. 3.2.0.0) and the PBE functional.^[31,32] All calculations used a plane wave basis set with an 'ultrafine' cutoff energy of 610 eV, and the 'fine' setting was used to establish the number of k-points used to sample the Brillouin zone (Monkhorst–Pack mesh).^[33]

Tuble 2. Crystan	lographic data for 5	onic boronic acid	s and esters ander	Study			
	A3	A5	A8	A9	C2 ^b	B6	B7
Formula	C ₈ H ₁₁ BO ₄	C ₇ H ₉ BO ₂	$C_7H_5BCIF_3O_2$	C ₇ H ₉ BO ₂ S	$C_{18}H_{12}B_3F_3O_3$	$C_{12}H_8BFO_2$	C ₁₂ H ₈ BClO ₂
FW	181.98	135.95	224.37	168.01	365.71	213.99	230.44
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P21/c	<i>P</i> -1	P21/c	P21/c	P21/m	P21/n	Pnma
a/Å	5.5550(18)	4.975(5)	4.930(6)	11.5921(3)	3.8571(4)	12.362(8)	19.6321(15)
b/Å	9.532(3)	6.180(6)	5.704(7)	5.15100	20.8400(17)	4.735(3)	11.0200(9)
c/Å	17.406(5)	12.206(11)	32.72(4)	14.5958(4)	10.4372(10)	17.487(11)	4.9630(3)
α/°	90	84.67(3)	90	90	90	90	90
β/°	95.269(4)	85.00(3)	90.007(15)	112.345(2)	97.423(5)	98.611(7)	90
γ/°	90	88.61(3)	90	90	90	90	90
V/Å ³	917.8(5)	372.2(6)	920.2(19)	806.09(3)	832.20(14)	1012.0(11)	1073.72(14)
Ζ	4	2	4	4	2	4	4
D _{calc} /g cm ⁻³	1.317	1.213	1.620	1.384	1.459	1.405	1.426
T/K	200(2)	296(2)	200(2)	296(2)	200(2)	200(2)	296(2)
θ(max)/deg	26.43	28.38	21.96	28.30	24.72	24.99	24.72
F(000)	384	144	448	352	372	440	472
GOF on F ²	1.047	1.037	1.063	1.020	1.071	1.012	1.015
$R_1[I > 2\sigma(I)]$	0.0354	0.0734	0.0379	0.0341	0.0714	0.0558	0.0626
wR ₂	0.1046	0.1754	0.0872	0.0893	0.1821	0.1198	0.1310

^aCrystallographic data for samples A1, A2, and B4 obtained using XRD in this work were consistent with those in the literature. These data are excluded from this table.

^bTrimeric anhydride form made from the recrystallization of **A6** from hot water.

Results and Discussion

X-ray crystallography

Among the arylboronic acids and catechol cyclic esters studied in this work, seven new crystallographic structures were obtained by single-crystal XRD. They are listed in Table 2. **A1** and **A3** each have two molecules in the asymmetric unit, that is, two nonequivalent boron sites, whereas the remaining samples have one molecule in their asymmetric unit. **C2** is the trimeric anhydride form of **A6**, obtained when the latter was recrystallized from hot water.

Carbon-boron bond lengths, intermolecular hydrogen bond lengths, and the dihedral angle formed by the C, C, B, and O atoms (ϕ_{CCBO}) are summarized in Table 3. As shown, the carbon-boron bond lengths are in the range of 1.526 to 1.575 Å and do not vary greatly within each compound class. All arylboronic acids studied have geometries which indicate the ability to form intermolecular hydrogen bonds [r(O...H) < 2 Å], as confirmed by IR spectroscopy (vide infra). When the idealized hydrogen atom positions reported in the XRD structures are optimized computationally, the intermolecular hydrogen bonding distances in solid arylboronic acids decreased by 0.080-0.201 Å. The $-B(OH)_2$ plane and the aromatic ring are twisted relative to each other for most arylboronic acids, while they are almost coplanar for the phenylboronic acid catechol cyclic esters. The CCBO dihedral angle in the arylboronic acids varied from 3.4° for one form of **A4** up to 40.0° for **A5**. On the other hand, CCBO dihedral angles of arylboronic acid catechol cyclic esters were below 3.5° and those in trimeric phenylboronic acid anhydrides were 8.6° for C1 and 4.9° for C2. A5 and A8, which have an ortho substituent, give the most twisted structures. This is attributable to the steric effect of the ortho substituent. **A5** has the shortest B-C bond length of all compounds investigated in this study. This may be due to the electron-donating methyl group located at the ortho position. The bond length between B and C atoms of **C1** is marginally shorter than that of **A1**. The same trend was found for **A4** and its anhydride structure.^[34] This may indicate a strengthening of this bond by the electron-withdrawing nature of the ring in the trimeric anhydride form.^[35]

