Synthesis, Characterization, and Antibacterial Activity of Structurally Complex 2-Acylated 2,3,1-Benzodiazaborines and Related Compounds

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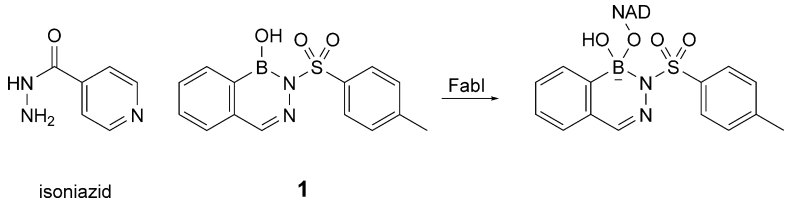
A set of 2-acylated 2,3,1-benzodiazaborines and some related boron heterocycles were synthesized, characterized, and tested for antibacterial activity against *Escherichia coli* and *Mycobacterium smegmatis*. By high-field solution NMR, the heretofore unknown class of 2-acyl-1-hydroxy-2,3,1-diazaborines has been found to be able to exist in several interconvertable structural forms along a continuum comprised of an open hydrazone **a**, a monomeric *B*-hydroxy diazaborine **b**, and an anhydro dimer **c**. X-Ray crystallography of one of the anhydro dimers, **17c**, revealed it to have an unprecedented structure featuring a double intramolecular O → B chelation. The crystal structure of another compound, **37**, showed it to be based on a new pentacyclic B heterocycle framework. Nine compounds were found to possess activities against *E. coli*, and two others were active against *M. smegmatis*. The finding that these two contain isoniazid covalently embedded in their structures suggests that they might possibly be acting as prodrugs of this well-known antituberculosis agent *in vivo*.

Introduction. – Although there are several drugs available to treat tuberculosis, the *Mycobacterium tuberculosis* organism responsible for this disease is adept at acquiring resistance. Additional drugs are needed to combat emergent organisms that are resistant to at least isoniazid (= isonictinylhydrazine) and rifampin, thereby causing multidrug-resistant tuberculosis (MDR TB) [1]. After 60 years, isoniazid (INH) is still one of the most effective anti-TB drugs used today. It is now well-known to interfere with fatty acid metabolism by inhibiting the mycobacterial FabI homolog (InhA) of enoyl-ACP reductase (ENR), an NAD-dependent redox enzyme responsible for catalyzing a late step in fatty acid biosynthesis. Lesser known is the fact that sulfonylated benzo- and other ring-fused 2,3,1-diazaborine heterocycles also possess antibacterial properties, particularly against *Gram*-negative organisms [2]. Early studies had indicated that these compounds affected lipopolysaccharide biosynthesis [3]. Subsequent structural studies [4] established that their biomacromolecular target is in fact the same ENR enzyme inhibited by the *in vivo* activated form of the prodrug INH. In these studies, diazaborine inhibitors of ENR like the sulfonylated boron

heterocycle **1** were shown to form a covalent B–O bond with the OH group at C(2′) of the NAD cofactor's ribose unit (*Scheme 1*). In turn, this borate-based bisubstrate analog species is bound tightly yet noncovalently at the active site of ENR. Interestingly, FabI is also the biomacromolecular target of the commonly used broad-spectrum (bacteria, fungi, viruses) bacteriostatic germicide triclosan [5].

Scheme 1



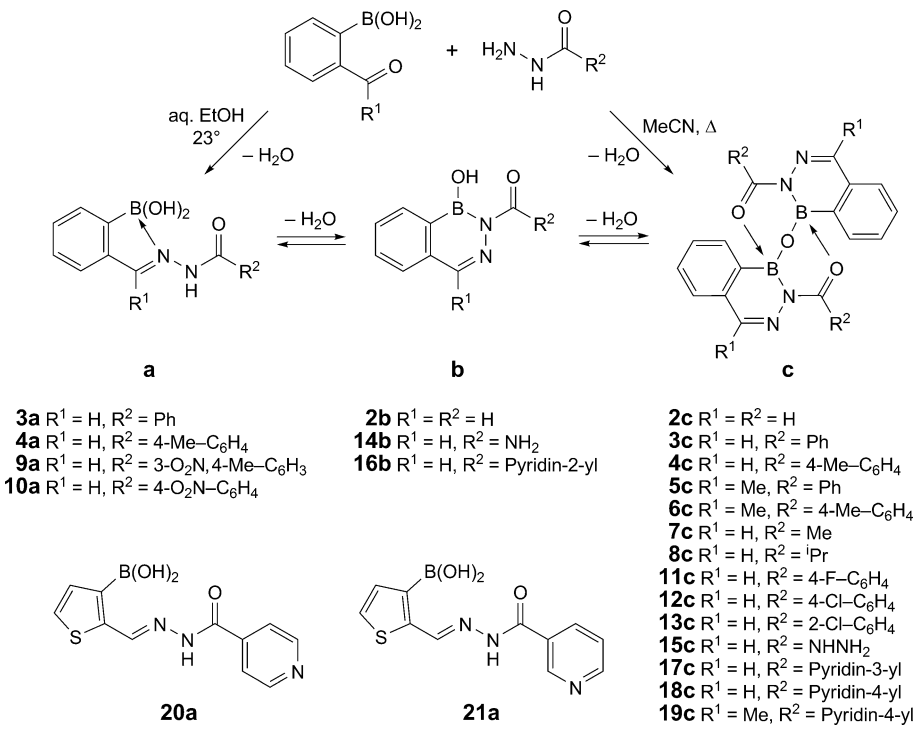
isoniazid **1**

Promising results had once been reported for a handful of benzodiazaborines prepared and tested against *M. tuberculosis* [6]. To follow up on this lead, we decided to explore the possibility that replacing the sulfonyl moiety in **1** with an acyl group would lead to a retention of antibacterial activity *via* FabI inhibition in some members of the relatively unexplored class of 2-acylated 2,3,1-diazaborines. Motivated by the continuing interest in fatty acid biosynthetic targets, particularly FabI [7], for developing new antibacterial agents [8], and by the attraction of developing B-based therapeutics in general [9], we synthesized, characterized, and tested several new acylated diazaborines. Further encouraged by the reported antimalarial activity of thiosemicarbazones [10], and especially by the antifungal activity of B heterocycle-forming ones [11], we also included in our investigation these types of compounds and others with a structural basis for possible antibacterial activity.

Results and Discussion. – *2-Acylated 1-Hydroxy-2,3,1-benzodiazaborines.* Results from the preparation of the simplest compound illustrate how the isolated structural form depended on the conditions of synthesis for many of the 2-acylated diazaborine compounds prepared. When 2-formylbenzeneboronic acid and formic acid hydrazide were condensed in H_2O or aqueous EtOH at room temperature (*Scheme 2*), the first-formed open hydrazone species **a** apparently underwent rapid intramolecular cyclization to produce monomer **2b**, isolated in 83% yield. The structure of **2b** was readily determined by its ^{1}H-NMR spectrum, which revealed seven signals – one of which (from the OH) exchanged upon addition of D_2O. Monomer forms like **b** were the most commonly encountered ones in our previous studies of 2-alkyl-1-hydroxy-2,3,1-benzodiazaborines [12]. By contrast, the same condensation conducted in MeCN at reflux (82°), followed by azeotropic removal of H_2O by distillation, gave not **2b** but its B–O–B anhydro dimer, **2c**, in 57% yield. The proclivity of 1-hydroxy-2,3,1-benzodiazaborines for undergoing dehydrative dimerization was first observed in the parent heterocycle some 50 years ago [13]. The ^{1}H-NMR spectrum of **2c** in $CDCl_3$ contained only six signals – none of which exchanged upon addition of D_2O. Interestingly, its ^{1}H-NMR spectrum in (D_6)DMSO revealed that **2c** had immediately undergone hydrolysis to **2b** by reacting with the propitious moisture in this NMR solvent. Based on

spectral data as well as the X-ray crystal structure determined of another compound (**17c**, *vide infra*), we now know that anhydro dimers like **2c** are stabilized by intramolecular chelation of the C=O O-atoms to the B-centers. We had once encountered a 2-formylbenzeneboronic acid hydrazone which formed a tridehydro trimer (a boroxine) with two intramolecular chelations [14]. Notably, chelation to form a borate mimics the trapping of the NAD HO–C(2′) group within FabI by the antibacterial boron heterocycle **1** [4b], and highlights the electrophilic character of the B-center in many of our compounds.

Scheme 2



3a R^1 = H, R^2 = Ph
4a R^1 = H, R^2 = 4-Me–C_6H_4
9a R^1 = H, R^2 = 3-O_2N,4-Me–C_6H_3
10a R^1 = H, R^2 = 4-O_2N–C_6H_4

2b R^1 = R^2 = H
14b R^1 = H, R^2 = NH_2
16b R^1 = H, R^2 = Pyridin-2-yl

2c R^1 = R^2 = H
3c R^1 = H, R^2 = Ph
4c R^1 = H, R^2 = 4-Me–C_6H_4
5c R^1 = Me, R^2 = Ph
6c R^1 = Me, R^2 = 4-Me–C_6H_4
7c R^1 = H, R^2 = Me
8c R^1 = H, R^2 = ^{i}Pr
11c R^1 = H, R^2 = 4-F–C_6H_4
12c R^1 = H, R^2 = 4-Cl–C_6H_4
13c R^1 = H, R^2 = 2-Cl–C_6H_4
15c R^1 = H, R^2 = $NHNH_2$
17c R^1 = H, R^2 = Pyridin-3-yl
18c R^1 = H, R^2 = Pyridin-4-yl
19c R^1 = Me, R^2 = Pyridin-4-yl

20a

21a

Further 2-acylated 2,3,1-diazaborines were prepared by condensation of 2-formyl- or 2-acetylbenzeneboronic acid with commercially available or readily prepared acyl hydrazides. Depending on the substitution pattern or conditions of synthesis, products were isolated in open **a**, monomer **b**, or anhydro dimer **c** form (*Scheme 2*). Although exceptions were encountered, preparation in 50% aqueous EtOH at ambient temperature typically favored the open **a** form, while those in anhydrous EtOH or MeCN at reflux, followed by azeotropic removal of H_2O by distillation, favored anhydro dimer form **c**. In aqueous EtOH at 23°, 2-formylbenzeneboronic acid condensed with benzoic acid hydrazide and 4-toluic acid hydrazide to give open forms **3a** and **4a**, respectively. These forms are likely intramolecularly N→B chelated as the 2-formylbenzeneboronic acid 2,4-dinitrophenylhydrazones we studied previously [15]. When the same condensations were conducted in refluxing EtOH (78°) or MeCN (82°), however, the

anhydro dimers **3c** and **4c**, respectively, were produced instead, *via* the intermediacy of their monomer **b** forms. Besides reaction conditions, the structural forms of the compounds obtained were also found to depend on the substitution pattern of the starting materials. With the slightly more electron-rich 2-acetylbenzeneboronic acid, benzoic acid hydrazide and 4-toluic acid hydrazide condensed to form only anhydro dimers **5c** and **6c**, respectively, even in aqueous EtOH at ambient temperature. Similarly, simple alkanoic acid hydrazides such as acetic and isobutyric acid hydrazides condensed with 2-formylbenzeneboronic acid to form anhydro dimers **7c** and **8c** exclusively. Nitro-substituted benzoic acid hydrazide reagents, on the other hand, gave only open forms **9a** and **10a**, but halogeno-substituted ones led only to anhydro dimers **11c**–**13c**.

