THE STRUCTURAL BASIS FOR HYDROLYSIS RESISTANCE IN THE ESTERS OF (2-FORMYLPHENYL)BORONIC ACID 2,4-DINITROPHENYLHYDRAZONES

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday.

Under conditions that typically afford bicyclic boron heterocycles directly, (2-formylphenyl)boronic acids react with 2,4-dinitrophenylhydrazine in ethanol to give highly water-resistant diethyl boronate esters. Two such 2,4-dinitrophenylhydrazones were prepared and their X-ray crystal structures determined. Contrary to a previous suggestion that their unusual stability is due to an intramolecular N→B coordination giving a six-membered BN_2C_3 ring system based on a (*Z*)-hydrazone, these compounds instead were found to be (*E*)-hydrazones internally stabilized by a weak intramolecular interaction between nitrogen and boron from within a five-membered ring. Further study revealed that the electron deficiency of the starting hydrazine reagent plays a key role in determining the structure of the hydrazone isolated, and that the water-resistant boronate esters can be hydrolyzed under forcing conditions to the boronic acids.

Keywords: Boron; Boraheterocycles; Heterocycles; Hydrazones; Cyclizations; Crystal structure determination; Steroid analogues; Estrogen mimics.

The arylboronic acids popularly used in the Suzuki cross-coupling reactions[1] are stable to hydrolysis, but their boronate esters in general are not. Considering the mechanistic aspects of phenylboronate ester hydrolysis[2], the interaction of a nucleophilic *ortho*-substituent with an arylboronate ester could retard the rate of this reaction, but it would be highly unusual if

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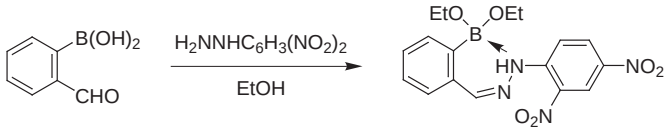
such an interaction actually rendered the boronate ester effectively stable to an aqueous environment. In this regard, the esters of certain hydrazone derivatives of (2-formylphenyl)boronic acid are exceptional, since they resist hydrolysis so strongly that they often can be recrystallized from water. To offer a structural explanation for the hydrolytic stability of the diethyl ester of (2-formylphenyl)boronic acid 2,4-dinitrophenylhydrazone, Tschampel and Snyder[3] proposed an intramolecular chelation of the hydrazone NH to the boronate ester from within a (*Z*)-hydrazone isomer (Scheme 1), giving a six-membered BN_2C_3 ring system in which the boronate ester is protected from hydrolysis.



SCHEME 1

We recently have been exploring the scope of 2,3,1-benzodiazaborine ring formation[4] in arylhydrazones derived from (2-formylphenyl)boronic acids to develop new bioactive boron heterocycles[5,6] as estrogen structural mimics (Chart 1)[7]. In our experience, condensation of (2-formylphenyl)-boronic acids with hydrazines in ethanol most often directly affords the desired bicyclic boron heterocycles, 2,3,1-benzodiazaborines[8], but we have encountered some hydrolysis-resistant diethyl boronate ester products clearly related to that described by Tschampel and Snyder. Therefore, we decided it would be useful and informative to use X-ray crystallography to investigate the structural basis for the unusual hydrolysis resistance exhibited by these compounds.

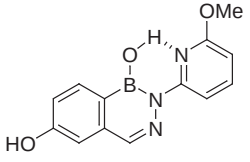
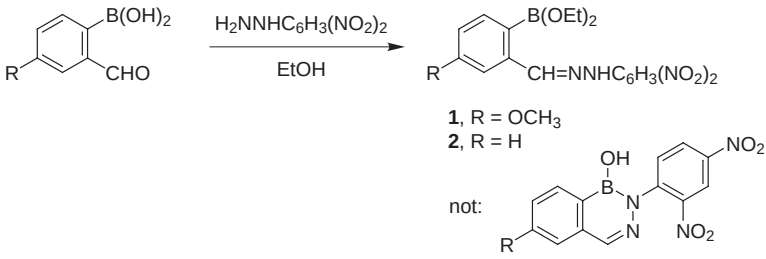


