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Boron Heterocycles Derived from 2-Guanidinobenzimidazole

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ABSTRACT: *The syntheses and structure determinations of a series of boron heterocycles derived from 2-guanidinobenzimidazole* **1** *are reported. Structures of new compounds, 2-guanidino-1-methyl-benzimidazole* **2,** *diphenyl-(2-guanidinobenzimidazole-N,N′)-borate* **3,** *diphenyl-(2-guanidino-1-methyl-benzimidazole-N,N′)borate* **4,** *hydroxy-phenyl-(2-guanidinobenzimidazole-N,N′)borate* **5,** *hydroxy-phenyl-(2-guanidino-1-methyl-benzimidazole-N,N′)borate* **6,** *methoxy-phenyl-(2-guanidinobenzimidazole-N,N′)borate* **7,** *isopropoxy-phenyl-(2-guanidinobenzimidazole-N,N′)borate* **8,** *acetoxy-phenyl-(2-guanidinobenzimidazole-N,N′)borate* **9,** *methoxy-phenyl-(2-guanidino-1-methyl-benzimidazole-N,N′)borate* **10,** *dihydroxy-(2-guanidino-1-methyl-benzimidazole-N,N′) borate* **16,** *difluoro-(2-guanidinobenzimidazole-N,N′)borate,* **17,** *dihydroxy-(2-guanidino-1-benzimidazole-N,N′)borate potassium salt* **19,** *diphenyl-(2-guanidinium-10H-benzimidazole-N,N′)borate hydrochloride* **20,** *methoxy-phenyl-(2-guanidinobenzimidazole-N,N′)borate hydrochloride* **21,** *and N10-borane-(diphenyl-2-guanidinobenzimidazole-N,N′)borate* **22,** *were determined based on* ^{1}H, ^{13}C, ^{15}N, *and* ^{11}B *spectroscopy. The X-ray diffraction structures of* **3–7,** **19,** *and* **20** *were obtained. The formation of N3-borane adducts* **11** *and* **12** *derived from compounds* **1** *and* **2,** *respectively, and the dihydride-(2-guanidinobenzimidazole-N,N′)borate* **13** *and dihydride-(2-guanidino-1-methyl-benzimidazole-N,N′)borate* **14** *were observed by* ^{11}B *NMR. The results show that 2-guanidinobenzimidazole gives stable borate heterocycles with a delocalized π electronic system. A dynamic exchange of N–H protons was observed with preferred protonation at N-12. The new heterocycles are protonated at N-10 by acidic substances to give pyridinium-type heterocycles or can lose a proton to give iminium salts.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:399–409, 1998

INTRODUCTION

2-Guanidinobenzimidazole **1** is a planar delocalized ligand formed with sp^2 nitrogen and carbon atoms that gives very stable metallic complexes by coordination to the lone pair of an imidazolic nitrogen atom and substitution of one acidic N–H of a guanidinic group [1,2]. It was of interest to investigate the ability of compound **1** to form diamagnetic complexes by coordination with acidic boron atoms such as boron difluoride, boron diphenyl, and boron hydroxyphenyl, which are models of metallic coordination easily studied by NMR techniques. Com-

Dedicated to Professor Heinrich Nöth on the occasion of his seventieth birthday.

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pound **1** is a complex molecule that can be depicted by several conformers and tautomers. In order to understand the complexing behavior of **1** in solution, we have previously studied the more stable conformers and tautomers in solution and prepared some diamagnetic metallic complexes [2].

To simplify the tautomeric behavior of compound **1,** the methylated compound **2** was prepared by treatment of the 2-guanidinobenzimidazole **1** with sodium, followed by methyl iodide, and then the analogous boron heterocycles were prepared.

RESULTS AND DISCUSSION

We have reacted compounds **1** and **2** with diphenylborinic and phenylboronic acids in THF or THF/methanol and at room temperature. The reaction products **3–6** are stable solids, and their structures were determined from the NMR spectra in DMSO-d6 solution and from X-ray diffraction studies (Figure 1).

The ^{11}B NMR spectra of compounds **3–6** show broad signals between +0.2 and 2.5 ppm characteristic of borates (Table 1). The ^{1}H NMR spectra of **3** and **5** did not show the tautomeric equilibria of imidazolic heterocycles, indicating a strong coordination of the imidazolic nitrogen atom. The four aromatic C–H protons of the benzimidazole and all the N–H groups present different resonances (Tables 2–4). Five H-tautomers (**I–V**) for the boron heterocycles **3** and **5** and four tautomers (**I–IV**) for **4** and **6** can be depicted (Figure 2).

In the ^{1}H NMR spectrum of **3** in DMSO-d6 taken at room temperature (Table 3), three N–H signals are observed that were attributed to an imidazolic N–H (δ = 11.81 ppm), a signal for an NH_2 group at 6.23 ppm, and another for one N–H at 6.42 ppm. The latter data could only be attributed to tautomers **I** and **IV.** In order to know which of them predominates, we examined the ^{13}C NMR spectra (Table 4), where all the carbon atoms have different chemical shifts. The ^{13}C δ of the C-2 in **3–6** compared with the same data in protonated **20** or coordinated species such as **22** or the zinc complex [2] (vide infra) were used as a probe to identify the protonation site (Figure 3). If N-10 is protonated or coordinated, its chemical shift appears between 143 and 149 ppm. This is not the case in compounds **3–6** that give a signal near 155 ppm (Table 4). The same preferred N-12 protonated tautomers (**I**) were also found in the solid state, as is shown from the X-ray diffraction structure of compounds **3–6** (Figures 4–7).