FT-IR

FT-IR ATR spectra of representative samples are shown in Fig. 1. The purpose of acquiring IR spectra was to provide an independent perspective on the formation of anhydrides, impurities, or decomposition products, so as to aid in the interpretation of the solid-state NMR spectra. Assignment of all vibrational bands is not our intention in this work. The C - H stretching mode of the benzene ring around 3000 cm⁻¹ from the FT-IR ATR spectra was very weak compared with normal FT-IR spectra $^{\left[16,38\right] }$ of $\boldsymbol{A1}$ and A4 obtained using a KBr disk. As shown in Fig. 1, pure A1, A3, B5, and C1 did not give any evidence that they contained any water or boric acid impurities. Boric acid was found to be a common impurity in boronic acids in our previous study.^[1] Other pure arylboronic acid samples have given the same result [see Supplementary Material (SM)]. Many arylboronic acids usually have their corresponding anhydride forms as an impurity in the solid state. These anhydride forms may either already be present as impurities or self-assemble from the acids as a result of heating (Scheme 2). To characterize the boronic acid compounds in the

Sample	Site	<i>r</i> (B-C)/Å	<i>r</i> (B-O)/Å	<i>r</i> (O … H)/Å		ϕ (CCBO)/ $^{\circ}$	Reference
				XRD data	Optimization of H position		
A1	а	1.566	1.364, 1.370	1.891, 1.896	1.753, 1.761	5.34, 6.63	T,34,35
	b	1.560	1.367, 1.368	1.891, 1.896	1.753, 1.761	20.42, 22.02	
A2	_	1.560	1.362, 1.374	1.969, 1.969	1.806, 1.806	19.64, 21.28	T, 36
A3	_	1.569	1.355, 1.371	2.003, 2.003	1.826, 1.826	21.59, 22.47	Т
A4	Α	1.554	1.354, 1.377	1.921, 1.927	1.766, 1.777	3.37, 4.63	37
	В	1.575	1.352, 1.362	1.921, 1.927	1.766, 1.777	20.28, 22.95	
A5	_	1.526	1.379, 1.396	1.944, 2.193	1.776, 1.776	36.44, 40.04	Т
A7	_	1.552	1.357, 1.364	1.860, 1.860	1.754, 1.754	26.19,26.28	Т
A8	_	1.558	1.347, 1.364	1.948, 1.948	1.778, 1.778	36.01, 38.49	Т
A9	_	1.563	1.354, 1.366	1.905, 1.905	1.830, 1.830	17.62, 19.55	Т
B1	_	1.536	1.394, 1.394	_	—	0.37, 0.37	T, 38
B2	_	1.533	1.396, 1.397	_	—	0, 0	G
B3	_	1.532	1.397, 1.398	_	_	0, 0	G
B4	_	1.533	1.383, 1.387	_	—	2.52, 3.45	T, 39
B5	_	1.542	1.396, 1.399	_	—	0, 0	G
B6	_	1.535	1.394, 1.394	_	_	0.42, 2.25	Т
B7	_	1.534	1.387, 1.387	_	_	0.69, 0.69	Т
C1	1	1.536	1.386, 1.390	_	—	2.10, 3.61	40
	2	1.544	1.379, 1.384	_		2.87, 3.38	
	3	1.542	1.386, 1.389	_		7.07, 8.56	
C2	1	1.538	1.379, 1.379	—	_	0.77, 0.77	Т
	2	1.539	1.373, 1.386	_		3.64, 4.92	
	3	1.539	1.373, 1.386	_	_	3.64, 4.92	

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Figure 1. IR spectra of representative boronic acids, a boronic ester, and an anhydride, along with spectra for boric acid (b) and water (w).

solid state, it is necessary to purify them. It is well known that the acid form and the anhydride form of arylboronic acids show different characteristic IR patterns.^[2,12,13,35–37] Pure arylboronic acids have a strong H-bonded O-H stretching mode (3300–3200 cm⁻¹) and a very strong band attributed to the B–O stretching mode (1380–1310 cm⁻¹).^[2] Upon anhydride formation, the O-H stretching mode disappears, and a new strong absorption appears at 680–705 cm⁻¹.^[2,16,36] Additionally, the BO₂ out-of-plane deformation mode^[38] at ~630 cm⁻¹ in arylboronic acids disappears in anhydrides. This information is particularly diagnostic of the presence of boronic anhydrides in the IR spectra. Before performing ¹¹B NMR experiments on pure solid arylboronic acids, it may be useful and convenient to confirm that an O-Hstretching mode around 3300 cm⁻¹ and a BO₂ deformation mode around 630 cm⁻¹ exist and that ring deformation modes of trimeric anhydrides around 700 cm⁻¹ do not exist. Unlike the other arylboronic acids, only A1 shows a vibrational mode around 700 cm⁻¹, which can also be seen in the IR spectrum of C1, a trimeric anhydride form of A1. This may be due to the out of plane phenyl ring deformation of monosubstituted benzenes^[38] rather than because of the ring deformation mode of trimeric anhydride. In addition to three vibrational bands, a B - O - H deformation $mode^{[38]}$ around 1000 cm⁻¹ and a B – C stretching mode around^[38] 1100 cm⁻¹ can be observed for the pure arylboronic acids. However, the latter is also observed for C1. So the latter modes may not be useful to diagnose the anhydride form of arylboronic acids.