^{1}H-NMR Spectroscopy was particularly useful in determining the various solution structures. The open forms **a** exhibited an extremely downfield-shifted, D_2O-exchangeable NH signal at δ(H) 12 and a 2-H D_2O-exchangeable *singlet* for $B(OH)_2$ at 8.5. Monomer forms **b** exhibited a sharp 1-H D_2O-exchangeable OH *singlet*, almost always at δ(H) 8.5–9.5. Anhydro dimer forms **c** displayed no D_2O-exchangeable peaks in their NMR spectrum. In addition, it was noted that their C=O stretching frequency had shifted to a lower wavenumber in the FT-IR spectrum compared to that of open forms **a**. Related by the removal or addition of H_2O, forms **a** – **c** sometimes readily interconverted simply by choice of NMR solvent. Loss (or gain) of H_2O was observed to be facile more often in (D_6)DMSO than in $CDCl_3$.

2-Formylbenzeneboronic acid condensed with semicarbazide to give B heterocycle **14b** displaying a structural sensitivity to solvents like **2b**. Heterocycle **14b** existed as a monomer in $CDCl_3$ but formed an anhydro dimer (**14c**; not shown) in (D_6)DMSO. In a 1:1 ratio with carbohydrazide, 2-formylbenzeneboronic acid condensed to form anhydro dimer **15c**. Using picolinic, nicotinic, and isonicotinic acid hydrazides as reagents, 2-formylbenzeneboronic acid furnished **16b**, **17c**, and **18c**. The ^{1}H-NMR data of **16b** indicated that this picolinic acid-based heterocycle must have an unusual structure, as its OH *singlet* resonance was uniquely found at a much higher than normal field (δ(H) 4.12), and it exchanged with D_2O only very slowly[1]). Benzo-fused nicotinic and isonicotinic **17c**–**19c** were formed as anhydro dimers, but the thiophene-fused versions **20a** and **21a** were obtained only in open form, even when prepared in MeCN at 82°, possibly because of the different substituent bond vector angles off of a thiophene ring.

Crystal Structure of **17c**. The structure of anhydro dimer **17c** was solved by single-crystal X-ray diffraction using a crystal grown *via* slow evaporation from anhydrous MeCN (*Fig. 1* and *Table 1*). The molecule has a crystallographic center of inversion. Its structure is unprecedented, but a molecule with the same central core has been reported previously [16]. For steric reasons, the nicotinyl C=O groups have chelated from opposite sides of the B–O–B linkage plane, producing a doubly chelated molecule

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[1]) *Note added in proof:* After this article was submitted, the crystal structure of **16b** was determined, revealing a zwitterion produced by the intramolecular addition of the picolinyl N-atom to the B-atom acting as a *Lewis* acid. Besides explaining the slow D_2O exchange of the OH in the ^{1}H-NMR spectrum, we note that this structure resembles that of diazaborine **1**, while inhibiting ENR. Details will be published elsewhere.

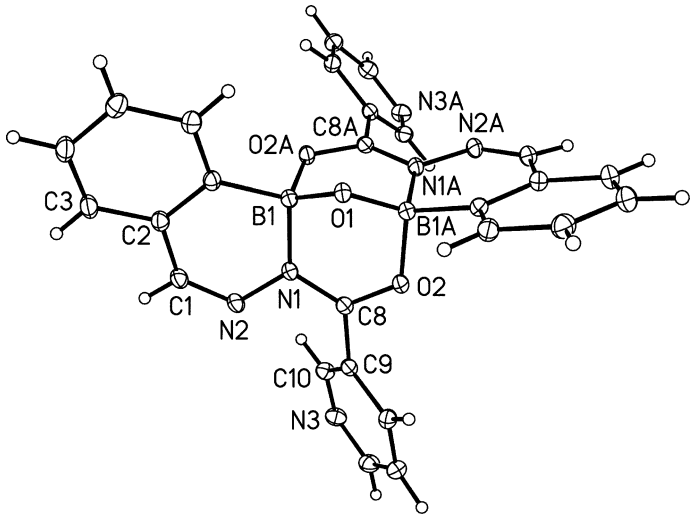


Fig. 1. *Molecular structure of* **17c** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: O(1)–B(1), 1.4173(10); O(2)–C(8), 1.2969(9); N(1)–C(8), 1.3201(10); N(1)–N(2), 1.4105(9); N(1)–B(1), 1.5960(11); N(2)–C(1), 1.2884(11); C(1)–C(2), 1.4620(12); C(7)–B(1), 1.5871(12); B(1)–O(2A), 1.5722(11); C(8)–C(9), 1.4862(11); B(1A)–O(1)–B(1), 111.62(9); C(8)–O(2)–B(1A), 121.03(6); C(8)–N(1)–N(2), 114.21(7); C(8)–N(1)–B(1), 119.98(7); N(2)–N(1)–B(1), 125.72(6); C(1)–N(2)–N(1), 115.69(7); N(2)–C(1)–C(2), 128.26(8); C(7)–C(2)–C(1), 120.02(7); C(2)–C(7)–B(1), 119.16(7); O(2)–C(8)–N(1), 121.28(7).

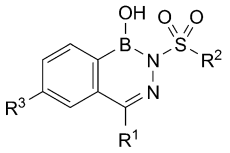
which is axially chiral and propeller-like in shape. Pairs of enantiomers are contained in the unit cell. The nicotinyl C=O bond length of 1.2969(9) Å in **17c** is significantly longer than that in nicotinamide (1.22 Å) [17], indicating a lowering of bond order due to the chelation. The B-atoms are tetrahedrally substituted, and the O–B chelate bond length of 1.5722(11) Å is longer than the O–B bond of 1.4173(10) Å in the boronic anhydride linkage, but close to the N–B bond length of 1.5960(11) Å and the C–B bond length of 1.5871(12) Å. The nicotinyl amide C–N bond length of 1.3201(10) Å is only slightly shorter than that in nicotinamide (1.34 Å) [17], but the amide C–C bond length of 1.4862(11) Å is longer than that in the same reference (1.42 Å). As expected, based on the presence of an sp^3-hybridized B-atom, the diazaborine ring is much more distorted from planarity than the benzene ring. Compound **17c** can be viewed as a double zwitterion with the nicotinyl N–C=O fragments delocalizing the positive charges which counterbalance the negative borate anionic charges. The double chelation in **17c** resembles that found in the triphenylboroxin of the 1,1-dimethylhydrazone of 2-formylbenzeneboronic acid [14].

Compounds from Sulfonyl Hydrazides and Thiosemicarbazides. To obtain reference compounds for potential bioactivity in our acylated B heterocycles, a set of sulfonylated ones was prepared. Members of this class of compounds are much more straightforward to characterize, and they have well-documented antibacterial properties [2e]. Besides the benchmark heterocycle **1**, **22**–**32** were synthesized. Without exception, these were obtained as monomeric 1-hydroxy-2,3,1-diazaborines exhibiting

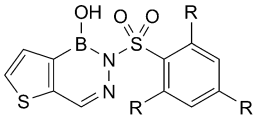
Table 1. *Crystallographic Data of* **17c** *and* **37**

	17c	**37**
Empirical formula	$C_{26}H_{18}B_2N_6O_3$	$C_{15}H_{10}B_2N_4O_2$
M_r	484.08	299.89
Crystal color and habit	colorless, parallelepiped	colorless, block
Crystal size [mm]	$0.50\times0.23\times0.20$	$0.50\times0.35\times0.26$
Diffractometer	*Bruker ApexII*	*Bruker ApexII*
Temp. [K]	90(2)	90(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
Z	4	8
Unit cell parameters:		
a [Å]	25.5569(11)	13.168(3)
b [Å]	5.7176(3)	13.741(3)
c [Å]	19.1584(9)	15.038(4)
β [°]	128.852(2)	102.980(3)
V [Å^3]	2180.17(18)	2651.5(11)
D_x (calc.) [g cm^{-3}]	1.475	1.502
Absorption coefficient [mm^{-1}]	0.099	0.101
F(000)	1000	1232
θ Range for data collection	2.73–30.03°	2.38–30.51°
Index ranges	$-35\le h\le35$, $-8\le k\le8$, $-26\le l\le26$	$-18\le h\le18$, $-17\le k\le19$, $-21\le l\le21$
Reflections collected	15880	15519
Independent reflections	3164 [$R_{int}=0.0131$]	4050 [$R_{int}=0.0133$]
Observed reflections ($I>2\sigma(I)$)	3001	3797
Completeness to $\theta=30.03°$ [%]	99.4	99.8
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.980; 0.952	0.746; 0.712
Solution method	SHELXS-97	SHELXS
Refinement method	SHELXL-97	SHELXL-2012
Data/restraints/parameters	3164/0/168	4050/0/209
Goodness-of-fit on F^2	1.055	1.057
Final *R* indices [$I>2\sigma(I)$]	$R^1=0.0358$, $wR^2=0.0998$	$R^1=0.0382$, $wR^2=0.1055$
R Indices (all data)	$R^1=0.0370$, $wR^2=0.1010$	$R^1=0.0397$, $wR^2=0.1075$
Largest diff. peak and hole [e Å^{-3}]	0.451; −0.224	0.483; −0.280

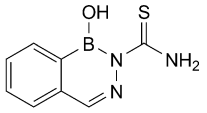
an OH resonance in the ^{1}H-NMR spectrum at δ(H) 7.3–7.4 in $CDCl_3$, and a narrow, medium-intensity OH stretching absorption in the FT-IR spectrum at 3500 cm^{-1}. A small set of thiosemicarbazones was also prepared. While the thiophene-derived **33a** and **34a** were obtained only in open **a** form, even from refluxing MeCN, the benzo-fused versions **35b** and **36b**, both first prepared and solved crystallographically as reported in [11], were obtained in monomer **b** form. None of the thiosemicarbazones formed anhydro dimers, possibly because their S-atoms do not chelate as well as an O-atom onto a B-center. Interestingly, monomer **36b** was found by ^{1}H-NMR to spontaneously hydrolyze to its open form (**36a**, not shown) when dissolved in (D_6)DMSO due to reaction with propitious H_2O in this solvent.



