

Synthesis of (azidomethyl)phenylboronic acids

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The synthesis of 2-, 3-, and 4-(azidomethyl)phenylboronic acids was carried out. The geometric and electronic structures were studied by quantum-chemical methods. The suggestion is made that there are weak intramolecular interactions between the boron atom and the nitrene nitrogen atom of the azido group.

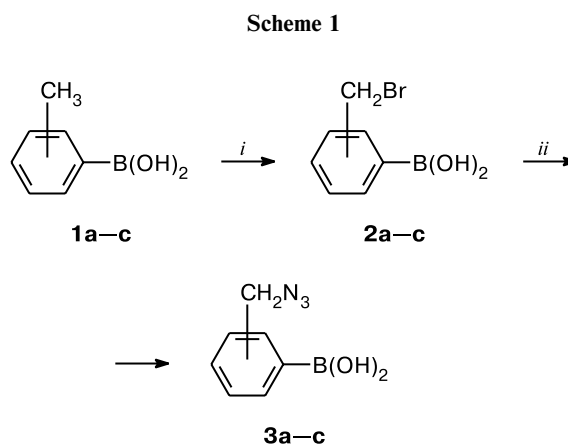
Key words: azidomethylphenylboronic acids, synthesis, quantum-chemical calculations.

Boronic acids have found wide use in fine organic synthesis. For example, Suzuki cross-coupling involving arylboronic acids^{1–10} is one of the most convenient and ecologically safe methods^{11,12} for the construction of new C–C bonds. In the presence of copper salts as catalysts, arylboronic acids serve as efficient *O*-,^{13,14} *N*-,¹⁵ and *S*-arylation reagents.¹⁶ Mild synthesis conditions, high regioselectivity of these processes, the possibility of performing arylation of optically active substrates without epimerization, and high yields of *N*-, *O*-, and *S*-arylation products favorably distinguish the reactions with arylboronic acids from the classical Ullmann reaction.¹⁷

In the present study, we synthesized previously unknown arylboronic acids containing the 2-, 3-, or 4-azidomethylphenyl groups and investigated their structures and the electron density distribution. Organic azides are extensively used for performing various chemical transformations.^{18,19} Hence, arylboronic acids, which allow one to insert the benzylazide fragments into organic substrates to form new C–C, C–N, C–O, and C–S bonds, are of considerable interest.

Radical bromination of known *ortho*-, *meta*-, and *para*-tolylboronic acids using NBS as a brominating agent afforded 2-, 3-, and 4-(bromomethyl)phenylboronic acids **2a–c** as polycrystalline products in 58, 37, and 39% yields, respectively. In the next step, (azidomethyl)phenylboronic acids **3a–c** were prepared in 46, 48, and

49% yields, respectively, as viscous oils by the reactions of (bromomethyl)phenylboronic acids with NaN₃ in dry DMF. Acids **3a–c** were obtained as solvates with DMF.



Reagents and conditions: *i*. NBS, (BzO)₂; *ii*. NaN₃, DMF.

All the derivatives synthesized were identified by ¹H, ¹³C, and ¹¹B NMR, IR, and UV spectroscopy as well as by elemental analysis. It should be noted that in the ¹H and ¹³C NMR spectra of some bromo- and azido-substituted derivatives, the protons of the methylene groups and aromatic rings and the corresponding carbon atoms appear as several signals with insignificantly different chemical shifts (the differences are 0.02–0.40 and 0.10–1.3 ppm for the ¹H and ¹³C NMR spectra, re-

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spectively). For example, in the ^1H NMR spectrum of 2-(bromomethyl)phenylboronic acid in CDCl_3 , the signals of the protons of the methylene group appear as three singlets at δ 4.75, 5.09, and 5.15 with the intensity ratio of 3 : 3 : 14. The relative intensities of the signals characteristic of the protons of the methylene groups as well as the number of these signals depend substantially on the concentration of the samples under study and the solvents used (CDCl_3 , acetone- d_6 , or $\text{DMSO}-d_6$). For instance, the ^1H NMR spectra of 2-(bromomethyl)phenylboronic acid in acetone- d_6 have one singlet at δ 5.00 belonging to the protons of the methylene group. In the spectra recorded in $\text{DMSO}-d_6$, the signals of the protons of the methylene group appear as two singlets at δ 4.93 and 5.00 with the intensity ratio of 9 : 1. It should be noted that the chemical shifts observed in the ^1H and ^{13}C NMR spectra belong to the methylene groups in the (monobromomethyl)phenyl and (monoazidomethyl)phenyl fragments. The presence of several signals in the ^1H and ^{13}C NMR spectra cannot be attributed to the fact that the reaction can afford not only the desired isomeric (monobromomethyl)phenylboronic acids **2a–c** but also their (dibromomethyl)phenyl analogs.²⁰ The dependence of the intensity ratio for these signals and the chemical shifts in the ^1H NMR spectra on the concentration of the samples under study as well as on the nature of the solvents used indicates that anhydrides of boronic acids with different degrees of oligomerization can exist along with monomeric forms of these derivatives ($\text{ArB}(\text{OH})_2$) in solutions of substituted arylboronic acids. The conclusions about the existence of oligomeric forms of boronic acids and the absence of by-products in the compounds isolated are supported by the results published earlier.²¹