CHART 1

RESULTS AND DISCUSSION

(2-Formyl-4-methoxyphenyl)boronic acid was condensed with 2,4-dinitrophenylhydrazine in ethanol in the open on a steam bath (Scheme 2), and the orange crystals that deposited upon cooling were collected and recrystallized repeatedly from absolute EtOH until an X-ray quality crystal of at least marginally acceptable size could be obtained. Rather than a

2-aryl-2,3,1-benzodiazaborine product, X-ray crystallography revealed the compound to be a diethyl boronate ester (**1**) of (2-formyl-4-methoxyphenyl)-boronic acid 2,4-dinitrophenylhydrazone with some unexpected structural features (Fig. 1).



SCHEME 2

Although its diethyl boronate group is orthogonal to the plane of the benzene ring exactly as Tschampel and Snyder had anticipated, **1** is an (*E*)- rather than a (*Z*)-hydrazone rotational isomer, and the intramolecular interaction between the nitrogen and boron occurs from within a five-membered ring. The hydrazone fragment is oriented with its N8 imine electron lone pair directed toward the boron atom. The intramolecular B1–N8 distance (2.750(7) Å) is 0.43 Å less than the sum[10] (3.18 Å) of the B and N packing radii, revealing an electrostatic interaction between these atoms.

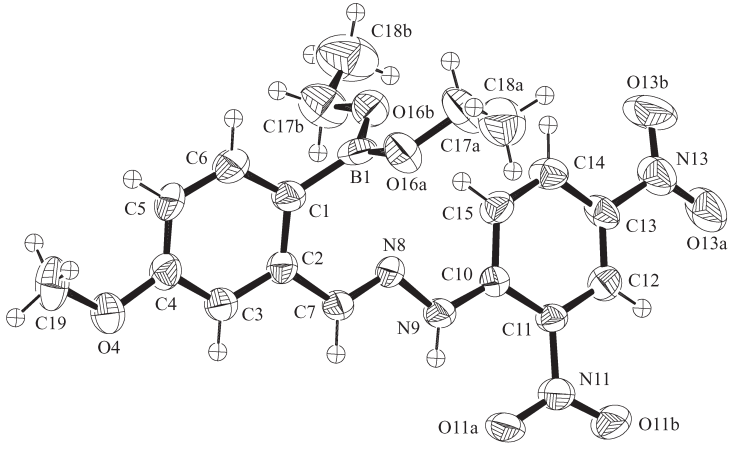


FIG. 1

Structure of compound **1** determined by X-ray crystallography. ORTEP[9] diagram (30% probability ellipsoids) showing the crystallographic atom numbering scheme and solid-state conformation; small spheres represent hydrogen atoms

Upon careful inspection of its position with respect to the plane defined by C1, O16a, and O16b, the boron atom is seen to be displaced towards N8 by 0.049(9) Å. This crystallographically confirmed weak interaction between N8 and B1 is likely responsible for the exceptional hydrolytic stability of **1**. It is strikingly similar to the transannular nitrogen–carbonyl interactions which take place in difunctional medium rings[11].

The orthogonal relationship of the diethyl boronate and benzene ring fragments in **1** is reminiscent of that reported for the solid state structure of (2-nitro-4-carboxyphenyl)boronic acid[12]. It is somewhat surprising to find this orientation in **1**, though, because the boron's empty p-orbital is orthogonal to, and thus does not interact with the symmetry-adapted lone pair orbital on the methoxy group O4. Still, a lack of conjugative interaction between O4 and the boron atom does help to explain why the C1–B1 length in **1** (1.569(7) Å) is so close to that in Tschampel and Snyder's original boronate ester **2** (1.580(8) Å), which we also obtained as X-ray-quality crystals.