Alver^[13] has observed four O – H stretching modes from 3480 to 3262 cm⁻¹ in the FT-IR spectrum of 2,4-dimethoxyphenylboronic acid. He suggested that the two sharper peaks at higher wavenumbers are caused by the formation of intramolecular hydrogen bonds, and the two broader peaks at lower wavenumber are caused by the formation of intermolecular hydrogen bonds. Among the various arylboronic acids studied in this work, three samples (**A2**, **A3**, and **A5**) have an additional sharp peak in their IR spectra. This may be caused by the formation of weak intramolecular hydrogen bonds, which can be expected in arylboronic acids substituted with a methoxy group or *ortho*-substituted by a methyl group. As shown in Fig. 2, the X-ray crystal structure



Figure 2. Short oxygen-hydrogen contacts, some of which could result in weak intramolecular hydrogen bonding in A2 (left) and A5 (right).

obtained in this work suggests that intramolecular hydrogen bonding may occur between O and the H atoms of the methoxy group of **A2**; on the other hand, it may occur between O and H atoms of different OH groups for **A5**.

When **A1** was heated in an electric oven at 80 °C overnight, its IR spectrum changed exactly to that of **C1** (Fig. 1). When **C1** was recrystallized from hot water, its IR spectrum changed exactly to that of **A1**. That is, phenylboronic acid and its trimeric anhydride can convert reversibly as shown in Scheme 2.

As shown in Fig. 1, any O – H stretching mode around 3300 cm⁻¹, which appears for pure arylboronic acids did not appear in the IR spectra of pure solid arylboronic acid catechol cyclic esters studied in this work. Most vibration modes are observed as in the literature,^[39] that is, C – O stretching modes were observed around 1237 and 1030 cm⁻¹, whereas B – O stretching modes were observed around 1329 and 1070 cm⁻¹. As in the case of the arylboronic acids, the C – C stretching mode was observed around 1600 cm⁻¹ for arylboronic acid catechol cyclic esters.

¹¹B NMR

Shown in Figs. 3–6 are ¹¹B NMR spectra acquired under MAS and static conditions at three different fields of 9.4, 11.75, and 21.1 T for some arylboronic acids and their catechol cyclic esters. Several more spectra for the other compounds are given in the SM. Presented in Table 4 are the ¹¹B EFG and CS tensor values obtained via analytical simulations of the ¹¹B NMR spectra of arylboronic acids (A1 through A9) and their catechol cyclic esters (B1 through B7). By simultaneously fitting data at three different fields, the C_{Q} , η_{Q} , and δ_{iso} values were determined from the MAS NMR spectra. The fitting is done using WSolids1 software in a heuristic fashion by cycling through the spectra acquired at all three fields and adjusting a single set of parameters manually until self-consistent results are obtained for all three spectral data sets. Spectra of stationary samples were then analyzed to determine the Ω , κ , and Euler angles relating the CS tensor PAS to the EFG PAS.^[40] As shown in Table 4, a small range in $C_{
m O},\,\delta_{
m iso},$ and Ω is observed. Incidentally, the clear resolution of the two crystallographically non-equivalent boron sites in A1 and A4 was not possible (Supplementary Material, Fig. 4S); however, slightly improved simulations were obtained using a two-site



Figure 3. Boron-11 MAS (left) and static (right) NMR spectra of A2 acquired at different three fields (21.1 T, 11.75 T, and 9.4 T from the top). Experimental spectra are in black, and simulated spectra are in red. The MAS rate was 10 kHz, and asterisks (*) indicate sidebands.



Figure 4. Boron-11 MAS (left) and static (right) NMR spectra of A8 acquired at different three fields (21.1 T, 11.75 T, and 9.4 T from the top). Experimental spectra are in black, and simulated spectra are in red. The MAS rate was 10 kHz, and asterisks (*) indicate sidebands.

model to fit the data, and so, two sets of parameters are listed in Table 4 for each of these compounds. Depending on the sample, the C_Q values vary from 2.64 MHz for compound **B6** to 3.05 MHz for compound **A5**; the δ_{iso} values vary over a very small range, from 28.6 ppm for **A2** to 31.5 ppm for **B3**, and the Ω values vary from 17.7 ppm for site *a* of **A1** to 28.3 ppm for **A5**. Although the ¹¹B NMR parameters vary over a small range, it is possible to divide the systems studied into two groups, that is, arylboronic acids and arylboronic acid catechol cyclic esters, using their NMR parameters, which is consistent with the trends reported previously for boronic acids and esters bearing different substituents.^[11] The C_Q , η_Q , and κ values for the arylboronic acids fall in the ranges 2.95–3.05 MHz, 0.30–0.45, and 0.35–1.0, respectively, whereas those for the arylboronic acid catechol esters fall in the ranges 2.64–2.71 MHz, 0.74–0.08, and -0.85 to -0.12, respectively. As seen previously^[11] for δ_{iso} and Ω , there is overlap in the ranges for each group of compound. The Ω values vary over a larger range (10.7 ppm) for arylboronic acids than for



Figure 5. Boron-11 MAS (left) and static (right) NMR spectra of B1 acquired at different three fields (11.75 T and 9.4 T from the top). Experimental spectra are in black, and simulated spectra are in red.



Figure 6. Boron-11 MAS (top) and static (bottom) NMR spectra of B3, B4, and B5 acquired at 9.4 T. The MAS rate was 10 kHz, and asterisks (*) indicate sidebands. Experimental spectra are in black, and simulated spectra are in red.

arylboronic acid catechol cyclic esters (5 ppm). The Euler angles suggest that the largest components of the CS and EFG tensors are coincident or nearly coincident.