It should be noted that (azidomethyl)phenylboronic acids were synthesized as solvates with DMF molecules. According to the ^1H NMR spectroscopic data for compound **3a–c**, there are two molecules of arylboronic acid per DMF molecule. It is also noteworthy that the signals for the protons of the $\text{C}(\text{O})\text{H}$ groups of the DMF molecules involved in complex formation with compounds **3a–c** are observed at higher field (δ 5.93, 5.86, and 5.77, respectively) compared to the standard chemical shift for this fragment of the DMF molecule in CDCl_3 (δ 8.02).²² This is indicative of the occurrence of rather strong donor-acceptor interactions between the molecules of arylboronic acids and DMF.²³ An insignificant difference in the ^{11}B chemical shifts of the singlets belonging to (azidomethyl)phenylboronic acids **3a–c** and the corresponding (bromomethyl)phenylboronic acids **2a–c** as well as broadening of these signals do not allow one to unambiguously assign these interactions to either hydrogen bonds or $\text{O}\rightarrow\text{B}$ coordination bonds.

Attempts to remove the solvent molecules from (azidomethyl)phenylboronic acids by repeated extraction of organic solutions of derivatives **3a–c** with water, repeated

precipitation with hexane from solutions in Et_2O , CH_2Cl_2 , or CHCl_3 , or careful heating under reduced pressure failed. Attempts to use azidating agents (LiN_3 in THF, $\text{Me}_3\text{SiN}_3\text{—SnCl}_4$, $\text{Me}_3\text{SiN}_3\text{—ZnI}_2$, $\text{Me}_3\text{SiN}_3\text{—ZnBr}_2$, or $\text{CH}_3\text{C}(\text{O})\text{N}_3$), which enable one to insert azido groups into organic substrates in solutions in other organic solvents (THF, Et_2O , CH_2Cl_2 , or CHCl_3),¹⁹ which are less prone to complex formation, were unsuccessful.

(Azidomethyl)phenylboronic acids prepared in the present study are of interest not merely from the synthetic standpoint. The $\text{N}\rightarrow\text{B}$ donor-acceptor interactions in arylboronic acids containing the electron-donating nitrogen atoms at the methyl group at position 2 of the aromatic fragment made it possible to create a new generation of selective fluorescence sensors for carbohydrates.^{24–26} In this connection, it was of interest to examine the possibility of coordination of the azido group to the boron atom in 2-(azidomethyl)phenylboronic acid and study the characteristics of the azido group in the organoboron compounds synthesized. To solve this problem, we used UV spectroscopy and quantum-chemical methods.

The absorption spectra of 2-(azidomethyl)phenylboronic acid **3a** in different solvents are shown in Fig. 1. The positions of the maxima in these spectra depend only slightly on the solvent used. The absorption of the azide chromophore at 296 nm depends on the polarity of the solvent in a complex way. Apparently, unlike the carbonyl and amino groups, the azido fragment cannot be efficiently coordinated at the boron atom. This fact is not surprising because the boron atom is already involved in complex formation with DMF. However, the possibility of coordination in the absence of DMF is still an open question.