The crystal structure of **2** shown in Fig. 2 reveals an intramolecular B1–N8 distance (2.721(10) Å) very close to that found in **1** – this time 0.46 Å less than the sum of the B and N packing radii. Selected bond lengths and angles for **1** and **2** are collected in Tables I and II, respectively. The important

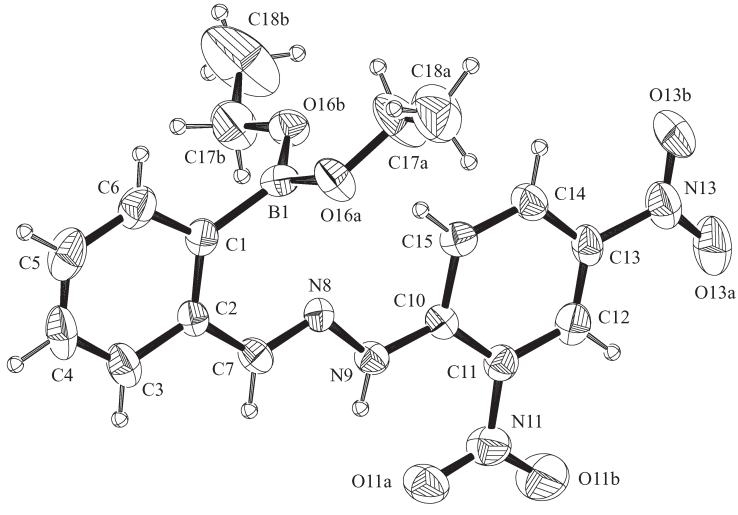


FIG. 2
Structure of compound **2** determined by X-ray crystallography. ORTEP[9] diagram (30% probability ellipsoids) showing the crystallographic atom numbering scheme and solid-state conformation; small spheres represent hydrogen atoms

TABLE I
Selected bond lengths (in Å) and angles (in °) for compound **1**

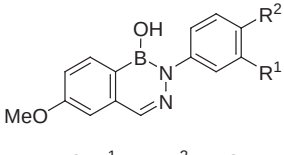
C1–C2	1.413(6)	C1–B1	1.569(7)
C2–C7	1.454(6)	N8–C7	1.279(5)
N8–N9	1.384(5)	N9–C10	1.365(6)
O16a–B1	1.364(7)	O16a–C17a	1.416(6)
O16b–B1	1.332(6)	O16b–C17b	1.412(6)
O4–C4	1.377(5)	O4–C19	1.428(5)
O16b–B1–O16a	118.9(5)	O16b–B1–C1	124.4(5)
O16a–B1–C1	116.3(5)	B1–O16a–C17a	122.7(4)
B1–O16b–C17b	119.4(5)	C7–N8–N9	115.2(4)
C10–N9–N8	119.2(4)	C2–C1–B1	124.7(4)
C1–C2–C7	122.2(5)	N8–C7–C2	120.1(5)
C4–O4–C19	117.4(4)		
C2–C1–B1–O16b	97.4(7)	C2–C1–B1–O16a	–89.0(6)
C7–N8–N9–C10	176.2(4)	B1–C1–C2–C7	–5.3(8)
N9–N8–C7–C2	–179.3(4)	C3–C2–C7–N8	168.3(5)
C1–C2–C7–N8	–12.8(7)	C19–O4–C4–C3	173.7(4)

