Supramolecular structures and spontaneous resolution: the case of *ortho*-substituted phenylboronic acids†

Matthias Filthaus,[a] Iris M. Oppel[b] and Holger F. Bettinger*[a]

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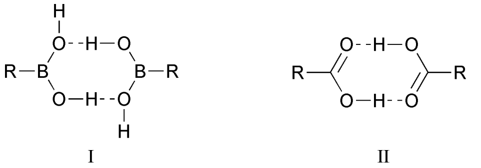
The solid state structures of a number of *ortho*-substituted arylboronic acids, *ortho*-bromophenyl, *ortho*-phenylphenyl, pentamethylphenyl, and 10-bromo-9-anthryl, were determined by X-ray diffraction techniques. All boronic acids investigated form dimers in the solid state, but the interconnection of dimers to ribbons differs from that of the parent phenylboronic acid. Pentamethylphenylboronic acid only uses *one* hydrogen bond but an additional OH–π interaction for connection of dimers, while all others investigated employ two hydrogen bonds for interconnection of dimers to ribbons. 10-Bromo-9-anthrylboronic acid is found to undergo spontaneous resolution of its enantiomers to a racemic conglomerate upon crystallization.

Introduction

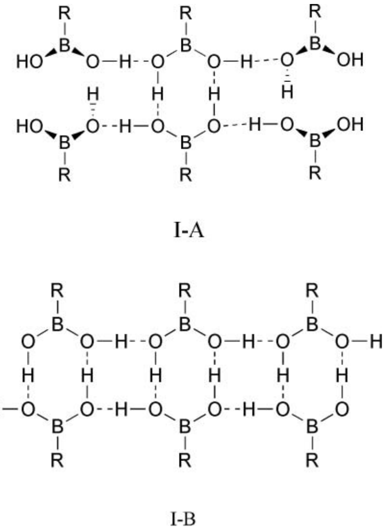
Boronic acids are invaluable reagents for transition metal catalyzed cross-coupling reactions[1] and thus comprise an important class of auxiliary compounds in modern organic synthesis.[2] Along with the boroxins, their cyclic trimeric anhydrides, boronic acids also are of current interest in supramolecular chemistry and crystal engineering.[3–8] The use of boronic acids as building blocks in the assembly of discrete supermolecules has been motivated by the formation of self-complementary dimers (**I**), akin to carboxylic acids (**II**; Scheme 1).[9]



Scheme 1 Homodimeric units of boronic acids (**I**) and carboxylic acids (**II**).

The formation of dimers is generally observed in the crystal structures of arylboronic acids, but there are some examples which do not crystallize within motif **I**.[10–13] Most of these examples have in common a hydrogen bond acceptor on the phenyl ring, which interacts with one of the $B(OH)_2$ hydroxyl groups of another molecule. Another exception is 4-methoxyphenylboronic acid where one molecule is hydrogen bonding to *four* other monomers.[14a]

The two additional hydrogen atoms in boronic acid dimers allow for interaction of homodimeric units in the solid state through hydrogen bonding, which is not available to carboxylic acid dimers. In prototypical phenylboronic acid **1**, the structure of which has been known since 1977,[15] each dimer unit is interacting with four other dimers by hydrogen bonds (Scheme 2, **I**-A). Here, the planes defined by the hydrogen bonding network within the *four* dimers are almost orthogonal to the plane of the central dimer.



Scheme 2 Schematic representation of the interaction of homodimeric arylboronic acid dimers in the solid state. In **I**-A a central dimer interacts with four other dimers (only monomers are shown for clarity) which are oriented almost perpendicularly to the central dimer. In **I**-B each dimer is interacting with two other dimers resulting in ribbons.

However, another connectivity of the homodimeric units was observed for a few arylboronic acids, like 2,6-difluorophenyl (**2**),[16] 2,6-bis(trifluoromethyl)phenyl (**3**)[17] and 2,2′-ethynylenedibenzeneboronic acid (**4**; Scheme 3).[18] In the solid state structures of these compounds each dimer is bound to only *two* other homodimers by hydrogen bonds (Scheme 2, **I**-B). This connectivity results in eight-membered rings with an almost coplanar arrangement of oxygen and hydrogen atoms. Compounds **2–4**

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[a] *Organische Chemie II, Ruhr-Universität Bochum, Universitätsstr. 150, 44780, Bochum, Germany. E-mail: Holger.Bettinger@rub.de; Fax: +49 234/322-4529*
[b] *Analytische Chemie, Ruhr-Universität Bochum, 44780, Bochum, Germany*