The X-ray diffraction structures of **3–6** (Figures 4–7, Tables 5–7) showed a tetracoordinated boron atom, the two boron–nitrogen bond lengths in each compound being similar, and they have an average value between a covalent and a coordinated bond (they were found in the range 1.55–1.57 Å). For the four compounds **3–6**, the N3–C2, N1–C2, N10–C2,

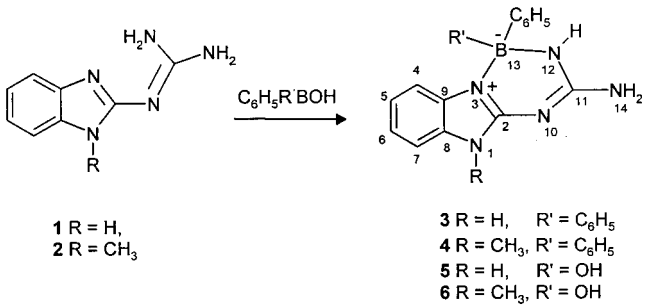

FIGURE 1 Reaction of compounds **1** and **2** with diphenylborinic and phenylboronic acids.

TABLE 1 ^{11}B NMR Data, δ(ppm), DMSO-d6

Compd.		*Compd*		*Compd*		*Compd*	
3	−2.5	**9**	0.1	**15**	1.8	**21**	0.8
4	−1.8	**10**	0.6	**16**	0.5	**22**	−2.5, −22.3
5	−1.8	**11**	−20.5	**17**	0.8	**23**	−2.6, +6.7
6	0.2	**12**	−21.8	**19**	−1.0	**24**	−2.6
7	0.8	**13**	−12.1	**20**	−1.5	**25**	+0.6
8	0.5	**14**	−10.5				

TABLE 2 ^{15}N NMR Data, δ(ppm), DMSO-d6

Compd.	*NH_2*	*NH-1*	*NH-12*	*Compd.*	*NH_2*	*NH-12*
2	−302.1			**17**	−299.0	
3	−300.1		−277.4	**20**	−300.5	−272.3
4	−301.2		−279.4	**22**	−299.8	−276.8
5	−303.3	−240.0				

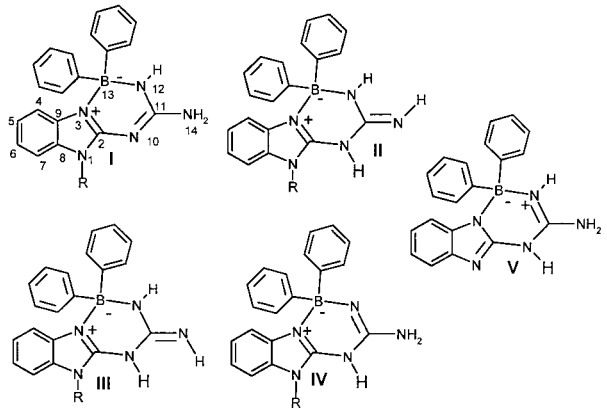

FIGURE 2 Proton tautomers for compounds **3** and **4.**

TABLE 3 ^{1}H NMR Data, in DMSO-d6 with TMS as an External Reference

Compd.	*NH-1*	*NH-10*	*NH-12*	*NH_2-14*	*H-4*	*H-5*	*H-6*	*H-7*	*CH*
1	11.12			6.89	7.20	6.92	6.92	7.20	
2				7.00	7.27	6.97	6.99	7.27	3.53
3	11.81		6.42	6.23	6.68	6.81	6.96	7.17	
4			6.45	6.33	6.71	6.85	7.02	7.08	
5	11.60		7.40	6.10	6.80	6.90	7.11	7.11	
6			6.19	6.28	7.44	7.06	7.06	7.29	
7	11.79		6.35	6.12	7.02	7.02	7.02	7.40	
8	11.64		6.10	6.19	6.92	6.92	6.92	6.92	0.70, 3.50
9	11.66		6.58	6.88	7.16	7.16	7.16	7.16	
10			5.75	6.39	7.04	7.04	7.04	7.42	
16			6.67	6.41	7.25	7.25	7.25	7.40	
17	12.00		6.53	6.89	7.34	7.15	7.15	7.26	
19		8.70		7.60	7.69	7.28	7.28	7.43	
20	11.80	8.37	7.58	7.67	6.80	7.20	7.20	7.20	
21	12.80	8.02	7.87	7.58	7.17	7.17	7.17	7.80	
22	12.33		6.77	6.73	6.97	7.21	7.21	7.21	
24	11.50		6.40	6.40	6.75	6.40	6.40	6.40	
25[a]			7.20	7.20	7.20	7.20	7.20	7.20	

[a]NH-1 not observed, broad signals.

TABLE 4 ^{13}C NMR Data, in DMSO-d6 with TMS as an External Reference

Compd.	*C-2*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-11*	*CH_3, CO*
1	158.90	111.69	119.36	119.36	111.69	135.70	135.70	158.73	
2	157.99	114.95	118.89	120.04	107.47	133.47	141.34	158.72	27.76
3	154.78	112.95	120.69	120.79	109.84	131.16	133.91	159.54	
4	154.12	112.92	120.78	121.28	108.64	(b)	132.78	159.64	
5	154.65	113.16	120.57	120.85	109.52	130.90	133.42	159.56	
6	154.69	113.71	121.43	121.74	108.39	132.75	133.04	160.37	
7	155.48	112.56	120.81	121.11	109.85	131.75	133.04	160.74	
8	155.27	113.77	120.59	120.90	109.47	130.58	133.32	160.32	
9	154.53	112.37	121.01	121.41	109.85	130.68	132.41	159.84	171.98
10	154.61	112.53	121.06	121.41	108.54	131.76	131.99	160.76	
16	153.53	111.22	121.73	121.73	109.11	130.61	131.80	159.54	27.68
17	154.62	112.49	122.00	122.60	110.62	130.43	131.38	160.52	
19	150.47	111.96	122.83	123.85	111.35	127.14	129.29	156.16	
20	143.05	114.61	123.46	124.00	112.63	130.06	131.97	151.52	
21	145.88	115.75	124.82	125.32	113.69	131.89	132.26	150.63	
22	149.05	114.21	122.53	122.53	112.17	130.50	132.97	155.47	
24	155.66	112.25	118.91	120.05	109.56	132.89	137.76	158.52	
25[a]	153.42	112.68	121.62	122.11	110.14	130.62	132.46	159.00	