TABLE II
Selected bond lengths (in Å) and angles (in °) for compound **2**

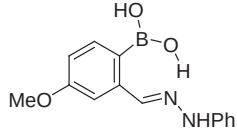
C1–C2	1.407(7)	C1–B1	1.580(8)
C2–C7	1.458(7)	N8–C7	1.282(6)
N8–N9	1.371(5)	N9–C10	1.357(6)
O16a–B1	1.331(7)	O16a–C17a	1.430(7)
O16b–B1	1.359(7)	O16b–C17b	1.439(7)
O16a–B1–O16b	119.3(6)	O16a–B1–C1	116.1(6)
O16b–B1–C1	124.2(6)	B1–O16a–C17a	120.2(5)
B1–O16b–C17b	123.6(5)	C7–N8–N9	114.6(5)
C10–N9–N8	120.2(5)	C2–C1–B1	125.1(5)
C1–C2–C7	121.5(5)	N8–C7–C2	121.1(5)
C2–C1–B1–O16a	–96.1(7)	C2–C1–B1–O16b	90.9(7)
C7–N8–N9–C10	–179.0(5)	B1–C1–C2–C7	–4.3(8)
N9–N8–C7–C2	–179.3(4)	C3–C2–C7–N8	176.6(5)
C1–C2–C7–N8	–2.9(7)		

bond lengths of C1–B1, C2–C7, C7–N8, and N9–C10 are quite close in the two compounds, and that of N8–N9 is only slightly different, at best. A big difference between **1** and **2** is seen in the interplanar angle between the two aromatic rings. In **2**, this angle is quite small at 1.5(3)°, while in **1** it is much larger at 20.7(2)°. This is related to the torsion angles in **1** of 168.3(5)° for C3–C2–C7–N8 and 174.0(4)° for N8–N9–C10–C11. The corresponding torsion angles in **2** are 176.6(5) and 177.6 (5)°. Thus, while the entire C and N framework of **2** is reasonably planar, **1** displays a distinctive twisting about the two σ bonds connecting the benzene rings to the central hydrazone unit. An explanation for this twisting is not apparent, but it may involve crystalline packing forces.

By ^{1}H NMR, the solution structures of **1** and **2** are identical to those determined by X-ray in the solid state. The failure of these 2,4-dinitrophenylhydrazones to close directly to 2,3,1-benzodiazaborines suggested to us that there might be a continuum of products whose structures are determined by the electron-withdrawing properties of the phenylhydrazine reagent employed. To explore this, we prepared the 4-nitrophenyl-, 3-nitrophenyl-, and phenylhydrazones of (2-formyl-4-methoxyphenyl)boronic acid (**3**–**5**, respectively; Chart 2) under conditions identical to those which gave **1** and **2**.



3, R^1 = H, R^2 = NO_2
4, R^1 = NO_2, R^2 = H

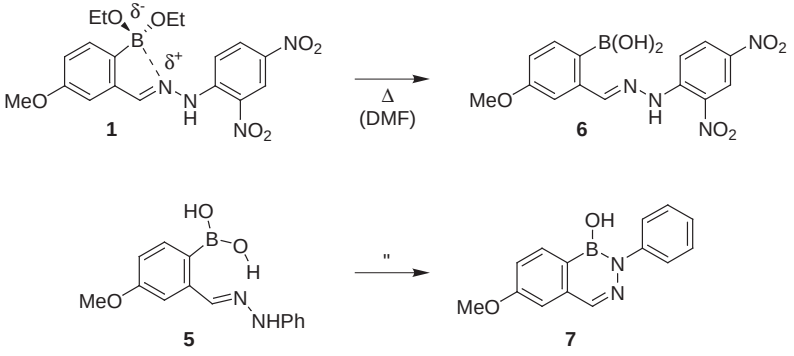


5

CHART 2

Although none of the three new adducts could be obtained as X-ray quality crystals, their structures were readily established from their ^{1}H NMR spectral data. The mononitrophenylhydrazone products **3** and **4** indeed turned out to be 2,3,1-benzodiazaborines – *i.e.*, these reactions had proceeded *via* the typically observed spontaneous boronate ester hydrolysis and dehydrative ring closure. Curiously, though, the phenylhydrazone **5** had undergone the boronate hydrolysis but not the dehydrative ring closure. In the ^{1}H NMR spectrum of **5** in DMSO-d_6, each of the boronic acid OH resonances appears as a discrete signal (δ 9.78 and 9.36 ppm), strongly suggesting that the more downfield shifted one donates an intramolecular hydrogen bond to hydrazone =N atom. This type of seven-membered ring hydrogen bond association has a direct precedent in the solid state structure of (2-formylphenyl)boronic acid *O*-methyl oxime[13].