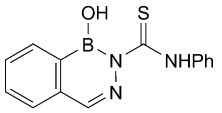
22 $R^1 = R^3 = H$, $R^2 = Ph$
23 $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}(Me)_3\text{–}C_6H_2$
24 $R^1 = H$, $R^2 = Ph$, $R^3 = MeO$
25 $R^1 = H$, $R^2 = 4\text{-}Me\text{–}C_6H_4$, $R^3 = MeO$
26 $R^1 = H$, $R^2 = 4\text{-}Me\text{–}C_6H_4$, $R^3 = OH$
27 $R^1 = H$, $R^2 = 2,4,6\text{-}(Me)_3\text{–}C_6H_2$, $R^3 = MeO$
28 $R^1 = Me$, $R^2 = Ph$, $R^3 = H$
29 $R^1 = Me$, $R^2 = 2,4,6\text{-}(Me)_3\text{–}C_6H_2$, $R^3 = H$
30 $R^1 = Me$, $R^2 = 4\text{-}Me\text{–}C_6H_4$, $R^3 = H$



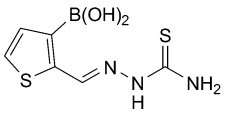
31 R = H
32 R = Me



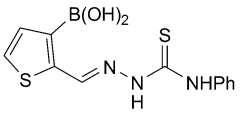
35b



36b



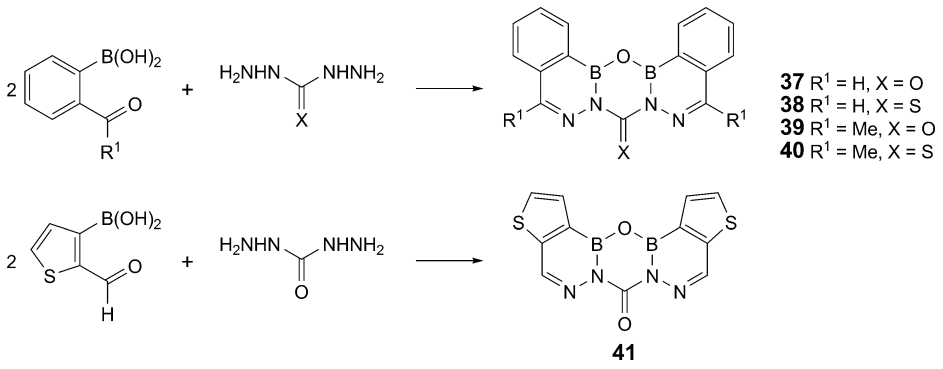
33a



34a

Pentacyclic Compounds from Carbohydrazides. Whereas, in a 1:1 ratio, 2-formylbenzeneboronic acid and carbohydrazide had condensed to form the anhydro dimer **15c**, in a 2:1 ratio, under dehydrating conditions they generated a new compound with a very simple ^{1}H-NMR spectrum exhibiting no D_2O-exchangeable resonances. This product was identified as the symmetric pentaheterocycle **37** by various analyses including X-ray crystallography (*Scheme 3*). Apparently, due to an extremely high effective concentration, the anhydro 'dimerization' of the two carbonyl-linked 1-hydroxy-2,3,1-benzodiazaborines to form the central 1,3,5,2,6-oxadiazadiborinane ring of **37** was facile and exclusive. Similar 2:1 condensations were used to obtain pentacyclic compounds **38**–**41**. Like **37**, these exhibited absorptions in the UV/VIS spectra at λ_{max} *ca.* 330–350 nm, diagnostic of their extended π-conjugated ring system. Interestingly, based on a C=O signal at δ(C) 150 in the ^{13}C-NMR spectrum and C=O stretching frequency at 1750 cm^{-1} in the FT-IR spectrum, B heterocycles **37**, **39**, and **41** appear to possess a rather ketone-like C=O group.

Scheme 3



37 $R^1 = H$, X = O
38 $R^1 = H$, X = S
39 $R^1 = Me$, X = O
40 $R^1 = Me$, X = S

41

Crystal Structure of **37**. The structure of the pentacyclic B heterocycle **37** was solved by single-crystal X-ray diffraction using a crystal grown from Et_2CO (*Fig. 2* and *Table 1*). Like **17c**, **37** has an unprecedented structure. A planar molecule with two

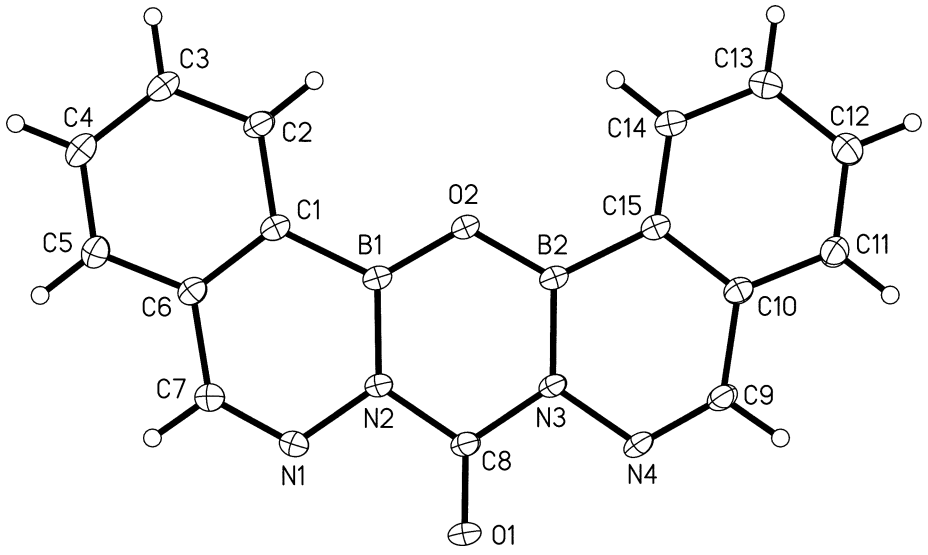
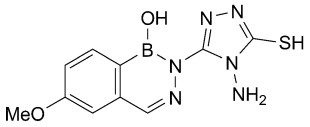


Fig. 2. *Molecular structure of* **37** (50% probability ellipsoids). Selected bond engths [Å] and angles [°]: O(1)–C(8), 1.2067(9); O(2)–B(1), 1.3708(10); O(2)–B(2), 1.3720(10); N(1)–C(7), 1.2944(10); N(1)–N(2), 1.3938(9); N(2)–C(8), 1.4140(10); N(2)–B(1), 1.4450(11); N(3)–N(4), 1.3979(9); N(3)–C(8), 1.4107(10); N(3)–B(2), 1.4485(10); N(4)–C(9), 1.2932(11); C(1)–B(1), 1.5301(11); C(6)–C(7), 1.4495(11); C(9)–C(10), 1.4528(11); C(15)–B(2), 1.5296(12); B(1)–O(2)–B(2), 120.09(6); C(7)–N(1)–N(2), 116.81(7); N(1)–N(2)–C(8), 111.81(6); N(1)–N(2)–B(1), 123.83(6); C(8)–N(2)–B(1), 124.33(7); N(4)–N(3)–C(8), 111.81(6); N(4)–N(3)–B(2), 123.82(7); C(8)–N(3)–B(2), 124.37(6); C(9)–N(4)–N(3), 116.29(7); C(6)–C(1)–B(1), 116.45(7); C(1)–C(6)–C(7), 118.41(7); N(1)–C(7)–C(6), 127.64(8); O(1)–C(8)–N(3), 124.27(7); O(1)–C(8)–N(2), 123.59(7); N(3)–C(8)–N(2), 112.14(6); O(2)–B(1)–N(2), 119.28(7); O(2)–B(2)–N(3), 119.25(7).

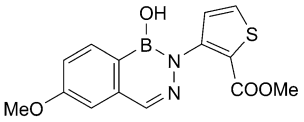
internal symmetry planes of reflection and one twofold axis of rotation was anticipated, but packing forces presumably caused it to deviate ever so slightly from that, making the path of the ring fusions somewhat curved. Examining the six internal angles of the central ring, the B–N–C ones are wide (124°), while the N–C–N angle is narrow (119°), a geometry clearly connected to the short C(8)–O(1) length of 1.2067(9) Å. While this C=O is formally of a urea-type, it is more ketone-like both crystallographically and spectroscopically (NMR and FT-IR, *vide supra*).

Miscellaneous Compounds. 2-Formyl-4-methoxybenzeneboronic acid was condensed with the aldehyde reagent *Purpald*® in refluxing EtOH to give **42b**, and with methyl 3-hydrazinylthiophene-2-carboxylate in MeOH at room temperature to give **43**. When the latter reaction was conducted in refluxing MeCN instead, lactone **44** was obtained. These three compounds were sought, hoping further stabilization of an NAD-adduct, if one should form, by H-bonding or acylation.

Antibacterial Assay Results. Most of the compounds were tested for activities against *Escherichia coli* and against *Mycobacterium smegmatis* as a surrogate for *M. tuberculosis* (*Table 2*). Nine compounds, **1**, **14b**, **22**, **24**, **25**, **28**, **31**, **35b**, and **39**, were found inactive against the latter but active against the former with *MIC* values of 2–



42b



43

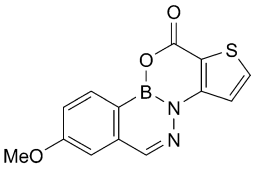


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Table 2. *Antibacterial Activity* (*MIC* values [μg ml^{-1}]) *for Compounds Tested*

Compound	*E. coli*	*M. smegmatis*	Compound	*E. coli*	*M. smegmatis*
1	32	>32	**28**	32	>32
2b	>32	>32	**29**	>32	>32
3c	>32	>32	**30**	>32	>32
4a	>32	>32	**31**	2	>32
4c	>32	>32	**32**	>32	>32
5c	>32	≥32	**33a**	>32	>32
6c	>32	≥32	**35b**	16	>32
14b	16	>32	**37**	>32	>32
15c	>32	>32	**38**	>32	>32
16b	>32	>32	**39**	32	>32
17c	>32	>32	**40**	>32	>32
18c	32	4	**41**	>32	>32
20a	>32	2	**42b**	>32	>32
22	4	>32	**44**	>32	>32
23	>32	>32	Amikacin	1	≤0.25
24	8	>32	Isoniazid	>32	2
25	16	>32	Pyrazinamide	>32	≥32
26	>32	>32	Triclosan	0.25	0.5
27	>32	>32			

32 μg ml^{-1}. Of those, six, *i.e.*, all except for **14b**, **35b**, and **39**, are members of the known class of antibacterial sulfonylated B heterocycles. Compound **1** had been reported active against *E. coli* with an *MIC* value of 25 μg ml^{-1} [2e]; we found 32 μg ml^{-1}. Compound **31** had been reported active against *E. coli* with an *MIC* value of 2.5 μg ml^{-1} [2a]; we found 2 μg ml^{-1}.

Also found active against *E. coli* (*MIC* values of 16 μg ml^{-1}) were the carbamoylated and thiocarbamoylated B heterocycles **14b** and **35b**, respectively. Semicarbazone **14b** is new, but thiosemicarbazone **35b** is one of those reported to show appreciable antifungal activity [11], and so it seems to have crossover activity. The pentacyclic B heterocycle **39** was weakly active against *E. coli* (*MIC* value of 32 μg ml^{-1}).

Although a handful were weakly active, two compounds, the anhydro dimer **18c** and the open semicarbazone **20a**, were found to have good activities (*MIC* values of 2–4 μg ml^{-1}) against *M. smegmatis* but not *E. coli*. Interestingly, both of these compounds were prepared using isonicotinic acid hydrazide, the tuberculosis drug INH, thus raising the possibility of an *in situ* hydrolysis which releases INH during the antibacterial assay.