Quantum-chemical calculations of the geometric and electronic structures of the organoboron compounds synthesized in the present study gave an estimate of this possibility. We carried out calculations using the density functional theory^{27–29} with the B3LYP hybrid functional^{30–32} and the 6-31G(d) basis set (B3LYP/6-31G(d))

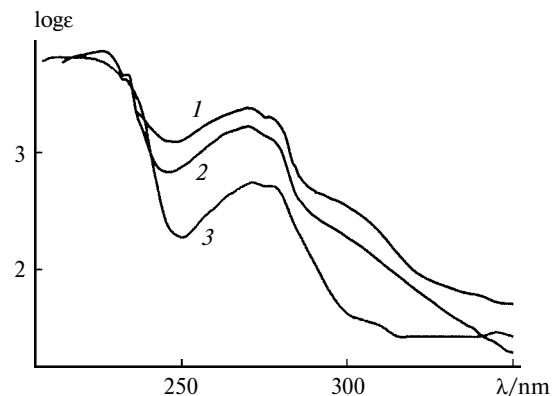


Fig. 1. Electronic spectra of 2-(azidomethyl)phenylboronic acid **3a** in different solvents: 1, CH_2Cl_2 ; 2, EtOH ; 3, hexane.

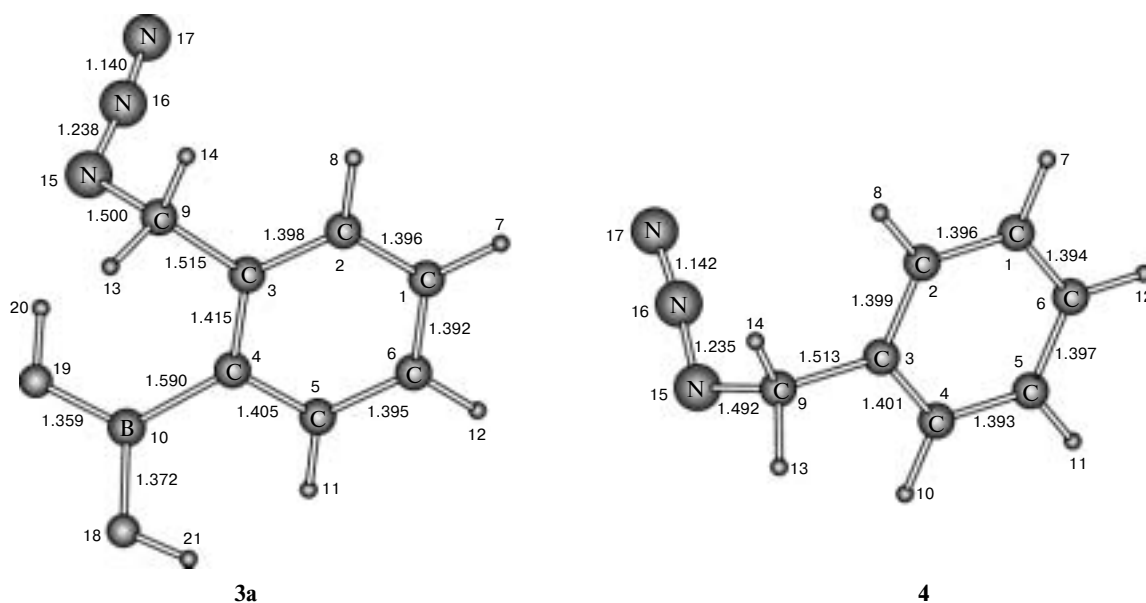


Fig. 2. Equilibrium geometric parameters of 2-(azidomethyl)phenylboronic acid **3a** and benzylazide **4** according to the results of quantum-chemical calculations by the B3LYP/6-31G(d) method.