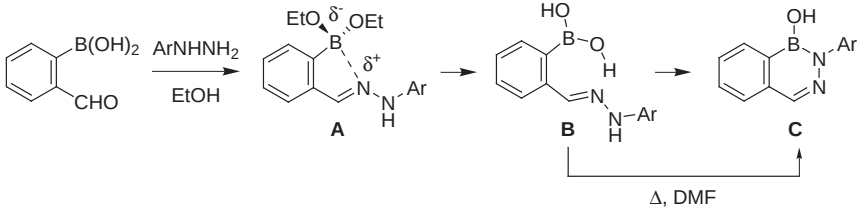
We developed conditions that promote the loss of ethanol from the stable boronate esters. Simply heating **1** briefly in DMF solution (90 °C, 15 min) liberated ethanol and gave a precipitate that was characterized as {4-methoxy-2-[(2,4-dinitrophenylhydrazono)methyl]phenyl}boronic acid (**6**) (Scheme 3). Efforts to cyclize this to the benzodiazaborine with prolonged heating were unsuccessful, but boronic acid **5** did smoothly form its corresponding benzodiazaborine, 2-phenyl-1-hydroxy-4-methoxy-1,2-dihydro-2,3,1-benzodiazaborin-1-ol (**7**), upon heating for a short time in DMF.



SCHEME 3

CONCLUSIONS

There does indeed appear to be a product continuum in these condensation reactions (**A**–C, Scheme 4) that is related to the electron-withdrawing property of the starting phenylhydrazine. With extremely electron-deficient reagents like 2,4-dinitrophenylhydrazine, the reaction stops at the diethyl boronate stage (**A**), where a five-membered ring intramolecular N→B chelate serves to protect the boronate ester from subsequent hydrolysis. With less electron-deficient hydrazines, the reaction proceeds further to the corresponding internally hydrogen-bonded boronic acid (**B**) or furthest to the intramolecular dehydration product, the 2,3,1-benzodiazaborine boron heterocycle (C).



SCHEME 4

The reason why the use of the unsubstituted phenylhydrazine would lead to a type **B** product whereas the use of a mononitrophenylhydrazine would give a type C one is not entirely clear, but this may simply reflect the solubility properties of the specific species produced. Importantly, though, some compounds of structural type **B** can be readily converted to the corresponding bicyclic boron heterocycle (C) simply upon heating in a polar aprotic solvent like DMF. Thus, the range of new bioactive boron heterocycles we are developing as estrogen structural mimics has been expanded.

EXPERIMENTAL

Diethyl {2-[(2,4-Dinitrophenylhydrazono)methyl]-4-methoxyphenyl}boronate (**1**)