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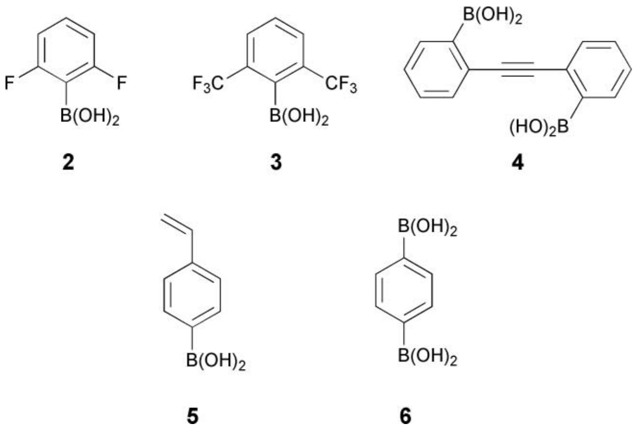


Scheme 3

have in common non-hydrogen substituents in positions *ortho* to the boronic acid functionality, and it is tempting to assume that the steric requirements of the *ortho* substituent might be responsible for the preference of structural motif **I**-B in the solid state. Establishing such an influence of the molecular structure on the crystal structure would be very valuable for crystal engineering applications utilizing arylboronic acid synthons.[4] However, the crystal structures of three other arylboronic acids indicate that the absence or presence of *ortho* substituents not necessarily results in the preferred formation of motif **I**-A or **I**-B, respectively. For example, *p*-styrylboronic acid (**5**) and 1,4-phenylenediboronic acid (**6**) also crystallize within motif **I**-B, but do not have any non-hydrogen groups in the *ortho* position.[19] On the other hand, in the crystal structure of pentafluorophenylboronic acid motif **I**-B is not observed in spite of the two fluorine atoms.[20]

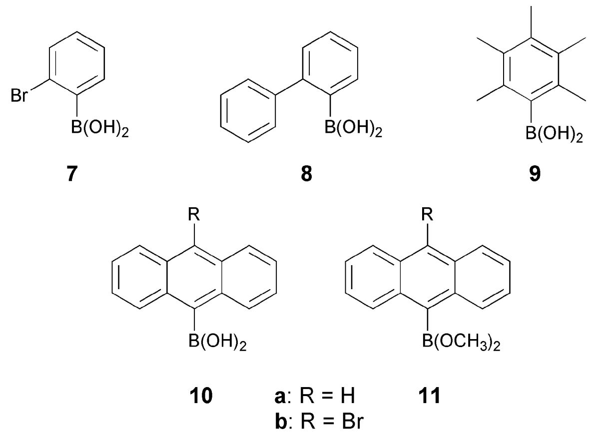
This brief survey of the crystal structures of arylboronic acids shows that it is difficult to clearly establish a link between molecular and crystal structures, even for such seemingly simple compounds. In view of the future utilization of arylboronic acids in crystal engineering, additional structural information is required to gain a deeper understanding of the influences of substituents at the arene ring on the crystal structures of phenylboronic acids. We have therefore investigated the solid state structures of α-substituted arylboronic acids **7–10** and 9-anthracenylboronic acid dimethyl ester (**11**; Scheme 4), which have not been described previously, and present our results here. We have selected these compounds because they are of interest in our ongoing research, which is aimed at the synthesis of kinetically stabilized benzoborirenes.

Results and discussion

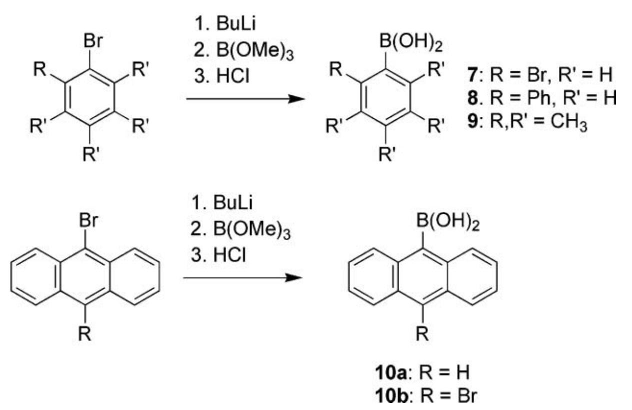
Synthesis and spectral properties

The phenylboronic acids **7**, **8**, and **10a** have been reported earlier as intermediates in complex syntheses, but their detailed preparations and spectroscopic properties have not yet been described. All phenylboronic acids studied in the present paper, including the novel compound **9**, were synthesized from the corresponding bromoarenes as depicted in Scheme 5.

All compounds showed the required ^{1}H, ^{13}C, and ^{11}B NMR and mass spectra, but obtaining acceptable elementary analyses can be difficult. This is most likely due to the equilibrium between the boronic acids and their cyclic anhydrides.[21,22]



Scheme 4



Scheme 5 General scheme for synthesis of substituted phenylboronic acids.

Solid state structures

Relevant crystallographic details for all compounds are compiled in Table 1. The molecular parameters (Table 2) are as expected for arylboronic acids. For example, the BC bond in **7**, 1.58 Å, is longer than in the *meta* or *para* isomer (1.53 Å),[23,24] but it is well within the range (1.57–1.59 Å) typically observed for α-substituted phenylboronic acids.[16–18,20,25–29] The tilt angles, which describe the relative rotations of the aryl rings and the BO_2 planes, range between 34–75° for the boronic acids **7–10b**. The BO bonds have similar lengths and do not deviate significantly from values in other phenylboronic acids.