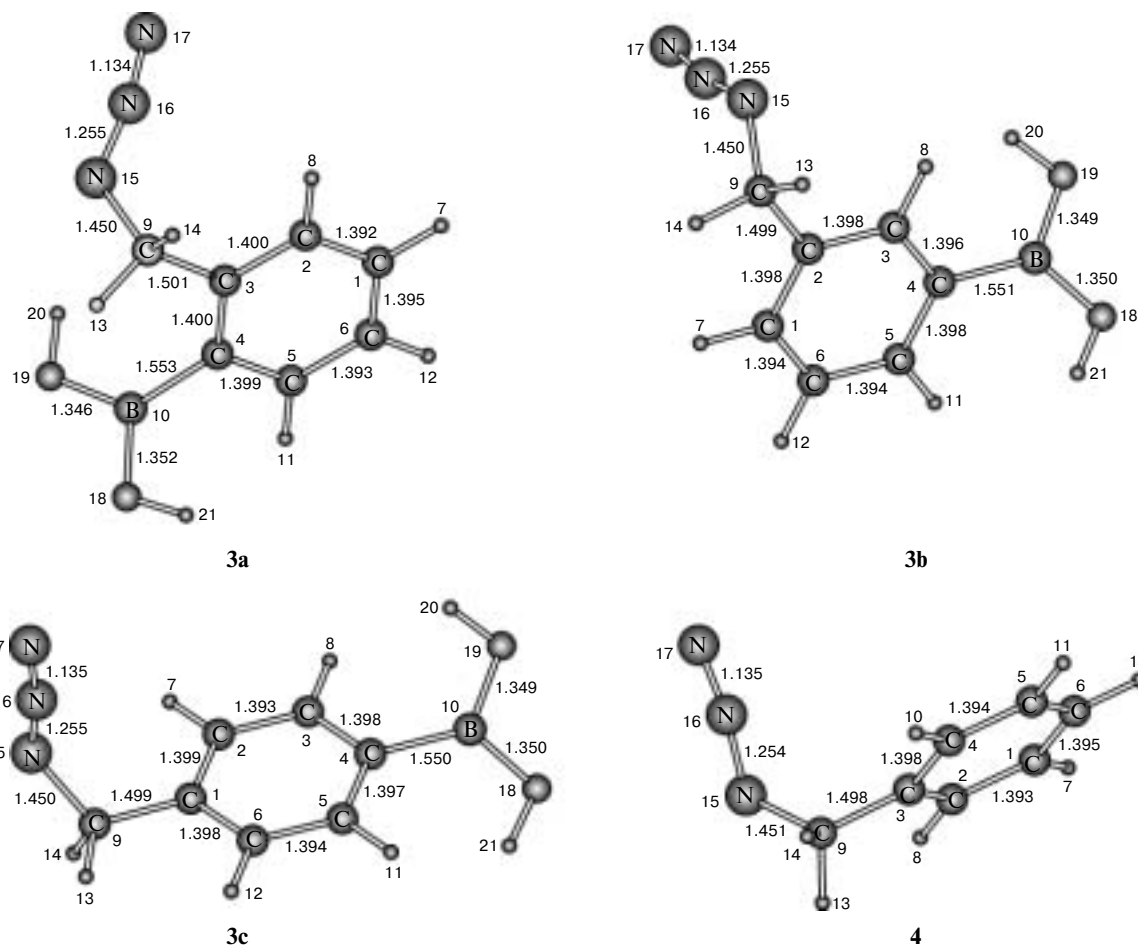


Fig. 3. Equilibrium geometric parameters of 2-, 3-, and 4-(azidomethyl)phenylboronic acids **3a-c** and benzylazide **4** according to the results of quantum-chemical calculations by the AM1 method.

Table 1. Comparison of the energies of the corresponding MOs for 2-(azidomethyl)phenylboronic acid **3a** and benzylazide **4**

MO ^a	ε/a.u. ^b		MO ^a	ε/a.u. ^b	
	3a	4		3a	4
-11	-0.41800	-0.46271	+1	-0.04973	-0.02955
-10	-0.39003	-0.44312	+2	-0.03272	-0.01081
-9	-0.38048	-0.42806	+3	-0.01966	-0.00727
-8	-0.36793	-0.42249	+4	-0.00349	+0.01497
-7	-0.36519	-0.40897	+5	+0.07270	+0.08800
-6	-0.35734	-0.36946	+6	+0.07777	+0.11382
-5	-0.32239	-0.35849	+7	+0.09183	+0.12368
-4	-0.30798	-0.34964	+8	+0.11042	+0.14541
-3	-0.30403	-0.30096	+9	+0.12664	+0.15039
-2	-0.27530	-0.26146	+10	+0.13807	+0.15939
-1	-0.26503	-0.25780	+11	+0.14553	+0.17757
0	-0.25886	-0.24693			

^a The numbering starts with the highest occupied molecular orbital (numbered 0); the negative numbers correspond to the occupied MOs; the positive numbers correspond to the virtual MOs.

^b The energy is expressed in atomic units (1 a.u. = 2625 kJ mol⁻¹).

as well as by the semiempirical AM1 method.³³ The structures of compound **3a** and benzylazide **4**, which were optimized at the B3LYP/6-31G(d) level of theory, are presented in Fig. 2. It appeared that the results obtained by the semiempirical AM1 method are in rather good agreement with those obtained by the B3LYP/6-31G(d) method. The geometric structures of compounds **3a**, **3b**, **3c**, and **4** calculated by the AM1 method are shown in Fig. 3.