This boronate ester was obtained by warming a solution of 2,4-dinitrophenylhydrazine (191 mg, 0.97 mmol) in 20 ml of EtOH on a steam bath and then dissolving solid (2-formyl-4-methoxyphenyl)boronic acid (173 mg, 0.96 mmol; Frontier Scientific, Inc.). Crystal formation began within minutes, and the mixture was allowed to cool to 23 °C and kept overnight. The orange crystals were collected by suction, washed with a minimum amount of absolute ethanol, and air-dried to give 379 mg (91%) of **1** as orange needles; m.p. 175–177 °C with re-solidification, and then m.p. 240 °C (dec.) (EtOH). The X-ray-quality crystals were grown from absolute ethanol under argon *via* repetitive slow evaporation. ^{1}H NMR ($CDCl_3$): 11.3 (bs, 1 H); 9.15 (s, 1 H, CH=N); 8.39 (d, *J* = 9.3, 1 H, ArH); 8.14 (d, *J* = 9.3, 1 H, ArH); 8.13 (s, 1 H, ArH); 7.37 (d, *J* = 8.0, 1 H, ArH); 7.06 (s, 1 H, ArH); 7.00 (d, *J* = 8.1, 1 H, ArH); 3.86 (s, 3 H, OCH_3); 3.85 (q, *J* = 7.1, 4 H, 2 × C**H**$_2$CH$_3$); 1.18 (t, *J* = 7.1, 6 H, 2 × CH$_2$C**H**$_3$). Low-resolution APCI (atmospheric pressure chemical ionization) mass spectrum: 416.8 (MH^+, 7.5%), 371.0 (M – EtO^-, 100%). For $C_{18}H_{21}BN_4O_7$ (416.2) calculated: 51.95% C, 4.94% H, 13.46% N; found: 51.90% C, 4.94% H, 13.58% N.

Diethyl {2-[(2,4-Dinitrophenylhydrazono)methyl]phenyl}boronate (**2**)

In a similar fashion, this compound, originally reported by Tschampel and Snyder[3], was obtained in 93% yield as orange needles; m.p. 223 °C (EtOH) (ref.[3] 249–250 °C). ^{1}H NMR ($CDCl_3$): 11.4 (bs, 1 H); 9.14 (s, 1 H, CH=N); 8.39 (d, 1 H, ArH); 8.17 (s, 1 H, ArH); 8.15 (d, 2 H, ArH); 7.46 (m, 4 H, ArH); 3.85 (q, *J* = 7.1, 4 H, 2 × C**H**$_2$CH$_3$); 1.18 (t, *J* = 7.1, 6 H, 2 × CH$_2$C**H**$_3$). Low-resolution APCI mass spectrum: 386.7 (MH^+, 15%), 341.0 (M – EtO^-, 100%). For $C_{17}H_{19}BN_4O_6$ (386.2) calculated: 52.87% C, 4.96% H, 14.51% N; found: 52.03% C, 4.62% H, 14.93% N. X-Ray-quality crystals of **2** were grown *via* slow evaporation of an absolute ethanol solution under argon. Similar to the conversion of **1** to **6** described below, heating a DMF solution of **2** on a steam bath for 15 min liberated the ethanol, but it did not promote diazaborine ring formation.

6-Methoxy-2-(4-nitrophenyl)-1,2-dihydro-2,3,1-benzodiazaborin-1-ol (**3**) and
6-Methoxy-2-(3-nitrophenyl)-1,2-dihydro-2,3,1-benzodiazaborin-1-ol (**4**)

The 4- and 3-nitrophenylhydrazones of (2-formyl-4-methoxyphenyl)boronic acid were prepared on a 1 mmol scale by condensing the aldehyde with 4-nitrophenylhydrazine or

3-nitrophenylhydrazine hydrochloride in 20 ml of EtOH, first on a steam bath, then at 23 °C, and then at 4 °C overnight. In this way, **3** was obtained in 88% yield as an orange powder, and **4** was obtained in 77% yield as a pale yellow microcrystalline solid. Immediate analysis by ^{1}H NMR revealed that diethyl boronate ester hydrolysis already had occurred to a large extent in both materials. After pumping dry at 23 °C overnight, ^{1}H NMR and elemental microanalysis revealed them to be the ring-closed 2,3,1-benzodiazaborine compounds.