As expected, all acids **7–10** form dimers, but they differ in the way dimers are interconnected in the solid state. Among the series investigated, the geometrically least hindered 2-bromophenylboronic acid (**7**) forms the motif **I**-B. Within each dimeric unit, the boron and oxygen atoms are coplanar. Each dimer in turn is connected by hydrogen bonds to two other dimers, one on either side, thereby creating a ribbon-like infinite structure (Fig. 1).

The boron and oxygen atoms within this ribbon are almost coplanar and the hydrogen atoms are only slightly above and below this plane. The aryl rings are tilted in the opposite direction,

Table 1 Crystallographic information for **7–11**

	7	**8**	**9**	**10b**	**11a**
Empirical formula	$C_6H_6BBrO_2$	$C_{12}H_{11}BO_2$	$C_{11}H_{17}BO_2$	$C_{14}H_{10}BBrO_2$	$C_{16}H_{15}BO_2$
Molecular weight	200.83	198.02	192.06	300.94	250.09
Temperature/K	108(2)	108(2)	108(2)	113(2)	294(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group, Z	$P\bar{1}$, 2	$P\bar{1}$, 4	$Aba2$, 16	$P2_12_12$, 4	$C2/c$, 8
a/Å	4.957(8)	8.264(1)	31.624(4)	8.264(1)	31.502(3)
b/Å	7.056(1)	9.289(1)	15.161(1)	17.094(1)	7.6126(6)
c/Å	10.757(2)	14.548(2)	9.156(1)	4.9200(2)	12.1156(7)
α/°	95.77(1)	98.51(1)	90.0	90.0	90.0
β/°	92.22(1)	105.00(1)	90.0	90.0	110.10(1)
γ/°	96.61(1)	99.90(1)	90.0	90.0	90.0
Volume/Å^3	371.4(1)	1040.7(2)	4390(1)	1216.8(1)	2728.5(4)
Density/g cm^{-3}	1.796	1.264	1.162	1.643	1.218
θ_{min}, θ_{max}/°	3.32, 27.49	2.95, 25.00	2.68, 27.49	2.82, 27.49	2.76, 25.23
R_1 (observed)	0.0241	0.0615	0.0406	0.0240	0.0530
wR_2 (all)	0.0595	0.1590	0.1014	0.0490	0.1597
Flack parameter	n. a.	n. a.	n. a.	−0.014(8)	n. a.

Table 2 Geometrical parameters (in Ångstroms and degrees) of molecules **7–11** as determined by crystal structure analysis

Parameter	**7**	**8**	**9**	**10b**	**11a**
r(CB)	1.583(3)	1.556(5)	1.574(4)	1.580(3)	1.581(3)
r(BO)	1.368(3); 1.369(3)	1.364(4); 1.374(4)	1.350(3); 1.377(3)	1.355(3); 1.359(3)	1.344(2); 1.346(2)
Averaged tilt angle	34.0	50.9	74.7	52.5	90.0

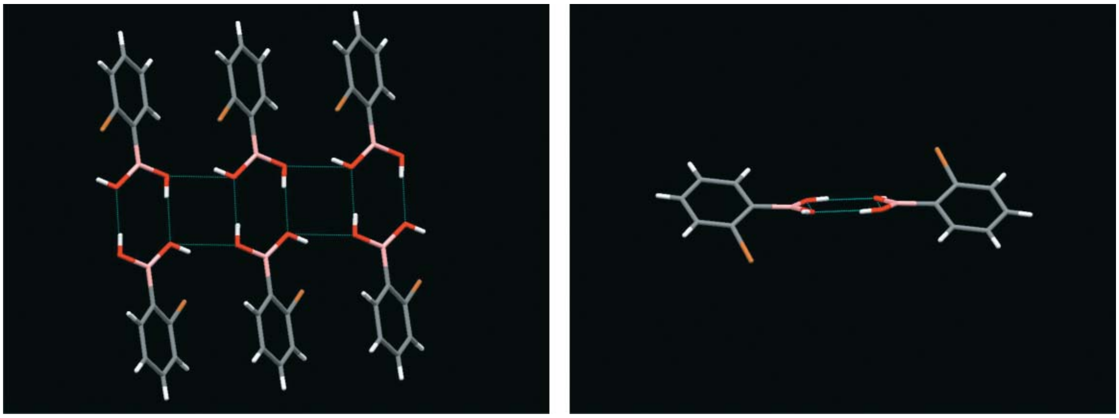


Fig. 1 Two different views of the arrangement of dimers of 2-bromophenylboronic acid (**7**) in the solid state.

if viewed along the B–C bond, giving rise to a symmetric arrangement of boronic acid monomers with respect to inversion in the center of the dimer. The compound crystallizes in the space group $P\bar{1}$, as does 1,1′-biphenyl-2-yl-boronic acid **8**. The latter also forms ribbons of dimer units in the solid similar to **7** and thus displays the hydrogen bonding motif **I-B**. The boron and oxygen atoms are no longer coplanar in the dimer units and these are strongly tilted with respect to each other (Fig. 2). It appears reasonable to ascribe these distortions compared to **7** to the sterically more demanding *ortho*-phenyl group in **8**.