Conclusions. – Based on the facility with which the new 2-acylated 2,3,1-diazaborines of this study undergo interconversion among open, monomer, and anhydro dimer forms (*i.e.*, **a**, **b**, and **c**, resp.), any one of these is potentially ultimately responsible for activity detected in the *E. coli* or *M. smegmatis* antibacterial assays. Moreover, although it was not observed in the chemical evaluation and characterization of these compounds, even a complete hydrolysis producing the starting materials used in their synthesis must be considered. In this scenario, since INH itself is a prodrug, a compound like **18c** or **20a** which releases it *in vivo* would be acting as a pro-prodrug. This consideration of hydrolysis is much less likely to be warranted for the more structure-stable pentacyclic or thiosemicarbazone-based B heterocycles, and, of course, is known not to be applicable in the case of the well-investigated 2-sulfonylated ones.

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Experimental Part

General. Starting materials, reagents, and solvents were purchased from *Sigma–Aldrich* or *Fisher Scientific* (*Acros*). UV Spectra: *Thermo Scientific NanoDrop 2000c* spectrophotometer; λ_{max} in nm. FT-IR Spectra: *PerkinElmer Spectrum Two* spectrophotometer with a *Pike Technologies MIRacle* ATR (attenuated total reflectance) accessory with a Ge crystal; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR Spectra: *Varian 500* FT-NMR spectrometer (500 MHz); δ in ppm rel. to Me_4Si as internal standard, *J* in Hz; Ψt, *pseudo-triplet*. *^{13}C-NMR Spectra: Varian 500* FT-NMR spectrometer (125 MHz); δ in ppm rel. to solvent C-atom resonances as internal standards. Recording of ^{13}C-NMR spectra was sometimes limited by solubility (often in $CDCl_3$), and when the quadrupolar relaxation did not obscure the ^{13}C-NMR signal of a C-atom attached to a B-atom, this signal was assigned based on its broadened lineshape. HR-ESI-TOF-MS: *The Scripps Center for Mass Spectrometry*, San Diego, CA, only for representative compounds; in *m*/*z*. These were determined using MeOH solns., in which the interconversion of forms **a**–**c** and the formation of MeOH adducts were facile. Elemental microanalyses: *Atlantic Microlab, Inc.*, Norcross, GA; in %.

General Procedure. Using commercially available starting materials, a 0.5–1.0M soln. of a substituted areneboronic acid was combined with a soln. of 1 equiv. of a substituted hydrazine in the same solvent. For **37**–**41**, a 2 :1 ratio of boronic acid to hydrazine was used. If the solvent was H_2O or 50% aq. EtOH, the mixture was allowed to evaporate slowly from an open beaker in the hood overnight, reducing its volume by at least half. Often, the product precipitated during this process. It was isolated by suction filtration, washed with a small amount of ice-cold H_2O, and dried *in vacuo*. If the solvent was anh. EtOH or MeCN, the mixture was heated at reflux overnight and then concentrated by reducing its volume by at least half *via* azeotropic distillation, removing H_2O. More anh. solvent was added, the mixture was heated at reflux for an additional 4–24 h, and the concentration of the mixture *via* azeotropic distillation was repeated. The product, which typically precipitated upon cooling to r.t. or 0°, was isolated as described above.

*2-[(4-Methylphenyl)sulfonyl]-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**1**). Solvent: MeCN, 82°. Yield: 65%. M.p. 159–161° ([2e]: 162–164°). Weakly active against *E. coli*, to the same degree as reported in [2e].

*1-Hydroxy-2,3,1-benzodiazaborinine-2(1*H*)-carbaldehyde* (**2b**). Solvent: 50% aq. EtOH, 23°. Yield: 83%. M.p. 90–93°, resolidifies to **2c** with m.p. 194–195°. UV (MeOH): 287. FT-IR: 3420 (OH), 1700 (C=O), 1615, 1288, 1078, 888, 760. ^{1}H-NMR ($CDCl_3$): 9.32 (*s*, CH–O); 8.44 (*s*, exchangeable, OH); 8.23 (*d*, *J* = 7.5, 1 H); 8.11 (*s*, HC=N); 7.79 (*Ψt*, 1 H); 7.71–7.65 (*m*, 2 H). ^{1}H-NMR ((D_6)DMSO): 10.00 (*s*, CH–O); 8.23 (*s*, exchangeable, OH); 8.22 (*d*, *J* = 7.5, 1 H); 8.02 (*s*, CH=N); 7.74–7.70 (*m*, 2 H); 7.60 (*Ψt*, 1 H). ^{13}C-NMR ($CDCl_3$): 175.9 (CH–O); 145.0 (C=N); 134.2; 133.1; 132.3; 130.8; 127.8. ^{13}C-NMR ((D_6)DMSO): 138.6; 135.8; 131.1; 130.3 (br., C–B); 128.4; 126.7. Dimerizes to **2c** in a concentration-dependent manner in $CDCl_3$, by NMR.

*1,1′-Oxybis(2,3,1-benzodiazaborinine-2(1*H*)-carbaldehyde)* (**2c**). Solvent: MeCN, 82°. Yield: 57%. M.p. 193.5–195.0°. UV (MeOH): 276. FT-IR: 1623, 1605 (C=O), 1399, 1323, 1312, 876, 771, 736. ^{1}H-NMR ($CDCl_3$): 8.55 (*s*, CH–O); 7.97 (*s*, CH=N); 7.86 (*d*, *J* = 7.0, 1 H); 7.56 (*Ψt*, 1 H); 7.52–7.45 (*m*, 2 H).

*{2-[(*E*)-(2-Benzoylhydrazinylidene)methyl]phenyl}boronic Acid* (**3a**). Solvent: EtOH, 23°. Yield: 99%. M.p. 200–203°. UV (MeOH): 299. FT-IR: 3299 (OH), 1643 (C=O), 1546, 1382, 1287. ^{1}H-NMR ((D_6)DMSO): 11.92 (*s*, exchangeable, NH); 8.77 (*s*, HC=N); 8.51 (*s*, exchangeable, $B(OH)_2$); 7.89 (*d*, *J* = 6.9, 2 H); 7.70–7.35 (*m*, 7 H). ^{13}C-NMR ((D_6)DMSO): 171.7 (C=O); 163.3; 153.0; 149.7; 137.5; 137.3 (br., C–B); 133.4; 130.4; 129.7; 128.6; 127.8; 125.9.

(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)bis(phenylmethanone) (**3c**). Solvent: EtOH, 78°. Yield: 81%. Solvent: MeCN, 82°. Yield: 91%. M.p. 233–237°. UV (MeOH): 297. FT-IR: 1546 (C=O), 1436, 1398, 1279. ^{1}H-NMR ($CDCl_3$): 8.07 (*s*, CH=N); 7.98 (*d*, *J* = 7.5, 1 H); 7.74 (*d*, *J* = 7.0, 2 H); 7.54–7.58 (*m*, 1 H); 7.47–7.51 (*m*, 3 H); 7.38 (*Ψt*, 2 H). ^{13}C-NMR ($CDCl_3$): 171.8; 153.0; 132.4; 132.0; 131.7; 131.5; 130.8; 130.7; 130.5; 129.9; 128.6; 128.2; 128.0; 127.7; 127.6.

*(2-{(*E*)-[2-(4-Methylbenzoyl)hydrazinylidene]methyl}phenyl)boronic Acid* (**4a**). Solvent: 50% aq. EtOH, 23°. Yield: 90%. M.p. 190–193°. UV (MeOH): 300. FT-IR: 3310 (OH), 1651 (C=O), 1551, 1440, 1389, 1281, 831. ^{1}H-NMR ((D_6)DMSO, only slightly soluble): 11.90 (*s*, exchangeable, NH); 8.76 (*s*, HC=N); 8.52 (*s*, exchangeable, $B(OH)_2$); 7.92 (*d*, *J* = 8.0, 1 H); 7.85 (*d*, *J* = 8.0, 2 H); 7.62 (*d*, *J* = 7.0, 1 H); 7.45 (*Ψt*, 1 H); 7.38 (*Ψt*, 1 H); 7.33 (*d*, *J* = 8.0, 2 H); 2.38 (*s*, Me). ^{13}C-NMR ((D_6)DMSO): 162.9 (C=O); 149.2; 141.8; 137.4; 137.2 (br., C–B); 134.0; 130.5; 129.1; 129.0; 128.8; 127.7; 125.7; 21.1 (Me). Insoluble in $CDCl_3$. HR-ESI-TOF-MS: 283.1262 ($[M+H]^+$, $C_{15}H_{16}BN_2O_3^+$; calc. 283.1248), 305.1089 ($[M+Na]^+$, $C_{15}H_{15}BN_2NaO_3^+$; calc. 305.1068).

(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)bis[(4-methylphenyl)methanone] (**4c**). Solvent: MeCN, 82°. Yield: 63%. M.p. >260°. UV (MeOH): 299. FT-IR: 1700, 1584 (C=O), 1549, 1438. ^{1}H-NMR ($CDCl_3$): 8.06 (*s*, HC=N); 7.97 (*d*, *J* = 7.5, 1 H); 7.64 (*d*, *J* = 8.5, 2 H); 7.53–7.57 (*m*, 1 H); 7.47 (*d*, *J* = 3.5, 2 H); 7.17 (*d*, *J* = 7.5, 2 H); 2.35 (*s*, Me). ^{1}H-NMR ((D_6)DMSO): 8.28 (*s*, CH=N); 7.74 (*d*, *J* = 5.9, 1 H); 7.66 (*d*, *J* = 8.0, 1 H); 7.59 (*d*, *J* = 8.5, 2 H); 7.53–7.57 (*m*, 2 H); 7.28 (*d*, *J* = 8.5, 2 H); 2.34 (*s*, Me). ^{13}C-NMR ((D_6)DMSO): 171.0 (C=O); 152.7 (C=N); 143.2; 131.5; 131.4; 130.4; 130.2; 128.6; 128.5; 128.4; 126.6; 21.2 (Me). HR-ESI-TOF-MS: 511.2123 ($[\mathbf{4c}+H]^+$, $C_{30}H_{25}B_2N_4O_3^+$; calc. 511.2107), 265.1161 ($[\mathbf{4b}+H]^+$, $C_{15}H_{14}BN_2O_2^+$; calc. 265.1143).

[Oxybis(4-methyl-2,3,1-benzodiazaborinine-1,2-diyl)]bis(phenylmethanone) (**5c**). Solvent: 50% aq. EtOH, 23°. Yield: 95%. M.p. 248–250°. UV (MeOH): 297. FT-IR: 1587, 1560, 1546, 1451, 1427, 1283, 798, 731. ^{1}H-NMR ((D_6)DMSO): 7.79 (*dd*, *J* = 5.0, 3.5, 1 H); 7.75 (*dd*, *J* = 5.0, 3.5, 1 H); 7.68 (*d*, *J* = 8.0, 2 H); 7.60 (*Ψt*, 1 H); 7.55 (*Ψt*, 1 H); 7.47 (*Ψt*, 1 H); 2.53 (*s*, Me). ^{13}C-NMR ((D_6)DMSO, 40°): 169.6 (C=O); 158.1 (C=N); 140.4 (br., C–B); 132.4; 131.1; 130.9; 130.8; 130.1; 129.5; 128.3; 127.7; 126.1; 20.7 (Me).