Compound **3**: m.p. > 275 °C. ^{1}H NMR ($(CD_3)_2SO$): 9.46 (bs, 1 H, OH); 8.35 (d, *J* = 8.4, 1 H, H-4); 8.29 (d, *J* = 9.3, 2 H, ArH); 8.25 (s, 1 H, H-4); 8.00 (d, *J* = 9.4, 2 H, ArH); 7.38 (d, *J* = 2.4, 1 H, ArH); 7.29 (dd, *J* = 8.4, 2.4, 1 H, ArH); 3.91 (s, 3 H, OCH_3). Low-resolution APCI mass spectrum: 326.1 (MH^+ + EtOH – H_2O, 100%), 298.1 (MH^+, 46%). For $C_{14}H_{12}BN_3O_4$ (297.1) calculated: 56.60% C, 4.07% H, 14.14% N; found: 56.73% C, 4.15% H, 13.93% N.

Compound **4**: m.p. 162 °C (partial only). ^{1}H NMR ($(CD_3)_2SO$): 9.36 (bs, 1 H, OH); 8.57 (t, *J* = 2.1, 1 H, H-4); 8.36 (d, *J* = 8.5, 1 H, ArH); 8.23 (s, 1 H, H-4); 8.17 (m, 1 H, ArH); 8.07 (m, 1 H, ArH); 7.70 (t, *J* = 8.2, 1 H, ArH); 7.37 (d, *J* = 2.4, 1 H, ArH); 7.29 (dd, *J* = 8.4, 2.4, 1 H, ArH); 3.91 (s, 3 H, OCH_3). Low-resolution APCI mass spectrum: 326.1 (MH^+ + EtOH – H_2O, 100%), 298.1 (MH^+, 10%). For $C_{14}H_{12}BN_3O_4$ (297.1) calculated: 56.60% C, 4.07% H, 14.14% N; found: 56.06% C, 4.21% H, 13.92% N.

{4-Methoxy-2-[(phenylhydrazono)methyl]phenyl}boronic Acid (**5**) and 6-Methoxy-2-phenyl-1,2-dihydro-2,3,1-benzodiazaborin-1-ol (**7**)

Compound **5** was prepared on a 1 mmol scale by combining (2-formyl-4-methoxyphenyl)-boronic acid and phenylhydrazine hydrochloride in 20 ml of warm EtOH, and keeping the solution at 23 °C for several hours and then at 4 °C overnight. Because no product had deposited, the solution was reduced in volume to 10 ml on a rotary evaporator, at which point a small amount of solid appeared. The flask was then transferred to a steam bath and the volume reduced slightly before the solution was allowed to cool to 23 °C and then kept at 4 °C overnight. The supernatant was decanted and the solid washed with a minimum amount of Et_2O, giving 85 mg of **5**. The supernatant and wash were combined and diluted with additional Et_2O to 50 ml, whereupon more white solid precipitated. This was decanted, washed with Et_2O, and pumped dry to give 108 mg (for a total of 193 mg, 72% yield) of **5** as a white powder; m.p. 231–232 °C (dec.). ^{1}H NMR ($(CD_3)_2SO$): 11.9 (s, 1 H, NH); 9.78 (s, 1 H, OH); 9.36 (s, 1 H, OH); 8.58 (d, *J* = 7.7, 1 H, ArH); 7.95 (m, 2 H, ArH); 7.83 (s, 1 H, CH=N); 7.75 (m, 3 H, ArH); 7.67 (d, *J* = 7.7, 1 H, ArH); 3.94 (s, 3 H, OCH_3). These data indicate an open hydrazone in which one of the $B(OH)_2$ hydroxy groups is intermolecularly hydrogen-bonded to the hydrazone =N atom. Microanalytical data were consistent with a hydrate of this open phenylboronic acid hydrazone. For $C_{14}H_{15}BN_2O_3 \cdot H_2O$ (288.1) calculated: 58.360% C, 5.95% H, 9.72% N; found: 58.28% C, 5.09% H, 9.55% N.