An aggregation of dimer units into ribbons with hydrogen bonding motif **I-B** is also obtained in (10-bromo-9-anthracenyl)boronic acid (**10b**). As with **8** coplanarity of the boron, oxygen, and hydrogen atoms is lost and the dimer units are tilted against each other, but the distortions are not as severe. Also some of the hydrogen atoms in the hydrogen bonding network are disordered (Fig. 3).

Most importantly, the aromatic rings are tilted in the same direction, looking along the B–C bond, on either side of the ribbon. Therefore, the inversion center is lost, and the compound crystallizes in the Sohncke space group $P2_12_12$. The molecule **10b** does not have an element of symmetry, and is thus dissymmetric, *i.e.*, it is not superimposable with its mirror image.[30] However, the barrier for rotation around the C–B bond is expected to be too low to allow separation of enantiomers at room temperature and thus a racemate of two very quickly equilibrating optical isomers exists in solution. Only one of the two enantiomers is found in the single crystal we have analyzed. Thus the crystal structure of **10b** provides an example of spontaneous resolution upon crystallization under formation of a *racemic conglomerate.*

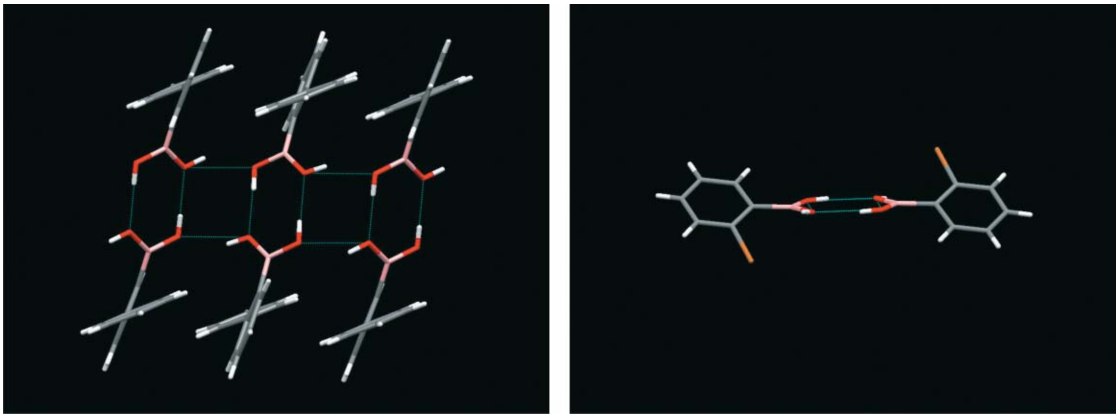


Fig. 2 Two views of the arrangement of dimeric units of 1,1′-biphenyl-2-yl-boronic acid (**8**) in the solid state.

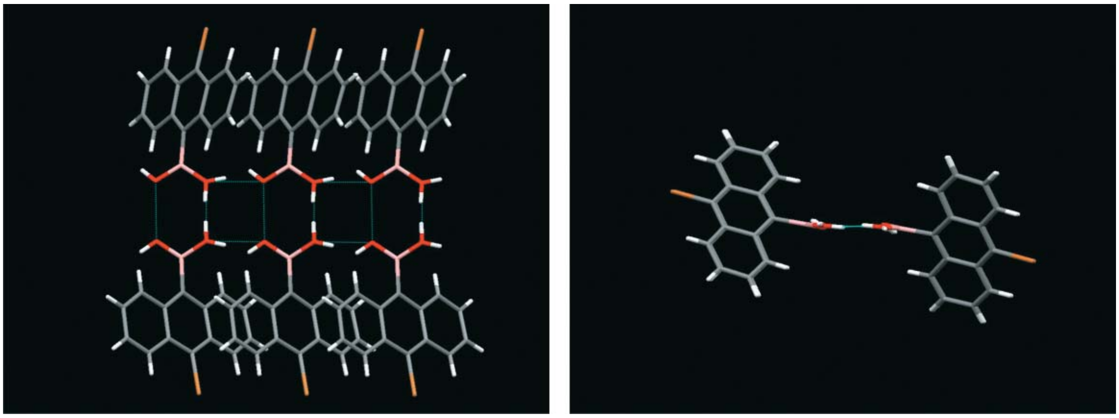


Fig. 3 Two views of the arrangement of dimeric units of 10-bromo-9-anthracenylboronic acid (**10b**) in the solid state.