[Oxybis(4-methyl-2,3,1-benzodiazaborinine-1,2-diyl)]bis[(4-methylphenyl)methanone] (**6c**). Solvent: 50% aq. EtOH, 23°. Yield: 96%. M.p. >260°. UV (MeOH): 297. FT-IR: 1581, 1544, 1510, 1428, 1283, 805, 783, 744. ^{1}H-NMR ($CDCl_3$): 7.78 (*d*, *J* = 3.0, 1 H); 7.74 (*d*, *J* = 3.0, 1 H); 7.58 (*d*, *J* = 8.0, 2 H); 7.52–7.56 (*m*, 2 H); 7.27 (*d*, *J* = 8.0, 2 H); 2.54 (*s*, Me); 2.35 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 169.8 (C=O); 158.0; 142.9; 132.1; 131.5; 131.3; 130.7; 128.2; 127.0; 125.6; 21.6; 21.1.

1,1′-(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)diethanone (**7c**). Solvent: 50% aq. EtOH, 23°. Yield: 99%. M.p. 216–218°. UV (MeOH): 290. FT-IR: 1574, 1555, 1476, 884. ^{1}H-NMR ($CDCl_3$): 7.92 (*s*, CH=N); 7.86 (*d*, *J* = 7.5, 1 H); 7.53 (*Ψt*, 1 H); 7.47–7.43 (*m*, 2 H); 1.63 (*s*, Me). ^{1}H-NMR ((D_6)DMSO): 8.15 (*s*, CH=N); 7.63 (*dd*, *J* = 6.5, 2.5, 1 H); 7.60 (*dd*, *J* = 6.5, 2.5, 1 H); 7.54–7.48 (*m*, 2 H); 2.39 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 177.1 (C=O); 151.7; 131.8; 130.8; 130.4; 128.5; 128.3; 19.0.

1,1′-(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)bis(2-methylpropan-1-one) (**8c**). Solvent: MeCN, 82°. Yield: 72%. M.p. 176–178°. UV (MeOH): 290. FT-IR: 1567 (C=O), 1551, 1479, 1438, 1086, 864. ^{1}H-NMR ($CDCl_3$): 7.90 (*s*, CH=N); 7.82 (*d*, *J* = 7.3, 1 H); 7.50 (*Ψt*, 1 H); 7.46–7.40 (*m*, 2 H); 3.88 (*sept.*, *J* = 6.8, Me_2CH); 1.11 (*d*, *J* = 6.8, Me); 1.05 (*d*, *J* = 6.8, Me). ^{13}C-NMR ($CDCl_3$): 182.5 (C=O); 151.3; 131.5; 130.6; 128.4; 28.7; 18.7; 18.3.

*(2-{(*E*)-[2-(4-Methyl-3-nitrobenzoyl)hydrazinylidene]methyl}phenyl)boronic Acid* (**9a**). Solvent: EtOH, 78°. Yield: 96%. M.p. 222–224°. UV (MeOH): 304. FT-IR: 3230 (OH), 3064 (NH), 1650 (C=O), 1524, 1344, 1311. ^{1}H-NMR ((D_6)DMSO): 12.17 (br. *s*, exchangeable, NH); 8.80 (*s*, CH=N); 8.56 (*d*, *J* = 1.5, 1 H); 8.52 (*s*, exchangeable, $B(OH)_2$); 8.19 (*dd*, *J* = 1.5, 8.3, 1 H); 7.96 (*d*, *J* = 7.8, 1 H); 7.69 (*d*, *J* = 8.3, 1 H); 7.62 (*d*, *J* = 8.3, 1 H); 7.46 (*Ψt*, 1 H); 7.40 (*Ψt*, 1 H); 2.60 (*s*, Me). ^{13}C-NMR ((D_6)DMSO): 160.9 (C=O); 150.1; 148.8; 137.2; 136.6; 133.9; 133.2; 132.2; 129.2; 129.0; 125.5; 123.6; 56.1.

*(2-{(*E*)-[2-(4-Nitrobenzoyl)hydrazinylidene]methyl}phenyl)boronic Acid* (**10a**). Solvent: EtOH, 23°. Yield: 81%. M.p. 205–208°. UV (MeOH): 308. FT-IR: 3232 (OH), 1650 (C=O), 1602, 1563, 1518, 1346, 1327, 1290. ^{1}H-NMR ((D_6)DMSO): 12.25 (*s*, exchangeable, NH); 8.82 (*s*, HC=N); 8.51 (*s*, exchangeable, $B(OH)_2$); 8.37 (*d*, *J* = 8.5, 2 H); 8.17 (*d*, *J* = 9.0, 2 H); 7.97 (*d*, *J* = 8.0, 1 H); 7.62 (*d*, *J* = 7.5, 1 H); 7.46 (*Ψt*, 1 H); 7.41 (*Ψt*, 1 H). ^{13}C-NMR ((D_6)DMSO): 161.5 (C=O); 150.5; 149.3; 139.1; 137.1; 133.8; 129.3; 125.5; 123.6.

(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)bis[(4-fluorophenyl)methanone] (**11c**). Solvent: MeCN, 82°. Yield: 82%. M.p. >225°. UV (MeOH): 299. FT-IR: 1603 (C=O), 1566, 1553, 1452, 1441, 1230. ^{1}H-NMR ((D_6)DMSO): 8.29 (*s*, CH=N); 7.81 (*Ψt*, 2 H); 7.75 (*d*, *J* = 6.5, 1 H); 7.66 (*d*, *J* = 6.5, 1 H); 7.60–7.52 (*m*, 2 H); 7.31 (*Ψt*, 2 H). ^{13}C-NMR ((D_6)DMSO): 170.3; 163.3; 152.9; 139.0 (br., C–B); 134.3; 131.6; 130.3; 128.7; 126.0; 115.1.

(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)bis[(4-chlorophenyl)methanone] (**12c**). Solvent: EtOH, 23°. Yield: 53%. M.p. >240°. UV (MeOH): 304. FT-IR: 1585, 1551, 1451, 1439, 1091, 1017, 878, 839, 817, 781, 759, 750, 729. ^{1}H-NMR ($CDCl_3$): 8.06 (*s*, CH=N); 7.95 (*d*, *J* = 7.5, 1 H); 7.72 (*d*, *J* = 9.0, 2 H); 7.55–7.59 (*m*, 1 H); 7.48–7.72 (*m*, 1 H); 7.36 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR ($CDCl_3$): 170.6 (C=O); 153.3 (C=N); 133.2; 132.1; 131.7; 130.7; 130.4; 128.7; 128.3; 128.0. Insoluble in (D_6)DMSO.

(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)bis[(2-chlorophenyl)methanone] (**13c**). Solvent: MeCN, 82°. Yield: 71%. M.p. >230°. UV (MeOH): 295. FT-IR: 1599 (C=O), 1570, 1434, 1053, 877, 772. ^{1}H-NMR ($CDCl_3$): 8.01 (*d*, *J* = 7.5, 1 H); 7.90 (*s*, HC=N); 7.47 (*Ψt*, 1 H); 7.48–7.30 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 172.9 (C=O); 153.3; 131.9; 131.4; 130.5; 129.9; 129.4; 129.0; 128.6; 126.7; 126.1.

*1-Hydroxy-2,3,1-benzodiazaborinine-2(1*H*)-carboxamide* (**14b**). Solvent: MeCN, 82°. Yield: 87%. M.p. >255°. UV (MeOH): 304. FT-IR: 3416 (OH), 3193 (NH), 1687 (C=O), 1417, 1323, 1298, 1154, 892, 811, 742. ^{1}H-NMR ($CDCl_3$): 9.31 (*s*, exchangeable, OH); 8.24 (*d*, *J* = 7.0, 1 H); 7.96 (*s*, CH=N); 7.74 (*Ψt*, 1 H); 7.68–7.63 (*m*, 2 H); 7.44 (br. *s*, exchangeable, NH); 5.17 (br. *s*, exchangeable, NH). Immediately forms anhydro dimer **14c**, releasing H_2O, when dissolved in (D_6)DMSO, by NMR: ^{1}H-NMR ((D_6)DMSO): 7.84 (*s*, exchangeable, NH); 7.83 (*s*, CH=N); 7.78 (*s*, exchangeable, NH); 7.62 (*d*, *J* = 7.0, 1 H); 7.48 (*d*, *J* = 7.0, 1 H); 7.46–7.40 (*m*, 2 H). ^{13}C-NMR ((D_6)DMSO): 160.7 (C=O); 145.5 (C=N); 135 (br., C–B); 131.2; 130.2; 130.0; 127.7; 127.3. Attempts to obtain **14c** *via* crystallization from MeCN gave only **14b**, likely due to the presence of propitious H_2O. Active against *E. coli*.

*1,1′-Oxybis(2,3,1-benzodiazaborinine-2(1*H*)-carbohydrazide)* (**15c**). Solvent: MeCN, 82°. Yield: 64%. M.p. 204–205°. UV (MeOH): 294, 326. FT-IR: 3343 (NH), 1699 (C=O), 1556, 1416, 1282, 782. ^{1}H-NMR ($CDCl_3$, only slightly soluble): 8.59 (*s*, CH=N); 8.56 (*d*, *J* = 8.0, 1 H); 7.93 (*Ψt*, 1 H); 7.90–7.80 (*m*, 3 H); 6.40 (br. *s*, exchangeable, NH); 3.68 (br. *s*, exchangeable, NH_2). ^{1}H-NMR ((D_6)DMSO): 8.14 (*s*, HC=N); 8.13 (*d*, *J* = 8.0, 1 H); 7.70–7.61 (*m*, 3 H); 7.47 (br. *s*, exchangeable, NH); 5.20 (br. *s*, exchangeable, NH_2). ^{13}C-NMR ((D_6)DMSO): 159.9 (C=O); 154.4 (C=N); 143.4; 133.4; 130.5; 130.3 (br., C–B); 129.7; 126.6.

*(1-Hydroxy-2,3,1-benzodiazaborinin-2(1*H*)-yl)(pyridin-2-yl)methanone* (**16b**). Picolinic acid hydrazide was prepared from the ethyl ester as described in [18]. Solvent: 50% aq. EtOH, 23°. Yield: 82%. M.p. >260°. FT-IR: 3436 (OH), 1680 (C=O), 1622, 1364, 1107, 1075, 1056, 846, 778. UV (MeOH): 292, 338. UV (MeOH, pH 2): 291, 340. UV (MeOH, pH 12): 299. ^{1}H-NMR ((D_6)DMSO): 9.37 (*d*, *J* = 5.4, 1 H); 8.55 (*Ψt*, 1 H); 8.21 (*d*, *J* = 7.8, 1 H); 8.11 (*Ψt*, 1 H); 8.05 (*s*, CH=N); 7.80 (*d*, *J* = 7.3, 1 H); 7.48 (*d*, *J* = 7.3, 1 H); 7.41–7.45 (*m*, 2 H); 4.12 (*s*, exchangeable very slowly, OH). ^{13}C-NMR ((D_6)DMSO): 157.6;

153.5; 146.9; 144.8; 143.5; 143 (br., C–B); 131.9; 130.4; 129.0; 128.9; 128.3; 127.4; 121.7. Insoluble in $CDCl_3$.