[a]Aminothiophenol: 127.80 (C-16), 114.80 C(17), 123.19 (C-18), 123.52 (C-19), 104.56 (C-20), 150.23 (C-21).

and N10–C11 bond lengths are very similar (between 1.33 and 1.37 Å), typical of a delocalized allylic system; the shortest bond is N12–C11 (around 1.32 Å): (Table 5). The boron atom has a borate structure with a formal negative charge, whereas a formal positive charge could be distributed between N3, C2, C11, and N12; however, the ^{13}C δ of C-11 does not change from the free 2-guanidine (159.5 ppm) to the boron complexes (159.5 ppm), whereas the C-2 resonances changes from 160 to 155 ppm. The latter fact indicates that the charge separation between the boron and the ring atoms is negligible. Similar delocalized systems for boron heterocycles have been reported and are depicted in Figure 8 [3–5].

To check the reactivity of the OH group in heterocycles **5** and **6** we have reacted compound **5** with methanol, isopropyl alcohol, and acetic acid in toluene with use of a Dean Stark trap to obtain the corresponding esters **7** and **8** and the anhydride **9.** Compound **6** was reacted with methanol to give compound **10** (Figure 9). The structures of the reaction products were deduced from the NMR data and the X-ray diffraction structure of compound **7** (Figure 10). The esters and the anhydride were sen-

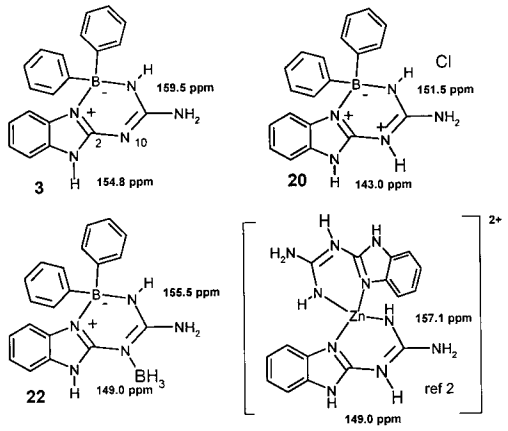

FIGURE 3 ^{13}C chemical shifts of C-2 and C-4 in boron and zinc heterocycles.

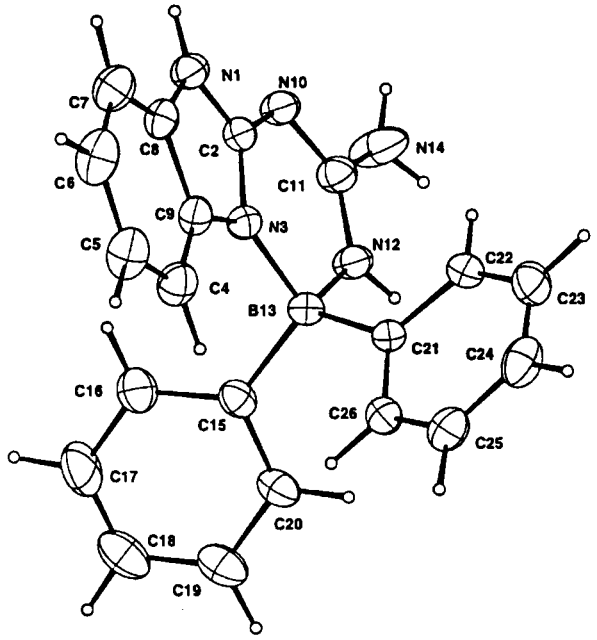

FIGURE 4 Structure of **3** obtained by X-ray diffraction analysis.

sitive to hydrolysis. The synthesis of an analogous borate ester is shown in Figure 8 [3–5].

The esterification mechanism must involve a stable aromatic intermediate with a planar boron atom, but we were unable to isolate such structures even after several attempts to prepare them. However, these aromatic structures were the parent peaks in the mass spectra of compounds **3, 4, 14,** and **17** (Figure 11). It is assumed that these compounds were not observed in the reaction mixtures because they add protonated substances (HY) very fast, as shown in Figure 11. We have tried to dehydrate compound

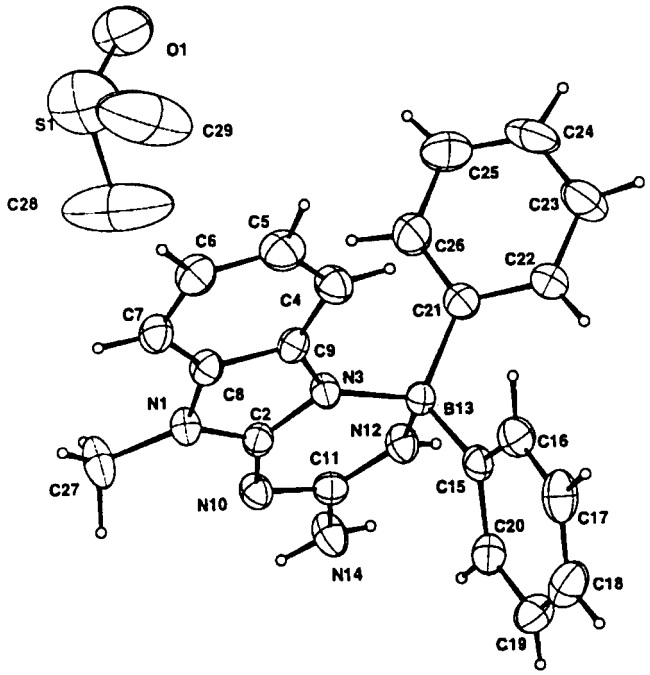

FIGURE 5 Structure of **4** obtained by X-ray diffraction analysis.