While this is not an uncommon phenomenon, it is less often observed in apparently achiral compounds.[31–36] The reason why homochiral chains are formed in **10b**, but not in the structurally closely related **7** and **8**, is unclear, as is so often the case when molecules resolve spontaneously upon crystallization.[34,37] Molecules with large permanent dipole moments appear to have a somewhat higher tendency towards conglomerate formation,[38] and the bromine substituent should cause an increased dipole moment in **10b**.

In an effort to learn if the formation of a racemic conglomerate is unique to the bromo derivative **10b**, parent compound **10a** was synthesized and crystals were grown from chloroform solution. Unfortunately, we could not obtain a satisfactory crystal structure. In order to grow better crystals, we transformed boronic acid **10a** into the novel dimethyl ester **11a**. It is obtained easily upon heating of **10a** in methanol, and during slow cooling needles of **11a** crystallize. Crystal structures of esters of arylboronic acids and small alcohols are rather scarce, possibly due to the fact that they are usually liquid and quickly hydrolyze. The large anthryl group efficiently protects the boron atom from attack of water as **11a** is stable under atmospheric conditions. Compound **11a** is no longer dissymmetric as the tilt angle is 90° (Fig. 4, Table 2). It appears that the lack of hydroxyl groups, which are necessary for formation of the supramolecular ribbon structure in **10b**, results in a packing which is dominated by weaker non-covalent interactions.

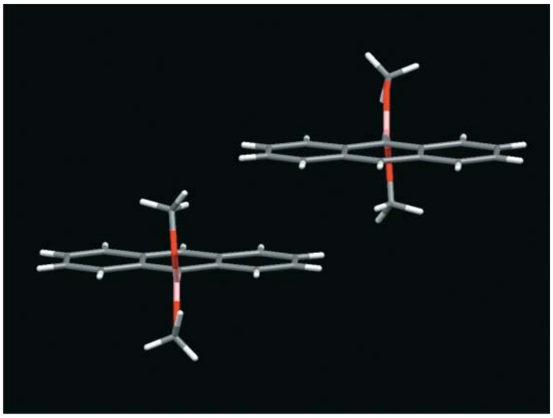


Fig. 4 Arrangement of two molecules of 9-anthracenylboronic acid dimethyl ester (**11a**) in the solid state with face to face interaction of the anthryl groups.

Lastly, a different packing mode than in boronic acids **7**, **8**, and **10b** is observed in (2,3,4,5,6-pentamethylphenyl)boronic acid (**9**), which also forms dimers in the solid state. Again, the boron and oxygen atoms are almost coplanar within a dimeric boronic acid unit (Fig. 5). But in contrast to the earlier examples, dimers of **9** are interconnected by only *one* hydrogen bond.

Which factors are responsible for giving up one hydrogen bond in **9** compared to having two such interactions between two dimeric

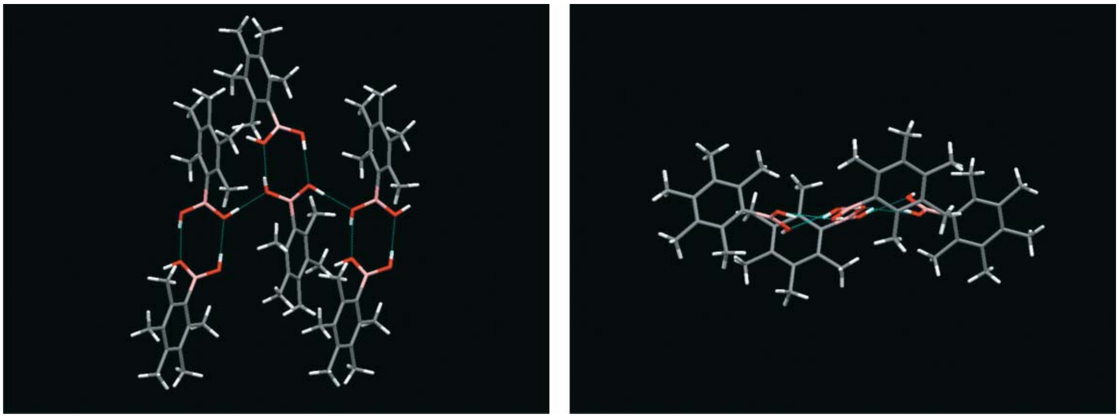


Fig. 5 Two views of the arrangement of dimeric units of (2,3,4,5,6-pentamethylphenyl)boronic acid (**9**) in the solid state.

building blocks in **7**, **8**, and **10b**? We observe the close proximity of the OH group, which is not engaged in a hydrogen bond, to the pentamethylphenyl ring. The OH group is not exactly located above the center of the aryl ring, resulting in three shorter (O · · · C_{aryl}: 3.05–3.22 Å) and three longer contacts (O. . .C_{aryl}: 3.45–3.58 Å). Such an attractive OH–π interaction[39–41] could partially compensate the loss of a more stable hydrogen bond.