(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)bis(pyridin-3-ylmethanone) (**17c**). Solvent: MeCN, 82°. Yield: 72%. M.p. 274–275° (dec.). UV (MeOH): 299. UV (MeOH, pH 2): 299. UV (MeOH, pH 12): 299. FT-IR: 1622, 1595, 1554, 1407. ^{1}H-NMR ((D_6)DMSO): 8.90 (*d*, *J* = 1.0, 1 H); 8.72 (*d*, *J* = 4.9, 1 H); 8.27 (*s*, CH=N); 8.10 (*d*, *J* = 8.0, 1 H); 7.75 (*d*, *J* = 6.5, 1 H); 7.66 (*d*, *J* = 7.5, 1 H); 7.58–7.49 (*m*, 3 H). ^{13}C-NMR ((D_6)DMSO): 170.4 (C=O); 153.0; 152.5; 151.2; 138.7; 131.7; 130.3; 128.8; 126.2; 123.0. HR-ESI-TOF-MS: 270.1074 ($[M+H]^+$, $C_{13}H_{13}BN_3O_3^+$; calc. 270.1044). X-Ray crystal structure determined.

(Oxydi-2,3,1-benzodiazaborinine-1,2-diyl)bis(pyridin-4-ylmethanone) (**18c**). Solvent: MeCN, 82°. Yield: 69%. M.p. 276–278° (dec.). UV (MeOH): 304. UV (MeOH, pH 2): 303. UV (MeOH, pH 12): 297. FT-IR: 1682, 1604, 1580, 1408. ^{1}H-NMR ((D_6)DMSO): 8.73 (*d*, *J* = 5.1, 2 H); 8.24 (*s*, HC=N); 7.76 (*d*, *J* = 6.8, 1 H); 7.69–7.64 (*m*, 3 H); 7.60–7.53 (*m*, 2 H). ^{13}C-NMR ((D_6)DMSO): 170.8 (C=O); 153.1; 149.5; 137.5; 131.8; 130.4; 130.2; 129.0; 128.9; 124.1. Active against *M. smegmatis*.

[Oxybis(4-methyl-2,3,1-benzodiazaborinine-1,2-diyl)]bis(pyridin-4-ylmethanone) (**19c**). Solvent: 50% aq. EtOH, 23°. Yield: 78%. M.p. >245°. UV (MeOH): 283. FT-IR: 1580, 1540, 1433, 1284. ^{1}H-NMR ($CDCl_3$, only slightly soluble): 8.77 (*d*, *J* = 8.7, 1 H); 7.96 (*d*, *J* = 8.3, 1 H); 7.70 (*d*, *J* = 7.8, 1 H); 7.63 (*d*, *J* = 6.1, 2 H); 7.58 (*Ψt*, 1 H); 7.51 (*Ψt*, 1 H); 2.58 (*s*, Me). ^{1}H-NMR ((D_6)DMSO): 8.73 (*d*, *J* = 6.0, 2 H); 7.79 (*d*, *J* = 8.5, 1 H); 7.76 (*d*, *J* = 6.0, 1 H); 7.66 (*d*, *J* = 6.0, 2 H); 7.56 (*Ψt*, 1 H); 7.56 (*Ψt*, 1 H); 2.50 (*s*, Me).

*(2-{(*E*)-[2-(Pyridin-4-ylcarbonyl)hydrazinylidene]methyl}thiophen-3-yl)boronic Acid* (**20a**). Solvent: MeCN, 82°. Yield: 95%. Solvent: 50% aq. EtOH, 23°. Yield: 79%. M.p. 205–206°. UV (MeOH): 329. FT-IR: 3313 (OH), 3009 (NH), 1682 (C=O), 1579, 1394, 1374, 1290, 697, 685. ^{1}H-NMR ((D_6)DMSO): 12.21 (*s*, exchangeable, NH); 9.14 (*s*, CH=N); 8.77 (*d*, *J* = 4.5, 2 H); 8.47 (*s*, exchangeable, $B(OH)_2$); 7.81 (*d*, *J* = 4.5, 2 H); 7.61 (*d*, *J* = 4.6, 1 H); 7.44 (*s*, *J* = 4.6, 1 H). ^{13}C-NMR ((D_6)DMSO): 161.5 (C=O); 150.3 (HC=N); 146.2; 145.8; 140.5; 139.7 (br., C–B); 134.4; 127.8; 121.6. HR-ESI-TOF-MS: 258.0501 ($[M+H]^+$, $C_{11}H_9BN_3O_2S^+$; calc. 258.0503), 276.0634 ($[M+H]^+$, $C_{11}H_{11}BN_3O_3S^+$; calc. 276.0609). Active against *M. smegmatis*.

*(2-{(*E*)-[2-(Pyridin-3-ylcarbonyl)hydrazinylidene]methyl}thiophen-3-yl)boronic Acid* (**21a**). Solvent: EtOH, 23°. Yield: 76%. M.p. 199–203°. UV (MeOH): 327. FT-IR: 3258 (OH), 3074, 1648 (C=O), 1556, 1411, 1387. ^{1}H-NMR ((D_6)DMSO): 12.15 (*s*, exchangeable, NH); 9.12 (*s*, 1 H); 9.06 (*s*, CH=N); 8.76 (*d*, *J* = 6.0, 1 H); 8.47 (*s*, exchangeable, $B(OH)_2$); 8.26 (*d*, *J* = 8.5, 1 H); 7.60 (*d*, *J* = 5.0, 1 H); 7.54–7.58 (*m*, 1 H); 7.44 (*d*, *J* = 5.0, 1 H). ^{13}C-NMR ((D_6)DMSO): 161.6 (C=O); 152.3; 148.7; 146.3; 145.2; 139.3 (br., C–B); 135.5; 134.3; 129.2; 127.6; 123.6.

*2-(Phenylsulfonyl)-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**22**). Solvent: EtOH, 78°. Yield: 73%. M.p. 160–161°. UV (MeOH): 292. FT-IR: 3509 (OH), 1548, 1446, 1284. ^{1}H-NMR ($CDCl_3$): 8.23 (*d*, *J* = 7.5, 1 H); 8.02–8.06 (*m*, 3 H); 7.73 (*Ψt*, 1 H); 7.67 (*Ψt*, 1 H); 7.64 (*Ψt*, 1 H); 7.55–7.59 (*m*, 3 H); 7.42 (*s*, exchangeable, OH). ^{13}C-NMR ($CDCl_3$): 143.8; 137.7; 134.0; 133.9; 132.8; 132.1; 130.8; 129.1; 128.3; 127.6. Active against *E. coli*.

*2-[(2,4,6-Trimethylphenyl)sulfonyl]-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**23**). Solvent: EtOH, 78°. Yield: 76%. M.p. 151–152°. UV (MeOH): 301. FT-IR: 3521 (OH), 1402, 1336, 1289, 985, 673. ^{1}H-NMR ($CDCl_3$): 8.24 (*d*, *J* = 6.0, 1 H); 7.95 (*s*, CH=N); 7.73 (*Ψt*, 1 H); 7.67 (*Ψt*, 1 H); 7.56 (*d*, *J* = 8.0, 1 H); 7.40 (*s*, exchangeable, OH); 7.26 (*s*, 1 H); 6.99 (*s*, 2 H); 2.67 (*s*, 2 *o*-Me); 2.31 (*s*, *p*-Me). ^{13}C-NMR ($CDCl_3$): 143.9 (C=O); 143.1; 141.0; 134.0; 132.7; 132.1; 132.0; 131.8; 130.6; 127.5; 22.9; 21.1.

*6-Methoxy-2-(phenylsulfonyl)-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**24**). Solvent: MeCN, 82°. Yield: 71%. M.p. 170–172°. UV (MeOH): 287. FT-IR: 3508 (OH), 1550, 1446, 1421, 1284. ^{1}H-NMR ($CDCl_3$): 8.13 (*d*, *J* = 8.5, 1 H); 8.03 (*d*, *J* = 7.0, 2 H); 7.96 (*s*, CH=N); 7.63 (*Ψt*, 1 H); 7.54 (*Ψt*, 2 H); 7.29 (*s*, exchangeable, OH); 7.21 (*dd*, *J* = 8.5, 2.0, 1 H); 6.98 (*d*, *J* = 2.5, 1 H); 3.89 (*s*, MeO). ^{13}C-NMR ($CDCl_3$): 163.2; 143.6; 137.9; 136.1; 134.0; 129.1; 128.2; 119.0; 110.3; 77.0; 55.5. HR-ESI-TOF-MS: 317.0771 ($[M+H]^+$, $C_{14}H_{14}BN_2O_4S^+$; calc. 317.0762). Active against *E. coli*.

*6-Methoxy-2-[(4-methylphenyl)sulfonyl]-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**25**). Solvent: EtOH, 78°. Yield: 90%. M.p. 175–177°. UV (MeOH): 289. FT-IR: 3500 (OH), 1596, 1399, 1347, 1264. ^{1}H-NMR ($CDCl_3$): 8.12 (*d*, *J* = 8.3, 1 H); 7.95 (*s*, CH=N); 7.92 (*d*, *J* = 8.3, 2 H); 7.33 (*d*, *J* = 8.1, 2 H); 7.31 (*s*, exchangeable, OH); 7.21 (*dd*, *J* = 8.3, 2.4, 1 H); 6.96 (*d*, *J* = 2.4, 1 H); 3.89 (*s*, MeO); 2.42

(*s*, Me). ^{1}H-NMR ((D$_6$)DMSO): 8.97 (*s*, exchangeable, OH); 8.14 (*d*, *J* = 7.8, 1 H); 8.13 (*s*, HC=N); 7.89 (*d*, *J* = 8.3, 2 H); 7.43 (*d*, *J* = 8.1, 2 H); 7.28–7.32 (*m*, 2 H); 3.63 (*s*, MeO); 2.38 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 162.9; 144.8; 142.5; 136.4; 134.0; 133.9; 130.0; 127.9; 119.1; 110.9; 55.7; 21.3. Anal. calc. for $C_{15}H_{15}BN_2O_4S$: C 54.57, H 4.58, N 8.48; found: C 54.80, H 4.72, N 8.50. Active against *E. coli*.