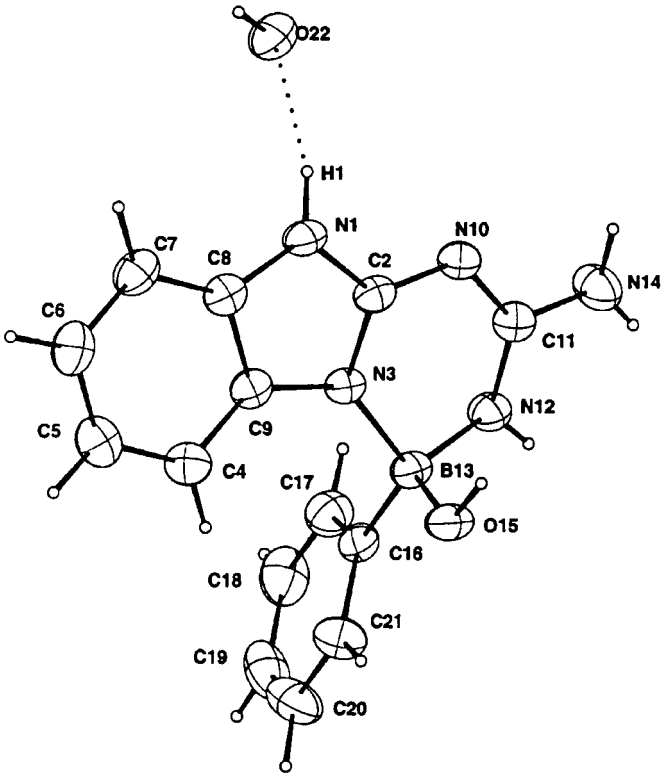

FIGURE 6 Structure of **5** obtained by X-ray diffraction analysis.

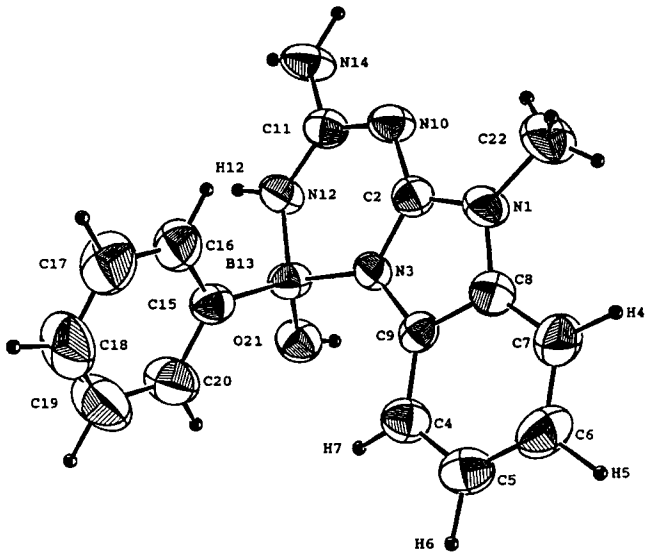

FIGURE 7 Structure of **6** obtained by X-ray diffraction analysis.

5 by heating it in the presence of dehydrating agents or by reacting compound **1** with dichlorophenylborane in the presence of base, but both attempts were unsuccessful. A similar equilibrium has been reported before for oxazaborolidines [6].

We have synthesized other boron derivatives to obtain information about the stability of the boron heterocycles. In particular, we have tried to prepare the boron hydrides by the reactions of **1** and **2** with BH_3 THF. The first reaction products observed by ^{11}B NMR spectroscopy were the N–BH_3 adducts **11** and **12** of the imidazole group (Figure 12), which gave a quartet in the ^{11}B NMR spectra (δ −20.5 and −21.8 ppm, respectively). These adducts are not stable because they react with the acidic guanidinic protons. Some few hours later the solutions of compounds **11** and **12** evolved to the boron heterocycles **13–14.** After that, the solutions gave a precipitate attributed to intractable material. Addition of water afforded the amides (**15,** ^{11}B $\delta = -1.8$; **16,** 0.5 ppm). Evidence for compounds **11–15** was only obtained by ^{11}B NMR spectroscopy. Our efforts to produce the amides **15–16** directly by reactions of **1** and **2** with boric acid did not yield good results.

The stability of the phenyl boron heterocycles could be attributed to the strong acidity of the boron atom produced by the electron-withdrawing behavior of the phenyl group. Therefore, it was assumed that the presence of a difluoroboron group could also give stable heterocycles. We performed the reaction of compound **1** with two equivalents of BF_3–OEt_2 that afforded the BF_2 heterocycle plus the protonated tetrafluoroborate derivative **18.** Compound **17** was separated from the reaction mixture using an alkaline chromatographic column (Figure 13).