Conclusions

Four structurally related arylboronic acids have been synthesized and their solid state structures have been analyzed by single-crystal X-ray crystallography. We find that all of them prefer the formation of dimeric units in the solid state, but the interconnection of dimeric units differs from that in the parent phenylboronic acid. Infinite ribbons are formed by **7**, **8**, and **10b**, in which the dimeric units are interconnected by two hydrogen bonds. In the sterically most crowded pentamethylphenylboronic acid (**9**), the two dimeric units within the ribbons are only connected by one hydrogen bond. We have found an example of a dissymmetric, but achiral molecule under ambient conditions, 10-bromo-9-anthrylboronic acid (**10b**), to undergo spontaneous resolution upon crystallization.

Experimental

General

All reactions were carried out under a dry argon atmosphere in oven dried Schlenk type glassware with magnetic stirring. Temperatures are reported as bath temperatures. Et_2O and THF were continuously refluxed and freshly distilled from sodium using benzophenone as indicator. MeOH was dried with activated 3 Å molecular sieves. All commercially available reagents were used without further purification, and were purchased from Aldrich Chemical Co., Acros Organics or Merck. *t*-BuLi was used as a 15% solution in pentane (1.48 M), and *n*-BuLi was used as a 15% solution in hexane (1.59 M). TLC was performed on Al-backed plates coated with silica gel with F_{254} indicator (Polygram SIL G/UV from Macherey-Nagel); the chromatograms were visualized under UV light (254 nm). R_f values refer to silica gel (eluent: pentane–ethyl acetate (4 : 1)). Melting points (uncorrected values, °C) were obtained with open capillary tubes. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX 400 calibrated on TMS (tetramethylsilane) as an internal standard ($\delta = 0.0$ ppm), and ^{11}B NMR spectra with a Bruker DPX 250 calibrated on $BF_3{\cdot}OEt_2$ ($\delta = 0.0$ ppm). All spectra were measured in acetone-d_6. Mass spectrometry (EI, 70 eV) was performed with a VG Autospec. The intensities are reported as a percentage relative to the base peak after the corresponding *m*/*z* value. Elemental analyses were determined with a Carlo-Erba Elemental Analyser 1106. FT-IR spectroscopy was performed with a Bruker Equinox 55 (KBr, ν in cm^{-1}). UV/Vis spectra were recorded with a Cary Varian 1 ($\lambda_{max.}$ in nm, ε in m^2 $mmol^{-1}$) in CH_2Cl_2.

X-Ray analysis

Intensity data for **7**, **8**, **9**, **10b** and **11a** were collected on an Oxford Diffraction Xcalibur2 CCD using MoK_α radiation and employing the ω scan method. The data were corrected for Lorentz, polarization and absorption (multi-scan) effects. All structures were solved by using direct methods (SHELXS-97)[42] and refined by using a full-matrix least-squares refinement procedure (SHELXL-97).[43] The protons bonded to carbon were placed at geometrically estimated positions while in all cases the proton bonded to oxygen was found in the Fourier difference synthesis and refined freely with only the distance fixed to the literature value. In **10b** the protons had to be split into two positions due to a disorder (2-fold axis). Compound **9** crystallizes in the polar space group *Aba*2. As **9** contains no heavy atom the absolute structure could not be determined. Therefore the Friedel pairs have been merged resulting in a meaningless Flack parameter of −10(10). In contrast **10b** contains a bromine atom. Here (space group $P2_12_12$) the absolute structure could be determined as 68% of the Friedel pairs had been measured. The Flack parameter refines to −0.014(8). Crystallographic data for the structure reported in this paper are available as ESI† (CIF format).

General procedure for the preparation of boronic acids (8, 9, 10). A solution of the arylbromine in THF was cooled to −90 °C with a nitrogen/isopropanol cooling bath and the lithium compound, *t*-BuLi (2.1 eq.) or *n*-BuLi (1.1 eq.), were added quickly. The coloured reaction mixture was stirred for 45 min, while the temperature rose to −65 °C. The reaction was treated with an excess of $B(OMe)_3$, warmed slowly to room temperature and stirred overnight. After the addition of water (80 cm^3) the reaction mixture was acidified with 0.5 M hydrochloric acid (pH ~ 3–5) and extracted with Et_2O (2 × 70 cm^3). The organic layer was washed with brine and water (2 × 25 cm^3) and dried over $MgSO_4$. The solvents of the organic layer were removed by rotary evaporation. The residue was refluxed in water for 2 h, and filtered scalding hot (recrystallization). The filtrate was cooled to 0 °C for 10 min and the white product was isolated by filtration, washed with pentane and water (2 × 20 cm^3).