In the ¹¹B MAS NMR spectra, an anomalous peak on the highfrequency edge of the powder pattern was sometimes observed, as shown for B6 and B7 (see SM). We were interested to determine whether this was caused by an impurity or the experimental conditions used to acquire the NMR spectra. Several verifications of sample purity were performed using IR spectroscopy and X-ray crystallography (vide supra) to ensure that the unexplained peaks were not due to boric acid or another decomposition product. We then decided to investigate the dependence of the secondorder quadrupolar line shape under MAS conditions as a function of relaxation delay and of the excitation pulse power and length. Some spectra demonstrating the results are presented in the Supplementary Material. Some of the findings are summarized in Fig. 7 for a typical case, compound **B6**, where it is seen that the high-frequency and low-frequency discontinuities of the powder pattern correspond to nuclei in crystallites which relax marginally more quickly ($T_1 = 19 \pm 2$ s and 16 ± 3 s for the high-frequency and low-frequency edges, respectively) than do the nuclei in crystallites corresponding to the central two maxima ($T_1 = 22 \pm 1$ s). Investigation of the effects of pulse length on the line shape (see SM, Fig. 12S) also revealed that a particularly long and weak pulse was optimal for achieving ideal lineshapes (i.e. up to 48 μ s for the CT-selective 90-degree pulse) and that short pulses (e.g. 1.5 μ s for the 90-degree pulse) contributed to the unwanted extra spectral intensity at the high-frequency edge of the MAS line shape.

For the anhydrides (**C1** and **C2**), ¹¹B MAS and static NMR spectra obtained at two magnetic fields are shown in Fig. 8 and in the Supplementary Material. Although the MAS NMR spectra at 9.4 T closely resemble those expected for an isolated ¹¹B nucleus, spectral analysis was not pursued further because of the existence of homonuclear ¹¹B-¹¹B dipolar couplings. More advanced methods may be amenable to analyzing the MAS NMR spectra;^[10,41] however, the analysis of the spectra of the stationary samples is complicated additionally by anisotropic chemical shift contributions from the multiple crystallographically non-equivalent sites.

¹³C NMR

Most of the samples studied in this work showed different ¹³C CP/MAS spectra before and after recrystallization. Phenylboronic acid (**A1**) is one such example. Shown in the Supplementary Material (Fig. 14S) are ¹³C CP/MAS spectra for the commercial sample and for the purified sample. The two spectra are completely

Table 4.	Table 4. Experimental ¹¹ B EFG and CS tensor parameters of the boronic acids and esters in this work ^a								
Sample	C _Q /MHz	η_{Q}	$\delta_{\rm iso}(^{11}{\rm B})/{\rm ppm}$	<i>Ω</i> /ppm	κ	α/°	β / $^{\circ}$	γ / °	
A1 (a) ^b	$\textbf{3.00}\pm\textbf{0.10}$	$\textbf{0.45}\pm\textbf{0.10}$	$\textbf{30.5} \pm \textbf{1.0}$	17.7 ± 1.3	$\textbf{0.80}\pm\textbf{0.20}$	0	0	90	
A1 (b) ^b	3.03 ± 0.10	$\textbf{0.40}\pm\textbf{0.10}$	31.0 ± 1.0	18.7 ± 1.3	1.00 ± 0.20	0	0	90	
A2	$\textbf{3.02}\pm\textbf{0.05}$	$\textbf{0.43} \pm \textbf{0.05}$	$\textbf{28.6} \pm \textbf{0.6}$	$\textbf{23.0} \pm \textbf{1.2}$	$\textbf{0.73} \pm \textbf{0.13}$	0	0	60	
A3	2.97 ± 0.05	$\textbf{0.40} \pm \textbf{0.05}$	28.7 ± 0.6	$\textbf{27.0} \pm \textbf{1.2}$	$\textbf{0.35}\pm\textbf{0.12}$	0	10	40	
A4 (a) ^b	$\textbf{3.00}\pm\textbf{0.10}$	$\textbf{0.42}\pm\textbf{0.10}$	$\textbf{30.2} \pm \textbf{1.0}$	17.7 ± 1.4	0.80 ± 0.20	0	5	0	
A4 (b) ^b	$\textbf{3.03}\pm\textbf{0.10}$	$\textbf{0.40}\pm\textbf{0.10}$	$\textbf{30.7} \pm \textbf{1.0}$	18.7 ± 1.4	1.00 ± 0.20	0	5	0	
A5	$\textbf{3.05}\pm\textbf{0.05}$	$\textbf{0.43}\pm\textbf{0.05}$	$\textbf{30.4} \pm \textbf{0.5}$	$\textbf{28.3} \pm \textbf{1.0}$	0.38 ± 0.13	0	8	40	
A7	$\textbf{3.03} \pm \textbf{0.05}$	$\textbf{0.40} \pm \textbf{0.05}$	29.7 ± 0.5	$\textbf{26.0} \pm \textbf{1.0}$	0.52 ± 0.10	0	13	40	
A8	2.97 ± 0.05	$\textbf{0.30}\pm\textbf{0.05}$	$\textbf{28.9}\pm\textbf{0.5}$	24.0 ± 1.0	0.57 ± 0.10	0	8	50	
A9	2.95 ± 0.05	$\textbf{0.37} \pm \textbf{0.05}$	$\textbf{28.8} \pm \textbf{0.5}$	25.7 ± 1.0	$\textbf{0.40}\pm\textbf{0.10}$	0	14	0	
B1	2.71 ± 0.05	$\textbf{0.78} \pm \textbf{0.05}$	$\textbf{30.8} \pm \textbf{0.5}$	$\textbf{26.0} \pm \textbf{1.0}$	-0.25 ± 0.10	0	0	0	
B2 ^c	2.68 ± 0.17	$\textbf{0.80}\pm\textbf{0.10}$	$\textbf{30.8} \pm \textbf{0.1}$	23 ± 1	-0.45 ± 0.05	0	5	0	
B3	2.68 ± 0.05	$\textbf{0.78} \pm \textbf{0.05}$	31.5 ± 0.5	25.5 ± 1.0	-0.85 ± 0.10	0	4	0	
B4	2.68 ± 0.05	$\textbf{0.78} \pm \textbf{0.05}$	$\textbf{30.4} \pm \textbf{0.5}$	$\textbf{28.0} \pm \textbf{1.0}$	-0.15 ± 0.10	0	0	0	
B5	2.64 ± 0.05	$\textbf{0.80} \pm \textbf{0.05}$	30.1 ± 0.5	$\textbf{28.0} \pm \textbf{1.0}$	-0.15 ± 0.10	0	0	0	
B6	2.64 ± 0.05	$\textbf{0.74} \pm \textbf{0.05}$	$\textbf{30.0} \pm \textbf{0.7}$	$\textbf{27.5} \pm \textbf{1.0}$	-0.22 ± 0.10	0	0	0	
B7	2.69 ± 0.05	0.76 ± 0.05	$\textbf{30.3} \pm \textbf{0.5}$	27.7 ± 1.0	-0.12 ± 0.10	0	0	12	