Reaction of the difluoroboron compound **17** with K_2CO_3 in a THF–water solution for 45 days gave colorless crystals. We have found that the product is the potassium salt **19** of the dihydroxyborate. The N–H protons were located in the X-ray diffraction structure, indicating only one N–H group and that the protonation site was found to be N-12 instead of N-1. Two hydrogen bonds were found between the solvated potassium atom and the NH_2 and N-H groups (Figures 14 and 15).

We were interested in evaluating the basic properties of these boron heterocycles; therefore, we decided to prepare the hydrochloride derivatives **20** and **21** of compounds **3** and **7** by reaction of these compounds with HCl in THF-methanol. After 24 hours, some colorless crystals were formed. Compound **21** was analyzed by X-ray diffraction (Figures 16 and 17), (Table 8).

The basicity of the sp^2 nitrogen 10 could be evaluated through the N–BH_3 adduct formation. Therefore, we have added one equivalent of BH_3 THF to compounds **3** and **5** and followed the reaction by ^{11}B NMR spectroscopy. The reaction of compound **3** with borane gave adduct N–BH_3 **22,** which is a yellow solid unstable to the air and soluble in THF, which presented two signals in the ^{11}B NMR spectrum ($\delta = +2.5$ and -22.3 ppm). For compound **5,** we have not observed the N-borane adduct but rather a BH_2 derivative, which presents in the ^{11}B NMR spectrum, in addition to the borate signal, a broad resonance at $+6.7$ ppm. Due to geometric restrictions of the possible rings formed, we assumed that **23** could be an eight-membered ring dimer, as depicted in Figure 18.

The possibility to link two 2-guanidinobenzimidazole molecules to one boron atom in order to obtain spiranic structures [7] was investigated. When two equivalents of compound **1** were reacted with one of borane and the solution was heated at 100°C, a sharp signal appeared in the ^{11}B NMR spectrum ($\delta = -2.6$ ppm), which corresponds to a spiranic compound **24** (Figure 19). The structure was confirmed by the ^{13}C and ^{1}H NMR spectra that showed different chemical shifts from that of compound **15.** Compound **24** has several tautomers because the N–H moieties are in equilibrium among the available lone pairs of the nitrogen atoms.

Another spiranic compound **25** was prepared by reaction of compound **1** with the 1,3,2-benzothiazaborole **26** [8], which has been identified by NMR spectroscopy (Figure 20).

TABLE 5 Bond Lengths of Boron Ring in the X-ray Diffraction Structures

Compd.	**3**	**4**	**5**	**6**	**7**	**19**	**21**
N1–C2	1.352(3)	1.366(9)	1.355(3)	1.364(8)	1.353(4)	1.34(1)	1.338(4)
N3–C2	1.346(3)	1.351(9)	1.345(3)	1.350(9)	1.345(5)	1.32(1)	1.332(4)
N3–B	1.568(3)	1.570(1)	1.571(3)	1.577(9)	1.568(5)	1.48(8)	1.604(4)
N12–B	1.566(3)	1.560(1)	1.560(3)	1.55(1)	1.550(5)	1.45(1)	1.546(5)
N10–C2	1.336(3)	1.329(9)	1.339(3)	1.33(1)	1.342(5)	1.35(1)	1.341(4)
N10–C11	1.334(3)	1.345(9)	1.340(3)	1.352(8)	1.347(4)	1.34(1)	1.374(4)
N14–C11	1.349(4)	1.350(1)	1.342(3)	1.33(1)	1.348(5)	1.34(1)	1.315(5)
N12–C11	1.318(3)	1.320(1)	1.327(3)	1.322(9)	1.314(5)	1.33(1)	1.322(4)
B–Ci	1.620(4)	1.620(1)	1.607(3)	1.60(1)	1.607(6)		1.623(5)
B–O			1.560(3)	1.447(9)	1.447(5)		1.430(5)

TABLE 6 Selected Bond Angles of the X-ray Diffraction Structures

Compd.	**3**	**4**	**5**	**6**	**7**	**19**	**21**
C2-N3-C9	107.4(2)	106.9(6)	107.6(2)	107.5(5)	107.2(3)	108.4(6)	107.1(3)
C9-N3-B	129.2(2)	131.1(6)	130.4(2)	129.1(6)	128.5(3)	128.9(6)	132.4(3)
C11-N12-B	126.9(2)	126.7(6)	125.1(2)	129.2(6)	128.1(3)	126.8(7)	126.2(3)
N1-C2-N3	109.9(2)	199.5(7)	110.0(2)	109.7(6)	110.5(3)	109.0(7)	110.6(3)
N3-C2-N10	127.3(2)	129.0(7)	127.3(2)	127.8(6)	126.5(3)	126.7(7)	123.5(3)
N1-C8-C9	106.0(2)	106.3(6)	106.4(2)	105.8(6)	106.9(3)	106.9(7)	105.9(3)
N3-C9-C4	131.4(3)	130.8(7)	131.9(2)	131.5(6)	130.8(3)	132.7(7)	132.3(3)
N10-C11-N14	115.9(2)	116.2(7)	116.8(2)	116.9(6)	115.5(4)	118.3(7)	117.9(3)
O-B-N3			110.7(2)	111.4(6)	111.8(3)	111.2(7)[g]	110.5(3)
N3-B-N12	102.2(2)	101.0(6)	101.0(2)	100.9(6)	101.2(3)	104.5(6)	101.4(2)
N3-B-C	111.7(2)[b]	110.0(6)[b]	111.9(2)[a]	110.8(5)[b]	110.5(3)[b]		110.4(3)[c]
C2-N1-C8	108.8(2)	108.6(6)	108.4(2)	108.5(6)	107.9(3)	109.2(6)	109.0(3)
C2-N3-B	123.0(2)	121.6(6)	122.0(2)	123.4(6)	124.3(3)	122.3(7)	120.3(3)
C2-N10-C11	115.6(2)	113.4(6)	114.9(2)	114.7(6)	115.0(3)	113.2(6)	120.7(3)
N1-C2-N10	122.8(2)	121.4(7)	122.6(2)	127.8(6)	123.0(3)	124.3(7)	125.9(3)
N3-C9-C8	107.9(2)	108.7(6)	107.6(2)	108.5(6)	107.5(3)	106.4(7)	107.4(3)
N10-C11-N12	124.7(2)	125.0(7)	123.8(2)	123.6(7)	124.3(4)	122.9(8)	117.5(3)
N12-C11-N14	119.55(3)	118.8(7)	119.4(2)	119.6(6)	120.2(4)	118.8(7)	124.6(3)
O-B-N12			111.4(2)	112.3(6)	111.9(3)	108.6(7)[g]	112.9(3)
O-B-C			110.2(2)[a]	109.6(6)[b]	110.0(3)[b]		109.5(3)[c]
N12-B-C	109.1(2)[b]	110.3(7)[b]	111.3(2)[a]	111.8(7)	111.2(3)		111.9(3)[c]
C15-B-C21	114.9(2)	115.7(6)					
N12-B-C21	110.4(2)	107.8(6)					
N3-B-C21	107.8(2)	111.1(6)					
C2-N1-C		124.9(7)[d]		126.5(7)[e]			