Heating a DMF solution of **5** on a steam bath for 15 min liberated water and promoted diazaborine ring formation. 6-Methoxy-2-phenyl-1,2-dihydro-2,3,1-benzodiazaborin-1-ol (**7**) was obtained in a 91% yield; m.p. 141–144 °C (EtOH). ^{1}H NMR ($(CD_3)_2SO$): 8.82 (bs, 1 H, OH); 8.34 (d, *J* = 8.4, 1 H, ArH); 8.15 (s, 1 H, H-4); 7.58 (d, *J* = 7.5, 2 H, ArH); 7.41 (t, *J* = 7.7, 2 H, ArH); 7.33 (d, *J* = 2.7, 1 H, ArH); 7.24 (m, 2 H, ArH); 3.90 (s, 3 H, OCH_3). Low-resolution APCI mass spectrum: 487.3 (2 M – H_2O + H^+, 6%), 281.2 (MH^+ + EtOH – H_2O, 100%), 253.2 (MH^+, 26%).

{4-Methoxy-2-[(2,4-dinitrophenylhydrazono)methyl]phenyl}boronic Acid (**6**)

Liberation of EtOH from **1** was accomplished by heating its solution in DMF on a steam bath for 15 min, then diluting with Et_2O, and collecting the solid product by suction. The filtrate was diluted still further with Et_2O to give additional **6** as a $CHCl_3$-insoluble orange solid; m.p. > 260 °C. ^{1}H NMR ($(CD_3)_2SO$): 11.67 (s, 1 H, NH); 8.92 (s, 1 H, CH=N); 8.84 (d, *J* = 3.0, 1 H, 2,4-di-NO_2-ArH); 8.34 (dd, *J* = 9.9, 2.4, 1 H, 2,4-di-NO_2-ArH); 8.13 (m, 3 H, 2,4-di-NO_2-ArH + $B(OH)_2$); 7.51 (d, *J* = 8.4, 1 H, ArH); 7.38 (d, *J* = 2.7, 1 H, ArH); 7.00 (dd, *J* = 8.1, 2.7, 1 H, ArH); 3.83 (s, 3 H, OCH_3). For $C_{14}H_{13}BN_4O_7$ (360.1) calculated: 46.70% C, 3.64% H, 15.56% N; found: 47.07% C, 3.77% H, 15.60% N.

X-Ray Crystallography

Diffraction data (Table III) were collected on a Rigaku AFC5-S four-circle diffractometer using a fine-focus, sealed-tube source, a graphite incident beam monochromator and MoKα radiation (λ = 0.71069 Å). For both structures, cell parameters were refined from 25 carefully centered reflections. The data were reduced using the TEXSAN package[14]. Structure **1** was solved with SIR92 [15] and structure **2** was solved with SHELXS [16], both direct methods pro-

TABLE III
Crystallographic data for compounds **1** and **2**

Parameter	Compound **1**	Compound **2**
Formula	$C_{18}H_{21}BN_4O_7$	$C_{17}H_{19}BN_4O_6$
Molecular weight	416.20	386.17
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P1$
a, Å	9.443(2)	11.194(3)
b, Å	15.436(2)	12.225(4)
c, Å	13.982(3)	8.1853(14)
α, °	90	93.32(2)
β, °	104.802(19)	107.331(17)
γ, °	90	64.68(3)
Z	4	2
Crystal	orange plate	yellow plate
$R[F^2 > 2\sigma(F^2)]$	0.052 (1 102 reflns.)	0.049 (893 reflns.)
$wR(F^2)$ (all data)	0.193 (3 494 reflns.)	0.201 (3 402 reflns.)
Parameters	274	255
GOF	0.973	0.951

grams. The structures were refined by full-matrix least-squares on F^2 using SHELXL97 [17]. The rotational orientation of the methyl groups were refined by the circular Fourier method available in SHELXL97. All H atoms are riding. The less than desirable quality of the two refinements is primarily a result of crystal morphology, both crystals being much thinner than was adequate for our data collection setup. Multiple attempts to grow thicker crystals met with failure. Thus the percentage of observed reflections was relatively small.

CCDC 183969 (**1**) and CCDC 183970 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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