The geometric parameters of the corresponding fragments in compounds **3a** and **4** have close values. The distance between the nitrene (N(15)) nitrogen atom (see Fig. 2) and the nearest hydrogen atom in the residue of boronic acid (0.1965 nm) is favorable for hydrogen bonding because it is smaller than the sum of the van der Waals radii of the hydrogen and nitrogen atoms. Although the distance between the nitrogen (N(15)) and the boron atoms (0.3392 nm) is larger than the sum of the van der Waals radii of these atoms (0.322 nm), the possibility of a weak donor-acceptor interaction is not ruled out. The energy levels in azides **3a** and **4** are given in Table 1. The

Table 2. Electron density distribution in 2-azidomethylphenylboronic acid **3a** and benzylazide **4**

3a		4	
Atom	Atomic charge*	Atom	Atomic charge*
C(1)	-0.129583	C(1)	-0.125372
C(2)	-0.169245	C(2)	-0.180997
C(3)	+0.091189	C(3)	+0.161466
C(4)	+0.009110	C(4)	-0.166365
C(5)	-0.222649	C(5)	-0.127988
C(6)	-0.111503	C(6)	-0.126673
H(7)	+0.139874	H(7)	+0.135695
H(8)	+0.131598	H(8)	+0.130766
C(9)	-0.256747	C(9)	-0.241161
B(10)	+0.384770	H(10)	+0.137907
H(11)	+0.128239	H(11)	+0.135782
H(12)	+0.138001	H(12)	+0.135082
H(13)	+0.196240	H(13)	+0.179307
H(14)	+0.170793	H(14)	+0.163966
N(15)	-0.409588	N(15)	-0.364637
N(16)	+0.440290	N(16)	+0.418706
N(17)	-0.243026	N(17)	-0.265484
O(18)	-0.552856		
O(19)	-0.568089		
H(20)	+0.433838		
H(21)	+0.399344		

* The charges are expressed in electron charge units.

theoretical bathochromic shift of the long-wavelength absorption maximum in the spectra of boron-containing azide **3a** compared to that of benzylazide is 8.3 nm. Earlier, the bathochromic shift has been observed experimentally.^{25,34}

The fact of formation of a weak donor-acceptor N(15)→B bond is supported by a slight increase (by 0.0009 electron charge units) of the sum of the charges of the nitrogen atoms in the azido group of compound **3a** compared to that of azide **4** (Table 2).

As can be seen from the above-described results of calculations, the geometric parameters of the azido group in the benzylazide fragment remain unchanged upon the insertion of boron-containing fragments at positions 2-, 3-, or 4 of the benzene ring (Table 3). The changes in the energy of orbitals upon the above replacements are

Table 3. Bond lengths (*d*), bond angles (*ω*), and atomic charges (*Z*) in the azido fragment of 2-, 3-, and 4-(azidomethyl)phenylboronic acids **3a–c** and benzylazide **4** (calculations by the AM1 method)

Compound	<i>d</i> /nm		ω/deg N(15)–N(16)–N(17)	<i>Z</i> /a.u.		
	N(15)–N(16)	N(16)–N(17)		N(15)	N(16)	N(17)
3a	0.126	0.113	169.0	-0.283	0.217	-0.053
3b	0.125	0.114	169.2	-0.285	0.218	-0.052
3c	0.126	0.114	169.0	-0.287	0.219	-0.050
4	0.125	0.114	169.1	-0.286	0.221	-0.057

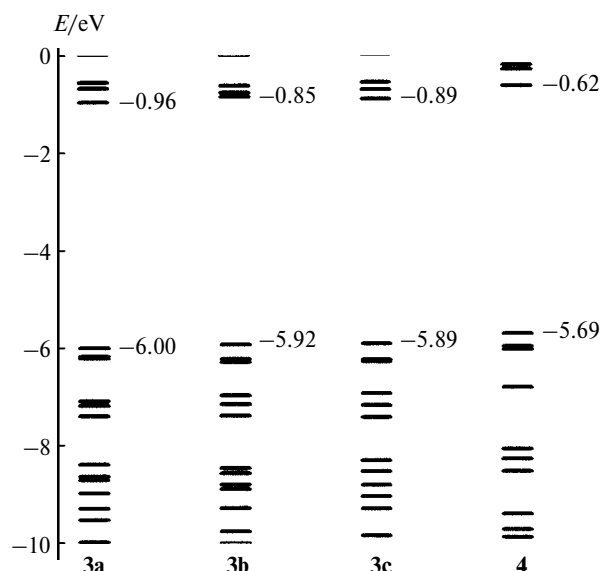


Fig. 4. Electronic levels in 2-, 3-, and 4-(azidomethyl)phenylboronic acids **3a–c** and benzylazide **4** according to the results of quantum-chemical calculations by the B3LYP/6-31G(d)//AM1 method.