*2-[(4-Methylphenyl)sulfonyl]-2,3,1-benzodiazaborinine-1,6(2*H*)-diol* (**26**). Yield: 44% (*via* BBr_3 demethylation of **25** in CH_2Cl_2). M.p. 172–174°. UV (MeOH): 275. FT-IR: 3438 (OH), 1681, 1604, 1582, 1542, 1408. ^{1}H-NMR ($CDCl_3$): 8.67 (br. *s*, exchangeable, OH); 8.04 (*d*, *J* = 8.0, 1 H); 7.91 (*s*, CH=N); 7.88 (*d*, *J* = 4.0, 2 H); 7.32 (*d*, *J* = 8.5, 2 H); 7.28 (*s*, exchangeable, OH); 7.14 (*dd*, *J* = 8.0, 2.0, 1 H); 6.95 (*d*, *J* = 2.5, 1 H); 2.42 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 161.0; 145.0; 143.6; 136.2; 134.9; 134.1; 129.7; 128.2; 119.8; 112.9; 21.6. HR-ESI-TOF-MS: 317.0770 ($[M+H]^+$, $C_{14}H_{14}BN_2O_4S^+$; calc. 317.0762).

*6-Methoxy-2-[(2,4,6-trimethylphenyl)sulfonyl]-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**27**). Solvent: EtOH, 78°. Yield: 91%. M.p. 161–162°. UV (MeOH): 286. FT-IR: 3470 (OH), 1610, 1593, 1397, 1332, 1267, 1161, 990, 762, 677. ^{1}H-NMR ($CDCl_3$): 8.13 (*d*, *J* = 6.5, 1 H); 7.87 (*s*, CH=N); 7.28 (*s*, exchangeable, OH); 7.22 (*dd*, *J* = 8.5, 2.5, 1 H); 6.98 (*s*, 2 H); 6.95 (*d*, *J* = 2.5, 1 H); 3.90 (*s*, MeO); 2.67 (*s*, 2 *o*-Me); 2.32 (*s*, *p*-Me). ^{13}C-NMR ($CDCl_3$): 163.2 (C=O); 143.8; 142.9; 140.9; 136.1; 134.0; 132.0; 118.8; 110.2; 55.4; 22.9; 21.1.

*4-Methyl-2-(phenylsulfonyl)-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**28**). Solvent: 50% aq. EtOH, 23°. Yield: 88%. M.p. 149–152°. UV (MeOH): 308. FT-IR: 3530 (OH), 1400, 1294, 1248, 1150, 937. ^{1}H-NMR ($CDCl_3$): 8.24 (*d*, *J* = 7.5, 1 H); 8.07 (*d*, *J* = 6.0, 2 H); 7.71–7.75 (*m*, 2 H); 7.62–7.66 (*m*, 2 H); 7.55 (*Ψt*, 2 H); 7.36 (*s*, exchangeable, OH); 2.50 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 148.6; 137.9; 134.6; 133.8; 132.7; 132.2; 130.3; 129.9; 128.4; 125.7; 20.5. Active against *E. coli*.

*4-Methyl-2-[(2,4,6-trimethylphenyl)sulfonyl]-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**29**). Solvent: MeCN, 82°. Yield: 80%. M.p. 153–154°. UV (MeOH): 288. FT-IR: 3502 (OH), 1605, 1402, 1336, 1292, 1254, 1172, 1020, 933, 666. ^{1}H-NMR ($CDCl_3$): 8.24 (*d*, *J* = 7.5, 1 H); 7.69–7.72 (*m*, 2 H); 7.64 (*Ψt*, 1 H); 7.32 (*s*, exchangeable, OH); 6.98 (*s*, 2 H); 2.71 (*s*, 2 *o*-Me); 2.42 (*s*, Me); 2.31 (*s*, *p*-Me). ^{13}C-NMR ($CDCl_3$): 147.7 (C=O); 143.6; 141.1; 134.6; 132.6; 132.3; 132.1; 131.9; 130.1; 125.6; 23.1; 21.1; 20.5.

*4-Methyl-2-[(4-methylphenyl)sulfonyl]-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**30**). Solvent: MeCN, 82°. Yield: 75%. M.p. 168–171° ([2e]: 179–180°). UV (MeOH): 286. FT-IR: 3504 (OH), 1398, 1348, 1298, 1248, 1150, 939, 671. ^{1}H-NMR ($CDCl_3$): 8.22 (*d*, *J* = 7.5, 1 H); 7.94 (*d*, *J* = 8.0, 2 H); 7.59–7.63 (*m*, 2 H); 7.61–7.65 (*m*, 1 H); 7.37 (*s*, exchangeable, OH); 7.33 (*d*, *J* = 8.0, 2 H); 2.49 (*s*, Me); 2.43 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 148.4 (C=O); 144.9; 135.0; 134.6; 132.6; 132.2; 130.2; 129.5; 128.4; 125.6; 21.7; 20.5.

*2-(Phenylsulfonyl)thieno[3,2-*d*][1,2,3]diazaborinin-1(2*H*)-ol* (**31**). Solvent: MeCN, 82°. Yield: 58%. M.p. 165–167° ([2a]: 168–172°). UV (MeOH): 299. FT-IR: 3499 (OH), 1513, 1419, 1366. ^{1}H-NMR ($CDCl_3$): 8.14 (*s*, CH=N); 8.05 (*d*, *J* = 8.5, 2 H); 7.62–7.66 (*m*, 3 H); 7.56 (*Ψt*, 2 H); 7.36 (*s*, exchangeable, OH). ^{13}C-NMR ($CDCl_3$): 144.7; 137.8; 136.5; 134.1; 130.9; 130.0; 129.1; 128.3. HR-ESI-TOF-MS: 293.0219 ($[M+H]^+$, $C_{11}H_{10}BN_2O_3S_2^+$; calc. 293.0220), 315.0048 ($[M+Na]^+$, $C_{11}H_9BN_2NaO_3S_2^+$; calc. 315.0040). Active against *E. coli*, to the same degree as reported in [2a].

*2-[(2,4,6-Trimethylphenyl)sulfonyl]thieno[3,2-*d*][1,2,3]diazaborinin-1(2*H*)-ol* (**32**). Solvent: EtOH, 78°. Yield: 40%. M.p. 158–159°. UV (MeOH): 310. FT-IR: 3499 (OH), 1420, 1359, 1334, 1254, 1151, 1001, 915, 660. ^{1}H-NMR ($CDCl_3$): 8.06 (*s*, CH=N); 7.64 (*s*, 2 H); 7.39 (*s*, exchangeable, OH); 6.99 (*s*, 2 H); 2.67 (*s*, 2 *o*-Me); 2.31 (*s*, *p*-Me). ^{13}C-NMR ($CDCl_3$): 144.7 (C=O); 144.1; 141.1; 135.8; 132.0; 130.5; 130.0; 23.0; 21.1.

*{2-[(*E*)-(2-Carbamothioylhydrazinylidene)methyl]thiophen-3-yl}boronic Acid* (**33a**). Solvent: 50% aq. EtOH, 23°. Yield: 95%. Solvent: MeCN, 82°. Yield: 64%. M.p. >250°. UV (MeOH): 336. FT-IR: 3432 (OH), 3243 (NH), 3056, 1608, 1547, 1504, 1377, 1310, 1185, 1070, 686. ^{1}H-NMR ((D$_6$)DMSO): 11.55 (*s*, exchangeable, NH); 8.77 (*s*, CH=N); 8.29 (*s*, exchangeable, $B(OH)_2$); 8.17 (*s*, exchangeable, NH); 7.52 (*d*, *J* = 5.0, 1 H); 7.40 (*s*, exchangeable, NH); 7.35 (*d*, *J* = 5.0, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 177.6 (C=S); 146.1 (HC=N); 140.2; 139.4 (br., C–B); 133.9; 127.1.

*(2-{(*E*)-[2-(Phenylcarbamothioyl)hydrazinylidene]methyl}thiophen-3-yl)boronic Acid* (**34a**). Solvent: EtOH; 23°. Yield: 84%. M.p. 153–155°. UV (MeOH): 346. FT-IR: 3335 (OH), 3218 (NH), 3041 (NH), 1548 (C=S), 1531, 1391, 1310, 1201, 1039. ^{1}H-NMR ((D$_6$)DMSO): 11.96 (*s*, exchangeable, NH); 9.69 (*s*, exchangeable, NH); 8.89 (*s*, CH=N); 8.35 (br. *s*, exchangeable, $B(OH)_2$); 7.60 (*d*, *J* = 7.5, 2 H); 7.57

(*d*, *J* = 5.0, 1 H); 7.39 (*d*, *J* = 5.0, 1 H); 7.35 (*Ψt*, 2 H); 7.17–7.21 (*m*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 175.4; 145.7; 140.6; 139.0; 134.0; 128.2; 127.4; 125.1; 125.0.

*1-Hydroxy-2,3,1-benzodiazaborinine-2(1*H*)-carbothioamide* (**35b**). Solvent: MeCN; yield: 68%. Solvent: 50% aq. EtOH; yield: 82%. M.p. 175–176° ([11]: 172–174°). UV (MeOH): 317. FT-IR: 3398 (OH), 3266 (NH), 3044 (NH), 1587 (C=S), 1408, 1299, 1255, 1131, 1023, 724. ^{1}H-NMR (CDCl$_3$): 10.46 (*s*, exchangeable, OH); 8.94 (*s*, exchangeable, NH); 8.27 (*d*, *J* = 7.0, 1 H); 7.97 (*s*, CH=N); 7.74 (*Ψt*, 1 H); 7.69 (*Ψt*, 1 H); 7.63 (*d*, *J* = 8.0, 1 H); 6.87 (*s*, exchangeable, NH). ^{1}H-NMR ((CD$_3$)$_2$CO): data in accordance with those in [11] (compound solved by X-ray). ^{1}H-NMR ((D$_6$)DMSO): 10.77 (*s*, exchangeable, OH); 9.72 (*s*, exchangeable, NH); 9.56 (*s*, exchangeable, NH); 8.27 (*s*, CH=N); 8.11 (*d*, *J* = 7.5, 1 H); 7.89 (*d*, *J* = 8.0, 1 H); 7.84 (*Ψt*, 1 H); 7.73 (*Ψt*, 1 H). Forms varying amounts of **35a** by reacting with the H$_2$O in (D$_6$)DMSO, by NMR: ^{1}H-NMR ((D$_6$)DMSO): 11.55 (*s*, exchangeable, NH); 8.28 (*s*, exchangeable, NH); 8.16 (*s*, CH=N); 8.12 (*s*, exchangeable, B(OH)$_2$); 7.63–7.61 (*m*, 1 H); 7.62 (*s*, exchangeable, NH); 7.37–7.34 (*m*, 3 H). Active against *E. coli*.

*1-Hydroxy-*N*-phenyl-2,3,1-benzodiazaborinine-2(1*H*)-carbothioamide* (**36b**). Solvent: 50% aq. EtOH, 23°. Yield: 75%. M.p. 149–151° ([11]: 149–150°). UV (MeOH): 326. FT-IR: 3382 (OH), 3223 (NH), 3047 (NH), 2928, 1557, 1504, 1477, 1417, 1293, 1142, 751, 711, 692. ^{1}H-NMR (CDCl$_3$): 11.24 (*s*, exchangeable, NH); 10.68 (*s*, exchangeable, OH); 8.31 (*d*, *J* = 7.0, 1 H); 8.05 (*s*, CH=N); 7.76 (*Ψt*, 1 H); 7.67–7.71 (*m*, 2 H); 7.47 (*d*, *J* = 7.0, 2 H); 7.45 (*Ψt*, 2 H); 7.34 (*Ψt*, 1 H). Immediately forms varying amounts of **36a** when dissolved in (D$_6$)DMSO, by NMR: ^{1}H-NMR ((D$_6$)DMSO): 11.99 (*s*, exchangeable, NH); 9.89 (*s*, very slowly exchangeable, NH); 8.26 (*s*, exchangeable, B(OH)$_2$); 8.23 (*s*, CH=N); 7.86 (*d*, *J* = 8.0, 2 H); 7.61–7.66 (*m*, 1 H); 7.36–7.42 (*m*, 5 H, 1 exchangeable); 7.17 (*Ψt*, 1 H); not in accordance with data in [11]. ^{13}C-NMR ((D$_6$)DMSO): 175.1 (C=S); 144.3; 139.1; 136.1; 131.8; 129.5; 128.7; 125.4; 124.0; 123.8; in accordance with data in [11] (compound solved by X-ray).