[a]C16; [b]C15; [c]C17; [d]C-27; [e]C-22; [f]O25-B-O26 110.7(7), O26-B-N12 111.6(7), O26-B-N12 111.6(7); [g]O25.

In conclusion, we have found that the 2-guanidinobenzimidazole molecule is a versatile ligand that gives new stable and delocalized borate heterocycles. The boron heterocycles can behave as Lewis bases or protonic acids.

EXPERIMENTAL

Materials and Methods

All new compounds were characterized by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopy and by heteronuclear correlation experiments. Boron compounds were handled under a nitrogen atmosphere using carefully dried glassware and dried solvents. 2-Guanidinobenzimidazole is a commercial compound. BH_3 THF was prepared according to reported methods [9]. The IR spectra were taken as KBr discs or in CH_2Cl_2, THF, or $CHCl_3$ solution using a Perkin Elmer 16F PC spectrometer. The mass spectra were obtained to 70 eV in an HP 5989 spectrometer. The NMR spectra were obtained on a Jeol GSX 270 spectrometer, ^{1}H (270.05 MHz), ^{13}C (67.80 MHz), ^{11}B (86.55 MHz), ^{15}N (27.25 MHz). Elemental analyses were performed by Oneida Research Services, Whitesboro, New York.

TABLE 7 Crystal Data of **3–6**

	$C_{20}H_{18}BN_5$ (**3**)	$C_{21}H_{20}BN_5 \cdot C_2H_6OS$ (**4**)	$C_{14}H_{13}BN_5O \cdot H_2O$ (**5**)	$C_{19}H_{24}BN_5O_2$ (**6**)
fw	339.21	431.36	296.11	365.25
Space group	P-1	P-1	$P2_1/a$	C2/c
a (Å)	9.360(1)	9.793(5)	10.816(1)	22.430(4)
b (Å)	9.353(5)	11.296(4)	9.545(2)	8.818(2)
c (Å)	12.801(3)	11.496(4)	14.601(2)	18.856(4)
α (°)	70.97(2)	72.16(3)	90.00	90.00
β(°)	67.82(2)	85.49(3)	110.02(1)	103.00(3)
γ(°)	60.18(1)	73.32(3)	90.00	90.00
V(Å^3)	887.0(3)	1159.7(8)	1416.4(3)	3633.8(3)
Z	2	2	4	8
F(000)	356	456	620	1552
Linear abs coeff cm^{-1}	0.73	1.55	0.90	0.80
r (calc) g/cm^{-3}	1.27	1.23	1.39	1.34
Scan range	0.75 + 0.69tgθ	0.34 + 0.55tgθ	0.47 + 0.49tgθ	0.5 + 0.570tgθ
θ limits (°)	1.0–25.0	2.0–25.0	2.09–25.0	2.4–24.0
Octants collected	−11,10; −11, 10;15,0	−11,11; −12, 13;0,13	0,12; −11,0; −17,16	0,27;0,12; − 21,23
No. of data collected	3265	4290	2790	3137
No. of unique data collected	3110	4067	2489	2100
No. of unique data used	1936	1828	1663	1672
R(int)		1.37	0.65	
Decay (%)	<1	<1	<1	<1
R	0.039	0.085	0.034	0.089
R_w	0.038 $w = 1.0$	0.084 $w = 1.0$	0.034 $w = 1.0$	0.088 $w = 1.0$
Goodness of fits	3.25	4.22	2.40	1.69
No. of variables	290	341	245	267
$\Delta\rho$min(e/Å^3)	−0.19	−0.65	−0.15	−0.77
$\Delta\rho$max(e/Å^3)	0.48	1.071	0.28	0.68

Diffractometer CAD4-Enraf-Nonius; radiation MoK_α (1 = 0.71069 Å); scan type $\omega/2\theta$; crystal size 0.2 × 0.2 × 0.2 mm; the measurements were at room temperature.