^aThe errors in the angles α and γ are approximately \pm 50 degrees, whereas the error in β is \pm 10 degrees.

^b(a) or (b) indicates one of two molecules in the asymmetric unit. Site (a) indicates a flat molecule in which the dihedral angle (ϕ_{CCBO}) is below 10 degrees, whereas site (b) indicates a twisted molecule in which a dihedral angle is larger than 10 degrees.

^cData for **B2** are from Weiss, J. W. E., M.Sc. Thesis, University of Ottawa, 2011.



Figure 7. Boron-11 T_1 relaxation anisotropy for **B6**. All data were taken from spectra obtained at 9.4 T. Data are fit to curves of the form $I = I_0 - fexp(-t/T_1)$. Values of T_1 obtained are 19 ± 2 , 22 ± 1 , 22 ± 1 , and 16 ± 3 s for the positions of the MAS powder pattern labelled A, B, C, and D, respectively.

different, and the as-received commercial sample was found to be mostly the anhydride form of phenylboronic acid. This phenomenon was also detected in the FT-IR spectra (*vide supra*).

Presented in the Supplementary Material (Fig. 15S) are representative ¹³C CP/MAS NMR spectra of pure arylboronic acids



Figure 8. Boron-11 MAS and static NMR spectra of C1 acquired at two fields (21.1 T and 9.4 T).

and their catechol cyclic esters. Of particular interest presently are the chemical shifts of the *ipso* carbons attached to boron. It can be difficult to determine these values because there is often spectral overlap with other aromatic carbons; the resonance is split into four peaks in principle due to coupling with ¹¹B or, alternatively, is split because of coupling to the other quadrupolar

boron isotope (¹⁰B). It is well known that spin-1/2 nuclei which are spin-coupled to quadrupolar nuclei are subjected to residual dipolar coupling effects under MAS conditions.^[14] That is, the dipolar coupling between the spin-1/2 nucleus and the guadrupole is not completely averaged as a result of MAS. This leads to broadening and/or splittings of the isotropic resonance of the spin-1/2 nucleus. These splittings are influenced by the values of the dipolar coupling constant between the two nuclei, the J coupling between them, the EFG tensor at the guadrupole, and the relative orientation of the EFG and dipolar tensors. Therefore, under favourable conditions, novel information on some or all of these NMR parameters may be determined through spectral line shape simulations. The NMR spectra here were fit using the dipolar coupling constants derived from the X-ray crystallographic atomic coordinates for boron and carbon (Table 3), the ¹¹B guadrupolar coupling data determined experimentally (Table 4), and an approximately perpendicular orientation of the largest component of the ¹¹B EFG tensor with respect to the ¹³C-¹¹B dipolar vector. A maximum of a few percent adjustment downwards in the value of the static dipolar coupling constant was permitted in the simulations to account for vibrational averaging and a small anisotropy in the indirect spin-spin coupling tensor (ΔJ). In all cases, the spectral simulations showed that the experimental data were consistent with a positive value of $C_{\rm O}(^{11}{\rm B})$ and a positive value of $R_{\rm DD}$ (¹³C,¹¹B), which is consistent with our quantum chemical data (vide infra) and our previous work.^[1]