2-Bromophenylboronic acid (7). A solution of *ortho*-dibromobenzene (0.5 cm^3, 4.15 mmol), THF–Et_2O (25 cm^3 : 25 cm^3) was cooled to −115 °C with a nitrogen/ethanol cooling bath and pre-cooled (−78 °C) *t*-BuLi (5.9 cm^3, 8.73 mmol) was added very quickly. The yellow reaction mixture was stirred for 35 min at −115 °C, and the reaction was treated with a pre-cooled solution (−78 °C) of $B(OMe)_3$ (5 cm^3, 44 mmol) in Et_2O (10 cm^3) and stirred for two hours at −115 to −105 °C. The solution was quenched with 5 cm^3 EtOH–conc. HCl (8 : 2) at −115 °C and warmed slowly to room temperature. Workup (see general procedure) and recrystallization from water (150 cm^3) gave **7** (0.55 g, 66%) as a white solid, mp 183 °C (from water), R_f 0.35. Single crystals (colourless needles) were obtained from chloroform solution by slow evaporation. δ_B 28.8; δ_H 7.25–7.35 (2 H, m), 7.51–7.54 (2 H, m); δ_C 126.38, 126.94, 131.16, 132.31, 135.09; MS (EI): *m*/*z* (%): 547 (39) 469 (6), 410 (13), 281 (8), 200 (91)[$M^{+\bullet}$], 156 (57), 130 (42), 103 (7), 77 (100), 50 (33); IR (KBr) in cm^{-1}: 3300, 1586, 1556, 3017, 2360, 1594, 1558, 1466, 1376, 1291, 1165, 1122, 1007, 822, 770, 736, 589; UV/Vis (CH_2Cl_2) $\lambda_{max.}$ (log ε) = 237 (3.76), 283 (3.02); calc. for $C_6H_6BBrO_2$: C 35.88, H 3.01; found: C 36.03, H 3.06. HRMS calc. 199.96442, found 199.96438.

1,1′-Biphenyl-2-yl-boronic acid (8). According to the general procedure, 2-bromo-1,1′-biphenyl (0.8 cm^3, 4.63 mmol) in THF (50 cm^3), *n*-BuLi (3.2 cm^3, 5.09 mmol) and $B(OMe)_3$ (5 cm^3, 44 mmol), gave **8** (0.74 g, 81%) as colourless needles after recrystallization from water (150 cm^3). Mp (from water) 194–196 °C, R_f 0.35. δ_B 30.6; δ_H 6.89 (2 H, s, O*H*), 7.34–7.54, (8 H, m), 7.67–7.71 (1 H, m); δ_C 126.43, 127.18, 128.47, 128.86, 129.10, 133.38, 143.80, 145.81; MS (EI): *m*/*z* (%): 540 (19) 198 (100)[$M^{+\bullet}$], 180 (43) (29), 154 (58), 128 (5), 77 (8), 51 (4); IR (KBr) in cm^{-1}: 3456, 3222, 3058, 3017, 2360, 1594, 1558, 1499, 1476, 1433, 1370, 1152, 1115, 1093, 1073, 1009, 824, 781, 742, 698; UV/Vis $\lambda_{max.}$ (log ε) = 250 (3.90); calc. for $C_{12}H_{11}BO_2$: C 72.78, H 5.60, found C 72.17, H 5.53. HRMS calc. 198.08562, found: 198.08542.

(2,3,4,5,6-Pentamethylphenyl)boronic acid (9). According to the general procedure, 1-bromo-2,3,4,5,6-pentamethylbenzene (3.0 g, 13.21 mmol) in THF (180 cm^3), *t*-BuLi (18.7 cm^3, 27.7 mmol) and $B(OMe)_3$ (10 cm^3, 88 mmol) afforded **9** after recrystallization from water (400 cm^3) as colourless needles (2.21 g, 87%), mp (from water) 185 °C, R_f 0.35. δ_B 31.8; δ_H 2.19 (6 H, s, *meta*-H), 2.23 (3 H, s, *para*-H), 2.30 (6 H, s, *ortho*-H), 4.45 (2 H, br s, O*H*); δ_C 20.16 (*meta*-C), 20.58 (*para*-C), 25.16 (*ortho*-C), 131.53, 131.70, 134.20; MS (EI): *m*/*z* (%): 192 (94)[$M^{+\bullet}$], 174 (29), 159 (37), 148 (30), 133 (100), 117 (15), 105 (13), 91 (19), 77 (9), 65 (6), 53 (6), 41 (8); IR (KBr) in cm^{-1}: 3488, 3408, 3229, 2924, 1574, 1477, 1224, 1152, 1086, 1022, 995, 941, 827, 746, 565; UV/Vis $\lambda_{max.}$ (log ε) = 229 (3.37), 273 (2.25); calc. for $C_{11}H_{17}BO_2$: C 68.79; H 8.92, found: C 68.53, H 8.96. HRMS calc. 192.13303, found: 192.13290.