2-Guanidino-1-methyl-benzimidazole **2.** A solution of 250 mg (1.4 mmol) of **1** in 20 mL of dry THF was reacted with 33 mg (1.4 mmol) of metallic sodium and refluxed for 5 hours. Then 200 mg of Na_2CO_3 and 0.9 mL (1.4 mmol) of CH_3I were added, and the reaction mixture was refluxed again for 30 minutes. The solvent was evaporated in vacuum, and a yellow powder was obtained that was dissolved in water and extracted with CH_2Cl_2. The organic solution was evaporated, a hygroscopic yellow solid being obtained: 158 mg (58%), mp 218–221°C, MS *m/z* (%) 189.4 (100). IR ν cm^{-1}, 3422 (N–H), 2926 (C–H), 1698 (C=N), 1636, 1542 (C=C), 1386, 1282 (C–N). $C_9H_{11}N_5$ (189.4). Calcd: C, 57.14; N, 37.03; H, 5.82; found: C, 57.03; N, 36.80, H, 5.84.

Diphenyl-(2-guanidinobenzimidazole-N,N′) borate **3.** A solution of 250 mg (1.4 mmol) of **1** in 20 mL of dry THF was reacted with 0.32 g (1.7 mmol) of diphenylborinic acid dissolved in 30 mL of methanol. The solvent was evaporated in vacuum, and a white solid was obtained (0.23 g, 48%). Compound **3** was recrystallized from a solution of 20 mL of ethanol and 10 mL of hexane to give colorless crystals, mp 273–277°C. IR ν cm^{-1}: 3382 (N–H), 1630, 1602 (C=N), 1288, 1148 (B–N). MS, *m/z,* (%): 338.1(1), 262 (100). $C_{20}H_{18}N_5B$ (339.2). Calcd: C, 70.82; N, 20.64; H, 5.34; found: C, 70.99; N, 20.63; H, 5.31.

Diphenyl-(2-guanidino-1-methyl-benzimidazole-N,N′)borate **4.** A solution of 160 mg (0.83 mmol) of compound **2** in 20 mL of dry THF was reacted with 0.32 g of diphenylborinic acid (1.7 mmol) dissolved in 30 mL of THF. The solvent was evaporated in vacuum, and a yellow solid was obtained (0.11 g, 37%). Compound **4** was recrystallized from a solution of 20 mL of DMSO, to give yellow crystals, mp 286–287°C. IR ν cm^{-1}: 3154 (N–H), 1654, 1624 (C=N), 1572, 1520 (C=C), 1176, 1132 (B–N). MS, *m/z,* (%): 352.3(1), 276.3 (100). $C_{21}H_{20}N_5B$ (353.21). Calcd: C, 71.41; N, 19.82; H, 5.70; found: C, 71.53; N, 19.83; H, 5.71.

Hydroxy-phenyl-(2-guanidinobenzimidazole-N,N′)borate **5.** A solution of 250 mg (1.4 mmol) of **1** in 20 mL of dry THF was reacted for 1 hour with 170 g (1.4 mmol) of phenylboronic acid dissolved in 20 mL of THF. A white precipitate was formed that was

TABLE 8 Crystal Data of **7, 19,** and **21**

	$C_{15}H_{16}BN_5O$ (**7**)	$C_8H_{25}BN_5O_9K$ (**19**)	$C_{15}H_{17}BClN_5O\cdot CH_3OH$ (**21**)
fw	293.4	385.22	361.64
Space group	P-1	C 2/c	P-2_1/a
a (Å)	8.293(3)	22.516(4)	13.326(2)
b (Å)	9.318(1)	6.477(7)	10.353(2)
c (Å)	11.168(2)	23.441(1)	14.410(2)
α(°)	71.29(1)	90.00	90.00
β(°)	79.19(2)	99.87(1)	112.23(1)
γ(°)	64.52(1)	90.00	90.00
V(Å^3)	748.63(6)	3368.0(1)	1840.33(1)
Z	2	8	4
Crystal size	0.1 × 0.1 × 0.1 mm	0.24 × 0.15 × 0.12 mm	0.2 × 0.2 × 0.2 mm
F(000)	308	1632	760
Linear abs coeff cm^{-1}	0.79	3.70	2.23
r (calc) g/cm^{-3}	1.30	1.55	1.31
Scan range	0.64 + 1.16tgθ	0.39 + 0.54tgθ	0.52 + 0.57tgθ
θ limits (°)	2.4–24	2.03–5	2–26
Octants collected	0,9–9,11;13,3	0,26; −7,0; −27,27	−16,0, −12,0;16,17
No. of data collected	2299	3330	3450
No. of unique data collected	2077	2460	3218
No. of unique data used	1158	2116	2325
R(int)	1.22	1.32	0.93
Decay (%)	2.34	<1	3.4
R	0.038	0.087	0.04484
R_w	0.039 w = 1.0	0.092 w = 1.0	0.0482 w = 1.0
Goodness of fits	0.64	3.91	1.57
No. of variables	248	268	287
$\Delta\rho$min (e/Å^3)	−0.16	−0.60	−0.27
$\Delta\rho$max(e/Å^3)	0.35	0.52	0.21

Diffractometer CAD4-Enraf-Nonius; radiation MoK_α (λ = 0.71069 Å); scan type $\omega/2\theta$; the measurements were at room temperature.

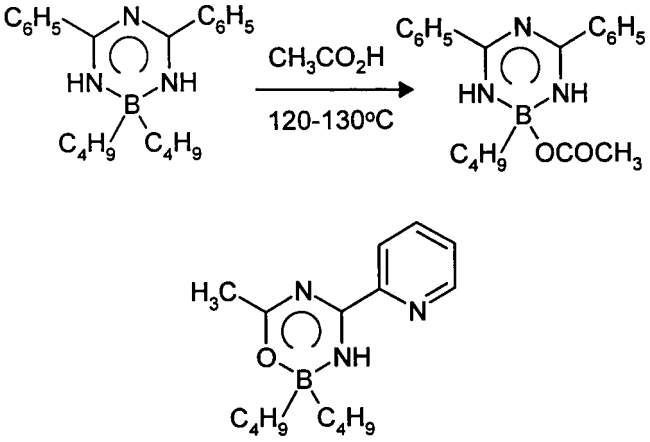

FIGURE 8 Boron delocalized heterocycles reported [3-5].