shown in Fig. 4. A decrease in the energy compared to the corresponding values in benzylazide is associated with the acceptor nature of the B(OH)₂ fragment.

Experimental

The ¹H and ¹³C NMR spectra were recorded on a Bruker AC-200P spectrometer; the chemical shifts are given in the δ scale relative to Me₄Si. The ¹¹B NMR spectra were measured on a Bruker AC-200P instrument; the chemical shifts are given in the δ scale relative to BF₃·OEt₂. The IR spectra were recorded on a Specord 75-IR spectrometer. The UV spectra were measured on a SF-46 spectrometer.

Methylphenylboronic acids **1a–c** were prepared according to known procedures.^{35,36}

Synthesis of (bromomethyl)phenylboronic acids 2a–c (general procedure). A mixture of methylphenylboronic acid **2a–c** (0.50 g, 3.68 mmol), NBS (0.69 g, 3.90 mmol), and (BzO)₂ (0.09 g, 0.39 mmol) in CCl₄ (30 mL) was refluxed for 2 h under irradiation with an incandescent lamp (300 W). Then the reaction mixture was cooled to 40 °C and twice filtered through a porous glass filter. The solvent was distilled off under reduced pressure. The reaction product was washed with cold Et₂O (7 mL) and recrystallized from a CH₂Cl₂–Et₂O–hexane mixture.

2-(Bromomethyl)phenylboronic acid 2a. Compound **2a** was prepared in a yield of 0.46 g (58%) as a white powder, m.p. 138 °C (CH₂Cl₂–Et₂O–hexane) (*cf.* lit. data³⁷: m.p. 139–146 °C). ¹H NMR (CDCl₃), δ: 4.75, 5.09, and 5.15 (all s, intensity ratio 3 : 3 : 14, 2 H, CH₂Br); 7.28–7.54 (m, 3 H, H(3), H(4), H(5)); 8.38 (d, 1 H, H(6), *J* = 8.1 Hz). ¹³C NMR (CDCl₃), δ: 33.7, 35.3 (CH₂Br); 128.2, 128.3, 130.6, 130.9, 132.7, 132.9, 137.7, 138.0 (C(3), C(4), C(5), C(6)); 145.4 (C(2)). ¹¹B NMR (CDCl₃), δ: 33.0.

3-(Bromomethyl)phenylboronic acid 2b. Compound **2b** was prepared in a yield of 0.29 g (37%) as a white powder, m.p. 217 °C (CH₂Cl₂–Et₂O–hexane) (*cf.* lit. data³⁸: m.p. 214–216 °C). ¹H NMR (CDCl₃), δ: 4.53 and 4.63 (both s, intensity ratio 3 : 5, 2 H, CH₂Br); 7.36–8.22 (m, 4 H, Ar–H). ¹³C NMR (CDCl₃), δ: 33.3, 33.5 (CH₂); 128.7 (C(5)); 131.9 (C(3)); 135.5; 135.8, 137.6 (C(2), C(4), C(6)). ¹¹B NMR (CDCl₃), δ: 28.4.

4-(Bromomethyl)phenylboronic acid 2c. Compound **2c** was prepared in a yield of 0.31 g (39%) as a white powder, m.p. 151 °C (CH₂Cl₂–Et₂O–hexane) (*cf.* lit. data³⁷: m.p. 138–144 °C). ¹H NMR (CDCl₃), δ: 4.55 (s, 2 H, CH₂); 7.50 (d, 2 H, H(3), H(5), *J* = 7.9 Hz); 8.12 (d, 2 H, H(2), H(6), *J* = 7.9 Hz). ¹³C NMR (CDCl₃), δ: 33.6 (CH₂); 129.2 (C(3)), (C(5)); 136.7 (C(2)), (C(6)); 142.9 (C(4)).