In Fig. 15S (see SM), the ¹³C CPMAS spectra of **A2** and **A3** show well-resolved peaks for the *ipso* carbons, whereas there is only partial resolution in the spectrum for **A9**, and there is no resolution in the spectrum of **A1**. To obtain the ¹³C isotropic chemical shift of the *ipso* carbons, fitting was straightforward in cases where the resonance was clearly resolved from other peaks. In the case of **A1** or **A9**, for example, CP/DD spectra were used instead of normal CP spectra to remove peaks from protonated carbons in the aromatic region. TOSS/DD spectra were used in some cases to deal with overlapping spinning sidebands (Supplementary Material). Spectra obtained at both 4.7 and 9.4 T were used for the simulations. Fits of the ¹³C CP/MAS NMR spectra of **A2** and **A3** are presented in Fig. 9, and an example of the deconvolution of the contributions caused by coupling to each of the two boron

isotopes to the ipso carbon is shown in the Supplementary Material for A2. In the simulation process, the isotope shift^[42] between ¹³C bonded to the two different boron isotopes, ¹¹B and ¹⁰B, was also considered. The one-bond ¹³C isotope shift, ${}^{[1]}\Delta^{13}C({}^{11/10}B)$, is defined as the chemical shift of ¹³C nuclei which are directly bonded to ¹¹B less the chemical shift of ¹³C nuclei which are directly bonded to ¹⁰B.^[43,44] On the basis of the theory of the isotope shift and from tabulated values for spin pairs of comparable mass, we anticipated a small negative isotope shift of less than 0.1 ppm.^[44] Simulations of all data show that a negative value of magnitude less than about 0.2 ppm for the isotope shift reproduces the experimental spectra. Spectral simulations are shown in detail for A2 in the Supplementary Material (Fig. 18S). The appropriate natural abundance ratio (80.1% for ¹¹B and 19.9% for ¹⁰B) was applied to all simulations. When this simulation was performed, one bond indirect nuclear spin-spin coupling constants (¹J) between ^{11/10}B and ¹³C were also determined. The ¹J(¹³C, ¹¹B) values are summarized with the ¹³C isotropic chemical shifts of the ipso carbons in Table 5. Isotope effects on the reduced coupling constants were assumed to be negligible. A weak correlation $(R^2 = 0.79)$ was found between the value of ${}^{1}J({}^{13}C, {}^{11}B)$ and the boron-carbon bond length (Fig. 10b); however, closer inspection of the data reveals that this apparent trend is mainly because the data for the boronic acids cluster together (long bond lengths and smaller coupling constants) and those for the boronate esters form a separate cluster (shorter bond lengths and larger coupling constants). Within each of the two compound classes, the experimental J coupling data are not precise enough to establish a clear correlation with bond length.

Quantum chemical calculations

Calculations of NMR parameters were carried out using two different approaches. The first is a cluster model approach, where one molecule of the compound of interest was used in the calculation. A second series of calculations using this approach was carried out using a dimer rather than a monomer in the case of some of the boronic acids, which are known to be hydrogen bonded according to their crystal structures. The second approach is the GIPAW DFT method, where the atomic coordinates



Figure 9. Fits of ¹³C CP/MAS NMR peaks of the *ipso* carbon attached to a boron atom for **A2** (left) and **A3** (right). Experimental spectra are in black, and simulated spectra are in red.

Table 5.	Experimental	and calculated	¹³ C chemica	I shifts of t	he ipso
carbons	and one-bond	¹³ C- ¹¹ B spin-sp	in coupling	constants	for the
boronic a	icids and cated	hol cyclic ester	s studied in	this work	

Sample		$\delta_{\rm iso}(^{13}{\rm C})$)/ppm	¹ J(¹³ C, ¹¹ B)/Hz ^b		
		Experiment	Calculation ^a	Experiment	Calculation	
A 1	Site a	129.4 ± 0.5	135.1	86 ± 10	86.4	
	Site b	130.8 ± 0.5	135.9	86 ± 10	85.9	
A2		123.8 ± 0.2	128.6	85 ± 5	87.2	
A3		124.8 ± 0.2	128.5	85 ± 5	86.7	
A4	Site a	123.0 ± 0.5	127.8	79 ± 10	78.9	
	Site b	128.0 ± 0.5	131.9	84 ± 20	84.0	
A5		132.0 ± 0.5	134.7	104 ± 10	103.9	
A7		128.0 ± 0.5	133.1	86 ± 10	85.9	
A8		130 ± 0.5	136.0	90 ± 10	89.8	
A9		127.5 ± 0.5	129.3	86 ± 10	85.8	
B1		126.4 ± 0.5	131.4	100 ± 10	100.1	
B3		116.5 ± 0.5	122.6	100 ± 10	101.0	
B4		123.0 ± 0.5	125.5	98 ± 10	97.9	
B5		125.3 ± 0.5	130.8	100 ± 10	98.7	
B6		122.1 ± 0.5	125.8	100 ± 10	99.8	
B7		123.9 ± 0.5	127.2	98 ± 10	98.2	

^aMonomer model, B3LYP/6-311 + G*. Shielding constants were placed on the chemical shift scale using the absolute shielding constant of 184.1 ppm for TMS (A. K. Jameson, C. J. Jameson, *Chem. Phys. Lett.* **1987**, *134*, 461).

^bOne bond spin-spin coupling constants [(¹*J*(¹³C,¹¹B)] were calculated using the heavy atom coordinates from XRD crystallographic data with the optimization of hydrogen positions.

from the crystal structure as well as the unit cell parameters are treated using periodic boundary conditions so as to model an infinite crystalline lattice.