9-Anthracenylboronic acid (10a). [44,45] According to the general procedure, 9-bromoanthracene (3.5 g, 13.61 mmol) in THF (140 cm^3), *n*-BuLi (10.0 cm^3, 15.9 mmol) and $B(OMe)_3$ (10 cm^3, 88 mmol), gave **10a** (1.94 g, 64%) as a pale yellow solid after recrystallization from water (650 cm^3), mp (from water) 217 °C. R_f 0.30; δ_B 32.5; δ_H 7.40–7.46 (4 H, m), 7.90 (2 H, s, O*H*), 7.97–8.00 (2 H, m), 8.12–8.14 (2 H, m), 8.42 (1 H, s); δ_C 125.01, 125.04, 126.60, 128.55, 129.04, 131.31, 133.47; MS (EI): *m*/*z* (%): 222 (7)[$M^{+\bullet}$], 204 (7), 178 (100), 151 (9), 139 (2), 126 (3), 89 (14), 76 (13), 63 (3), 51 (2), 40 (2); IR (KBr) in cm^{-1}: 3268, 3047, 1621, 1558, 1511, 1485, 1415, 1353, 1303, 1181, 1069, 888, 849, 834, 728, 607; UV/Vis $\lambda_{max.}$ (log ε) = 244 (4.17), 329 (3.44), 345 (3.72), 363 (3.88), 382 (3.85); calc. for $C_{14}H_{11}BO_2$: C 75.73, H 4.99, found: C 75.62, H 5.00. HRMS calc. 222.08495, found: 222.08482. Hydrolysis and recrystallization of **11a** in hydrochloric acid (1000 cm^3, 0.5 M) for 2 h at 100 °C gave **10a** as pale yellow needles of higher purity.

(10-Bromo-9-anthracenyl)boronic acid (10b). According to the general procedure, 9,10-dibromoanthracene (4.0 g, 11.90 mmol) in THF (180 cm^3), *n*-BuLi (8.24 cm^3, 13.1 mmol) and $B(OMe)_3$ (15 cm^3, 132 mmol), gave **10b** (2.48 g, 69%) as a pale yellow solid after column chromatography on silica (eluent: pentane–ethyl acetate (4 : 1)) and washing with pentane (50 cm^3), mp (ethyl acetate) 179 °C. R_f = 0.3; δ_B 32.0; δ_H 7.55–7.68 (4 H, m), 7.95 (2 H, s, O*H*), 8.15–8.17 (2 H, m), 8.50–8.52 (2 H, m); δ_C 123.58, 127.06, 128.93, 129.11, 131.38, 131.64, 135.65; MS (EI): *m*/*z* (%): 300 (8)[$M^{+\bullet}$], 282 (6), 256 (100), 208 (11), 176 (54), 151 (22), 128 (16), 88 (37), 75 (13), 63 (3), 43 (3); IR (KBr) in cm^{-1}: 3298, 1954, 1928, 1620, 1546, 1483, 1413, 1298, 1261, 1149, 1036, 947, 883, 828, 753, 655, 618; UV/Vis $\lambda_{max.}$ (log ε) = 246 (4.14), 338 (3.45), 355 (3.73), 374 (3.87), 395 (3.85); calc. for $C_{14}H_{10}BBrO_2$: C 55.87, H 3.35, found: C 56.11, H 3.19. HRMS calc. 298.99771, found: 298.99710.

9-Anthracenylboronic acid dimethyl ester (11a). Recrystallization of dry **10a** (5.2 g, 23.42 mmol) from sparse $MeOH_{abs.}$ under argon gave **11a** (3.26 g, 56%) as pale yellow needles, mp (MeOH) 81 °C. R_f 0.35; δ_B 32.3; δ_H 3.61 (6 H, s, O-CH_3), 7.43–7.53 (4 H, m), 7.86–7.89 (2 H, m), 7.99–8.08 (2 H, m), 8.52 (1 H, s); δ_C 52.70, 126.09, 126.59, 128.08, 128.91, 129.74, 132.15, 134.32; MS (EI): *m*/*z* (%): 250 (100)[$M^{+\bullet}$], 234 (4), 219 (5), 204 (41), 192 (78), 178 (52), 165 (6), 151 (9), 139 (2), 126 (3), 88 (4), 73 (11), 43 (5); IR (KBr) in cm^{-1}: 3301, 2950, 2871, 1622, 1473, 1452, 1415, 1414, 1329, 1266, 1165, 1049, 1003, 888, 839, 736, 663; UV/Vis $\lambda_{max.}$ (log ε) = 245 (3.83), 315 (3.13), 329 (3.40), 346 (3.58), 364 (3.64), 382 (3.61); calc. for $C_{16}H_{15}BO_2$: C 76.84, H 6.05, found: C 76.69, H 5.88. HRMS calc. 250.11798, found: 250.11733. Hydrolysis and recrystallization of **11a** in hydrochloric acid (1000 cm^3, 0.5 M) for 2 h at 100 °C gave **10a** as pale yellow needles of higher purity.

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