Synthesis of azidomethylphenylboronic acids 3a–c (general procedure). (Bromomethyl)phenylboronic acid **2a–c** (0.16 g, 0.74 mmol) was dissolved in dry DMF (5 mL) and then NaN₃ (0.14 g, 2.2 mmol) was added. The reaction was carried out at 20 °C with vigorous stirring for 14 h. Then CHCl₃ (30 mL) was added to the reaction mixture. The organic layer was washed with water (5×20 mL) and dried over anhydrous Na₂SO₄. Volatile products were distilled off under reduced pressure. The reaction product was precipitated with hexane from a solution in CHCl₃.

2-(Azidomethyl)phenylboronic acid (3a). Solvate **3a**·0.5 DMF was obtained in a yield of 0.07 g (46%) as a viscous oil. Found (%): C, 47.98; H, 5.04; N, 23.31. C₁₇H₂₃B₂N₇O₅. Calculated (%): C, 47.81; H, 5.43; N, 22.96. UV (EtOH), λ/nm (log ϵ): 226 (3.868), 262 (3.159), 270 (3.229), 278 (3.096). ¹H NMR (CDCl₃), δ: 2.98 and 3.02 (both s, 3 H each, Me); 4.48 and 4.88 (both s, intensity ratio 2 : 9, 4 H, CH₂); 5.93 (s, 1 H, CHO); 7.27–7.68 (m, 6 H, H(3), H(4), H(5)); 8.09–8.24 (m, 2 H, H(6)). ¹³C NMR (CDCl₃), δ: 32.8, 37.9 (Me); 51.2 (CH₂); 128.0; 129.8; 132.4; 136.7 (C(3), C(4), C(5), C(6)); 141.4 (C(2)); 163.6 (C=O). ¹¹B NMR (CDCl₃), δ: 28.9. IR (Nujol mulls), ν/cm⁻¹: 2080 (N₃).

3-(Azidomethyl)phenylboronic acid (3b). Solvate **3b**·0.5 DMF was obtained in a yield of 0.077 g (48%) as a viscous oil. Found (%): C, 48.09; H, 4.98; N, 23.31. C₁₇H₂₃B₂N₇O₅. Calculated (%): C, 47.81; H, 5.43; N, 22.96. UV (EtOH), λ/nm (log ϵ): 225 (3.197), 264 (2.693), 270 (2.751), 277 (2.680). ¹H NMR (CDCl₃), δ: 2.89 and 2.96 (both s, 3 H each, Me); 4.46 (br.s, 4 H, CH₂); 5.86 (s, 1 H, CHO); 7.51–8.19 (m, 8 H, Ar–H). ¹³C NMR (CDCl₃), δ: 32.8 (Me); 36.9 (Me); 54.8 (CH₂); 128.5 (C(5)); 132.1 (C(3)); 135.0, 135.1, 137.4 (C(2), C(4), C(6)); 162.9 (C=O). ¹¹B NMR (CDCl₃), δ: 27.4. IR (Nujol mulls), ν/cm⁻¹: 2070 (N₃).

4-(Azidomethyl)phenylboronic acid (3c). Solvate **3c**·0.5 DMF was obtained in a yield of 0.075 g (49%) as a viscous oil. Found (%): C, 48.06; H, 5.01, N, 23.38. C₁₇H₂₃B₂N₇O₅. Calculated (%): C, 47.81; H, 5.43; N, 22.96. UV (EtOH), λ/nm (log ϵ): 232 (3.457), 264 (3.018), 269 (3.019), 276 (2.950). ¹H NMR (CDCl₃), δ: 2.88 and 2.95 (both s, 3 H each, Me); 4.37 (s, 4 H, CH₂); 5.77 (s, 1 H, HCO); 7.31–7.46 (m, 4 H, H(3), H(5)); 8.11–8.24 (m, 4 H, H(2), H(6)). ¹³C NMR (CDCl₃), δ: 32.7 (Me); 36.8 (Me); 54.7 (CH₂); 127.6 (C(3)), (C(5)); 136.1 (C(2)), (C-6); 139.9 (C(4)), 163.1 (C=O). IR (Nujol mulls), ν/cm⁻¹: 2070 (N₃).

Quantum-chemical calculations. The DFT and semiempirical calculations were carried out using the GAMESS program.³⁹

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 01-03-33113 and 02-03-33021), the Competition Center for Basic Natural Science (PD02-1.3-443), and INTAS (Grant YSF 2002-122).

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Received November 1, 2002;
in revised form July 1, 2003