Calculated ¹³C chemical shifts and ¹J(¹³C, ¹¹B) values are summarized in Table 5. The ¹³C chemical shifts are systematically overestimated by the B3LYP calculations by about 2-5 ppm when using a monomer as the model. The values of ${}^{1}J({}^{13}C,{}^{11}B)$ are very well reproduced by the calculations (Fig. 10a), with a R^2 value of 0.9897. Calculated ¹¹B NMR parameters are listed in Table 6. Comparison with the experimental data reveals several points of interest. First, in the cases where there are two crystallographically distinct molecules in the unit cell (compounds A1, A4), the calculations are consistent with the experimental finding that the values of $C_Q(^{11}B)$, η_Q , and δ_{iso} are too close to distinguish the two boron sites. Second, as shown in Fig. 11, the experimental trends in $C_{\rm O}(^{11}{\rm B})$ are well reproduced using a monomer (cluster, B3LYP), dimer (cluster, B3LYP), or infinite lattice (GIPAW DFT), with essentially negligible improvements noted upon increasing the model size from a monomer to a dimer. The GIPAW DFT Co values are systematically larger than the values obtained using a cluster model, and the former are also further from the experimental values. In the case of $\eta_{\rm Q}$, both the cluster model and the periodic models reproduce the experimental data fairly well, with the GIPAW DFT method providing slightly better agreement with experiment both in terms of absolute values and in terms of the correlation coefficient (see SM). Likely as a result of the small overall range in the values of $\delta_{\rm iso}$ and $\Omega,$ both types of calculations do not provide good correlations with the experimental data. Experimental chemical shifts are overestimated by both types of calculations when the experimental absolute shielding scale of Jackowski et al. is used ($\sigma = 110.9 \text{ ppm}$ for liquid BF₃OEt₂).^[45]



Figure 10. (a) Relation between experimental and calculated one bond spin-spin coupling constants for arylboronic acids and their catechol cyclic esters. ${}^{1}J({}^{13}C,{}^{11}B)$ calc = 0.9701(${}^{1}J({}^{13}C,{}^{11}B)$ expt) + 2.9426 Hz; R^{2} = 0.9897. (b) Correlation between experimental values of ${}^{1}J({}^{13}C,{}^{11}B)$ and the experimental boron–carbon bond lengths. ${}^{1}J({}^{13}C,{}^{11}B)$ = -453.87r + 795.04 Hz; R^{2} = 0.7862.

Calculated CS tensor spans are in approximate agreement with the experimental data, but the trends are not reproduced.

Overall, given that the use of a dimer model did not significantly alter the results obtained when using a monomer model, it would seem that the notably different values obtained from the GIPAW DFT approach are largely because of the difference in the density functional and basis set/energy cutoff, rather than because of the inclusion or exclusion of the surrounding molecules from the model used for the calculation. This is perhaps not surprising given that the boron atoms in the molecules studied presently are covalently bound within the centre of each molecule, and there are no ions in the lattice.

Boron-11 NMR parameters were calculated for **A1**, **A4**, and **A5** using a monomer model as the CCBO dihedral angle was varied. **A4** and **A5** are arylboronic acids, which have only methyl groups as substituents on the phenyl ring. The results are shown in Fig. 12 and in the SM. The observed dependence and its relationship with the electronic structure at boron has been discussed by Weiss and Bryce.^[11] The inclusion of a methyl group as a *para* substituent (**A1** vs **A4**) did not alter the manner in which the energy and the ¹¹B NMR parameters vary as a function of the CCBO dihedral angle; however, a difference in the behaviour of the computed parameters when the methyl group was substituted at

		Site b	3.563	0.431	64.87	30.34
A2	1		3.132	0.459	73.98	27.29
	3		3.155	0.590	74.13	26.54
			3.525	0.415	66.61	30.90
A3	1		3.099	0.652	76.00	28.10
	2		3.114	0.511	74.55	31.46
			3.469	0.370	66.46	30.73
A4 ^a	1 site a		3.119	0.296	74.54	28.36
	1 site b		3.150	0.434	74.62	27.45
	2 site a		3.135	0.515	74.54	26.86
	2 site b		3.142	0.494	74.21	30.54
		Site a	3.582	0.289	64.88	32.15
		Site b	3.956	0.356	60.32	29.54
A5	1		3.182	0.759	77.73	37.83
	2		3.195	0.636	70.85	39.81
			3.593	0.542	62.83	38.81
A7	1		3.170	0.440	74.19	29.30
	2		3.161	0.502	74.02	32.25
			3.585	0.402	65.21	31.32
A8	1		3.113	0.311	74.56	33.36
	2		3.116	0.372	74.19	32.41
			3.559	0.283	66.18	29.55
A9	1		3.129	0.439	74.61	26.43
	3		3.137	0.477	74.98	25.81
			3.517	0.396	67.11	29.90
B1	1		2.768	0.880	71.09	24.77
			3.120	0.855	64.71	34.24
B4	1		2.786	0.859	71.22	25.25
			3.123	0.806	65.12	34.08
B6	1		2.753	0.853	70.89	23.86
			3.083	0.824	65.39	31.59
B7	1		2.760	0.840	71.50	24.09
			3.109	0.812	64.92	33.39
C1	1 site a1		3.301	0.678	73.06	25.92
	1 site a2		3.314	0.691	73.27	26.14
	1 site a3		3.305	0.659	73.45	24.68
		Site a1	3.616	0.638	66.10	32.89
		Site a2	3.677	0.617	66.38	31.89
		Site a3	3.392	0.577	66.82	29.71
C2	1 site a1		3.283	0.645	74.11	24.43
	1 site a2 ^c		3.277	0.643	74.22	25.26
	1 site a3 ^c		3.277	0.643	74.22	25.26
		Site a1	3.673	0.586	66.85	34.19
		Site a2 ^c	3.678	0.583	66.58	30.70
		Site a3 ^c	3.678	0.583	66.58	30.70