*[2,3,1]Benzodiazaborinino[2′,1′:5,6][1,3,5,2,6]oxadiazadiborinino[2,3-*a*][2,3,1]benzodiazaborinin-8-one* (**37**). Solvent: MeCN, 82°. Yield: 66%. M.p. >290° (Et$_2$CO). UV (MeOH): 287 (sh), 296, 329. FT-IR: 1751 (C=O), 1435, 1402, 1279, 782. ^{1}H-NMR (CDCl$_3$): 8.58 (*s*, CH=N); 8.26 (*d*, *J* = 7.5, 2 H); 7.92 (*Ψt*, 2 H); 7.87–7.82 (*m*, 4 H). ^{1}H-NMR ((D$_6$)DMSO): 8.31 (*s*, HC=N); 8.26 (*d*, *J* = 7.5, 2 H); 7.83–7.72 (*m*, 6 H). ^{13}C-NMR ((D$_6$)DMSO): 153.8 (C=O); 143.8 (C=N); 133.7; 133 (br., C–B); 131.2; 130.5; 130.1; 127.2. X-Ray crystal structure determined.

*[2,3,1]Benzodiazaborinino[2′,1′:5,6][1,3,5,2,6]oxadiazadiborinino[2,3-*a*][2,3,1]benzodiazaborinine-8-thione* (**38**). Solvent: MeCN, 82°. Yield: 88%. M.p. >260°. UV (MeOH): 284, 345. FT-IR: 1484, 1422, 1395 (C=S), 1226, 1127, 899, 771. ^{1}H-NMR ((D$_6$)DMSO): 8.33 (*s*, CH=N); 8.17 (*d*, *J* = 6.5, 2 H); 7.75–7.65 (*m*, 6 H). ^{13}C-NMR ((D$_6$)DMSO): 185.8 (C=S); 145.7; 135 (br., C–B); 132.8; 130.6; 130.5; 130.3; 127.0.

*5,11-Dimethyl[2,3,1]benzodiazaborinino[2′,1′:5,6][1,3,5,2,6]oxadiazadiborinino[2,3-*a*][2,3,1]benzodiazaborinin-8-one* (**39**). Solvent: MeCN, 82°. Yield: 82%. M.p. >260°. UV (MeOH): 288(sh), 296, 326. FT-IR: 1748 (C=O), 1486, 1456, 1425, 1405, 1365, 1321, 1129, 783, 732. ^{1}H-NMR (CDCl$_3$): 8.51 (*d*, *J* = 7.5, 2 H); 7.96 (*d*, *J* = 7.5, 2 H); 7.88 (*Ψt*, 2 H); 7.78 (*Ψt*, 2 H); 2.83 (*s*, Me). ^{1}H-NMR ((D$_6$)DMSO): 8.29 (*d*, *J* = 7.5, 2 H); 7.90 (*d*, *J* = 8.0, 2 H); 7.80–7.72 (*m*, 4 H); 2.61 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 151.2 (C=O); 133.5; 132.2; 130.2; 126.2; 21.0. Weakly active against *E. coli*.

*5,11-Dimethyl[2,3,1]benzodiazaborinino[2′,1′:5,6][1,3,5,2,6]oxadiazadiborinino[2,3-*a*][2,3,1]benzodiazaborinine-8-thione* (**40**). Solvent: 50% aq. EtOH, 23°. Yield: 91%. M.p. >260°. UV (MeOH): 283, 345. FT-IR: 1494, 1443, 1354, 1277 (C=S), 1018, 823, 773. ^{1}H-NMR ((D$_6$)DMSO): 8.16 (*d*, *J* = 6.5, 2 H); 7.79 (*d*, *J* = 7.5, 2 H); 7.65–7.68 (*m*, 4 H); 2.58 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 183.5 (C=S); 151.7; 137.5 (br., C–B); 132.7; 130.6; 130.2; 125.8; 20.3. HR-ESI-TOF-MS: 345.1159 ([*M* + H]$^+$, $C_{17}H_{15}B_2N_4OS^+$; calc. 345.1147), 367.0992 ([*M* + Na]$^+$, $C_{17}H_{14}B_2N_4NaOS^+$, calc. 367.0967).

*Bisthieno[3′,2′:4,5][1,2,3]diazaborinino[3,2-*b*:2′,3′-*e*][1,3,5,2,6]oxadiazadiborinin-7-one* (**41**). Solvent: EtOH, 23°. Yield: 99%. M.p. >260°. UV (MeOH): 299, 350. FT-IR: 1755 (C=O), 1494, 1416, 1364, 1334. ^{1}H-NMR (CDCl$_3$): 8.71 (*s*, 2 H); 7.89 (*d*, *J* = 4.8, 2 H); 7.83 (*d*, *J* = 4.8, 2 H). ^{1}H-NMR ((D$_6$)DMSO): 8.62 (*s*, 2 H); 8.05 (*d*, *J* = 4.8, 2 H); 7.73 (*d*, *J* = 4.8, 2 H). ^{13}C-NMR ((D$_6$)DMSO): 153.5 (C=O); 144.2; 139.7 (br., C–B); 137.3; 131.9; 129.1.

*2-(4-Amino-5-sulfanyl-4*H*-1,2,4-triazol-3-yl)-6-methoxy-2,3,1-benzodiazaborinin-1(2*H*)-ol* (**42b**). Solvent: EtOH, 78°. Yield: 84%. M.p. >300°. UV (MeOH): 271. FT-IR: 3313, 3196, 1614, 1580, 1553,

1373, 1282, 1083, 956. ^{1}H-NMR ((D$_6$)DMSO): 13.8 (*s*, exchangeable, SH); 9.22 (*s*, exchangeable, OH); 8.24 (*d*, *J* = 8.3, 1 H); 8.16 (*s*, CH=N); 7.39 (*d*, *J* = 2.0, 1 H); 7.25 (*dd*, *J* = 8.3, 2.0, 1 H); 5.44 (*s*, exchangeable, NH); 3.90 (*s*, MeO). ^{13}C-NMR ((D$_6$)DMSO): 165.9; 162.2; 149.7; 141.1; 137.1; 133.7; 122 (br., C–B); 118.4; 110.2; 55.4 (Me). HR-ESI-TOF-MS: 291.0833 ([*M* + H]$^+$, $C_{10}H_{12}BN_6O_2S^+$; calc. 291.0830).

*Methyl 3-(1-hydroxy-6-methoxy-2,3,1-benzodiazaborinin-2(1*H*)-yl)thiophene-2-carboxylate* (**43**). Solvent: MeOH, 23°. Yield: 27%. M.p. 127–129°. UV (MeOH): 357. FT-IR: 1364 (OH), 1705 (C=O), 1395, 1262, 1250. ^{1}H-NMR ((D$_6$)DMSO): 8.73 (*s*, exchangeable, OH); 8.24 (*d*, *J* = 8.5, 1 H); 8.06 (*s*, HC=N); 7.85 (*d*, *J* = 5.5, 1 H); 7.32 (*s*, 1 H); 7.21–7.25 (*m*, 2 H); 3.89 (*s*, MeO); 3.34 (*s*, MeOCO).

*8-Methoxy-13*H*-thieno[3′,2′:4,5][1,3,2]oxazaborinino[2,3-*a*][2,3,1]benzodiazaborinin-13-one* (**44**). Solvent: MeCN, 82°. Yield: 58%. M.p. 251–253°. UV (MeOH): 271. FT-IR: 1708 (C=O), 1559, 1496, 1348, 1176, 1025, 774. ^{1}H-NMR ($CDCl_3$): 8.33 (*s*, CH=N); 8.31 (*d*, *J* = 8.5, 1 H); 7.84 (*d*, *J* = 5.4, 1 H); 7.71 (*d*, *J* = 5.4, 1 H); 7.34 (*dd*, *J* = 8.3, 2.2, 1 H); 7.22 (*d*, *J* = 2.2, 1 H); 3.98 (*s*, MeO). HR-ESI-TOF-MS: 285.0509 ([*M* + H]$^+$, $C_{13}H_{10}BN_2O_3S^+$; calc. 285.0500), 307.0418 ([*M* + Na]$^+$, $C_{13}H_9BN_2NaO_3S^+$; calc. 307.0319).

Antimicrobial Susceptibility Testing. Minimal inhibitory concentrations (*MIC*s) for *E. coli* ATCC#25922 strain (*ATCC*, Manassas, VA) were determined by broth microdilution procedures based on CLSI standards [19], with modifications [20]. To determine *MIC*s against *M. smegmatis* ATCC#700084 (*ATCC*, Manassas, VA), the broth microdilution method was further modified according to an accepted protocol [21]. Briefly, the *M. smegmatis* stock was streaked onto sheep blood agar plates (*Hardy Diagnostics*, Santa Maria, CA), which were incubated for 2 d at 35° to obtain discrete colonies. To prepare inoculum for *MIC* assays, 3–5 similar colonies were taken with a sterile disposable inoculation loop and inoculated into a 125-ml *Erlenmeyer* flask containing 10 ml of tryptic soy broth and incubated at 35° in a shaker/incubator for 18–24 h until its OD_{600} reached 0.08–0.1. Compounds were initially dissolved in 100% DMSO and subsequently diluted into a series of two-fold dilutions using 5% DMSO. After the inoculum with appropriate $5 \cdot 10^5$ CFU ml^{-1} was combined with serial dilutions of compound in microplates, the microplates were incubated at 35°, and *MIC* values were read at 72 h. The *MIC* was the lowest concentration of a given compound which prevented visible growth of *M. smegmatis* at the incubation time point.

X-Ray Crystallography. Crystals suitable for data collection were mounted in the N_2 cold stream provided by *Cryo Industries* low-temp. apparatus on the goniometer head of a *Bruker ApexII* diffractometer. Data were collected with the use of a MoK_α sealed tube. A multi-scan absorption correction was applied using the program SADABS 2008/2 [22]. The structures were solved by direct methods (SHELXS-97) [23] and refined by full-matrix least-squares on F^2 (SHELXL-97 (**17c**) [23] or SHELXL-2012 (**37**) [24]). Anisotropic thermal parameters were used for all non-H atoms. The H-atoms were treated as riding on their parent C-atoms. Crystal data are compiled in *Table 1*. CCDC-973490 and -973491 contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk.

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