Number of molecules

included in the cluster model for GIAO calculation

GIPAW

Site a

GIA0^b

1 site a

1 site b

2 site a

2 site b

Sample

A1^a

Table 6. Calculated ¹¹B EFG and magnetic shielding tensor parameters for arylboronic acids, esters, and anhydrides

 $C_{\rm O}/\rm MHz$

3.130

3.165

3.132

3.155

3.513

 η_{Q}

0.452

0.467

0.508

0.529

0.399

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κ

0.79

0.89

0.02

0.11

0.87

0.54 0.88 0.60 0.73 0.58 0.13 0.55 0.45 0.91 0.12 0.11 0.68 0.25 0.36 0.00 0.31 0.91 0.18 0.65 0.58 0.41 0.85 0.90 0.55 0.75 -0.71 -0.04-0.83 -0.06 -0.77 -0.04 -0.73 0.00 -0.47 -0.42 -0.40 -0.05 0.02 0.22 -0.39 -0.39 -0.39 0.10 0.08 0.08

 Ω/ppm

24.95

28.19

27.41

31.53

22.17

 $\sigma_{\rm iso}(^{11}{\rm B})/{\rm ppm}$

74.64

73.74

74.48

73.41

65.16

was performed for a dimer or trimer. ^cSites a2 and a3 are crystallographically equivalent.

^bNumerical value of 2 or 3 means that intermolecular H-bonding was involved in the model used for the GIAO calculation. That is, the calculation



Figure 11. Correlations between experimental and calculated ¹¹B quadrupolar coupling constants for boronic catechol acids and esters. Results are presented using Gaussian 09 software [cluster model; monomer (red circles) and dimer (open black circles)] as well as CASTEP (GIPAW-DFT) using periodic boundary conditions (blue triangles). The equations of best fit are as follows: $C_Q(calc) = 1.13C_Q(expt) - 0.26$ MHz, adjusted $R^2 = 0.986$ (monomer); $C_Q(calc) = 1.27C_Q(expt) - 0.27$ MHz, adjusted $R^2 = 0.977$ (GIPAW DFT).



Figure 12. Calculated $(B3LYP/6-311 + G^*)^{11}B$ magnetic shielding tensor parameters *versus* dihedral angle (CCBO) for **A5**.

the *ortho* position (**A5**) was noted. The computed energy explains why the experimental value of ϕ_{CCBO} of **A5** is large (~ 40°) relative to the values for **A1** and **A4**, as shown in Table 3. Inspection of the plots of computed energy and ¹¹B NMR parameters as a function of ϕ_{CCBO} shows that we would anticipate a larger ¹¹B CS tensor span in

A5 versus **A1** and **A4**. This is in agreement with the experimental data in Tables 3 and 4. Additional calculations of various ¹¹B and ¹³C NMR parameters for boronic acids as a function of geometry are presented in the Supplementary Material.

Conclusions

In conclusion, this study has revealed new insights into the relationship between the NMR parameters of boronic acids and boronate esters, and their molecular structures. X-ray crystal structures of seven compounds have been newly determined. Along with X-ray crystallography, IR spectroscopy of powdered samples was very useful in identifying anhydride impurities in the samples and to understand the conversion between acid and anhydride forms of various samples. Proper consideration of T_1 relaxation anisotropy and excitation pulse power was found to be critical for the acquisition of undistorted ¹¹B solid-state NMR spectra. Boron-11 chemical shift and electric field gradient tensors were characterized for several samples, and, in agreement with our previous work, it was noted that the acids and esters may be easily differentiated on the basis of the value of the ¹¹B quadrupolar coupling constant. Small boron chemical shift anisotropies were measureable because of the use of spectrometer equipped with a 21.1 T magnet. The magnitude of these small anisotropies was well reproduced with quantum chemical calculations; however, the experimental trends were not. The importance of the CCBO dihedral angle and the local hydrogen bonding environment was noted. Careful analysis of the ¹³C CP/ MAS NMR spectra of the same samples allowed for the accurate measurement of ipso carbon chemical shifts as well as boroncarbon J coupling constants. Both of these values were wellreproduced with quantum chemical calculations, suggesting the potential utility of the NMR parameters for providing insight into structure in boronic acids and esters.

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Supporting Information

Additional ¹¹B and ¹³C solid-state NMR spectra, figure showing the effects of pulse delay and pulse length on ¹¹B NMR spectra, additional computational results, correlations between experimental and calculated data, cif data.

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