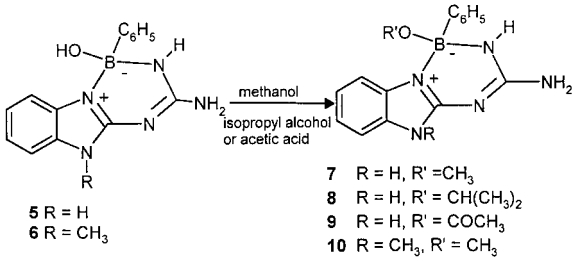

FIGURE 9 Compounds **5-6** give esters or anhydrides.

separated by filtration and dried in vacuum (240 mg, 52%). The solid was recrystallized from a saturated solution of THF. Dec. 250°C. IR ν cm^{-1}: 3378 (N–H), 1630, 1606 (C=N), 1596, 1516 (C=C), 1340 (B–O), 1142 (B–N). $C_{14}H_{14}N_5BO\cdot 1/4H_2O$ (283.6). Calcd: C, 59.29; N, 24.69; H, 5.06; found: C, 59.52; N, 23.97; H, 5.04.

Phenyl-(2-guanidino-1-methyl-benzimidazole-N,N′)borate **6.** A solution of 800 mg (0.95 mmol) of compound **2** in 20 mL of dry THF was reacted for 5 hours with 170 mg (1.4 mmol) of phenylboronic acid dissolved in 5 mL of THF. A white precipitate was formed that was separated by filtration and dried in vacuum (0.125 g, 30%). Dec. 270°C, IR ν cm^{-1}: 3376 (N–H), 1626, 1646 (C=N), 1580, 1542 (C=C), 1332 (B–O), 1196 (B–N).

Methoxy-phenyl-(2-guanidinobenzimidazole-N,N′)borate **7.** A solution of 0.24 g (0.85 mmol) of

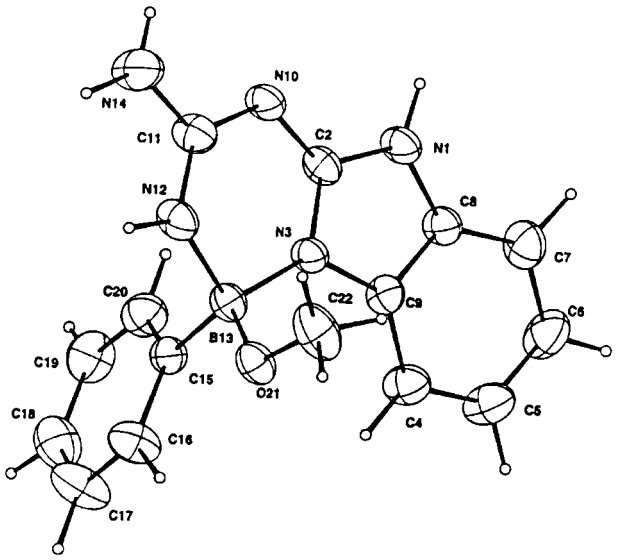

FIGURE 10 Structure of compound **7** obtained by X-ray diffraction analysis.

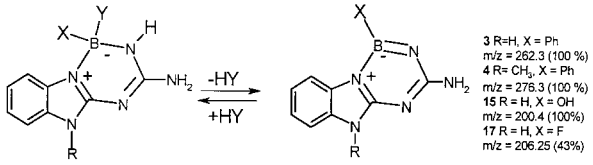

FIGURE 11 Proposed equilibria between the tetracoordinated borate heterocycles and the tricoordinated boron compounds. The parent peak of the mass spectra of some derivatives is given.

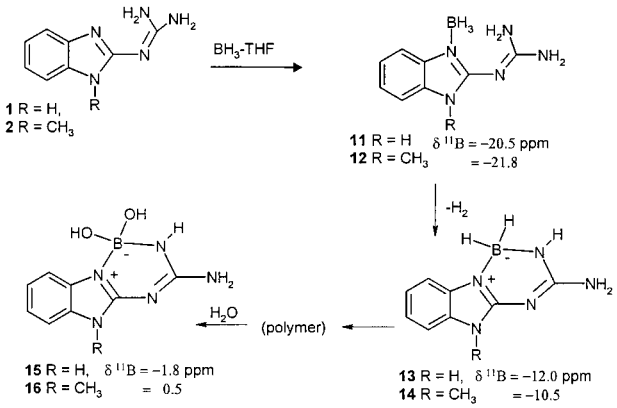

FIGURE 12 Products of the reaction of 1-2 with borane.

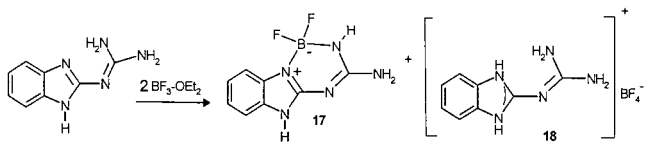

FIGURE 13 Products of the reaction of 1 with BF_3-OEt_2.

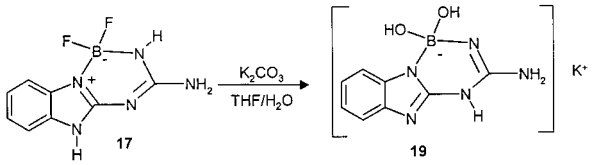

FIGURE 14 Alkaline hydrolosis of 17.

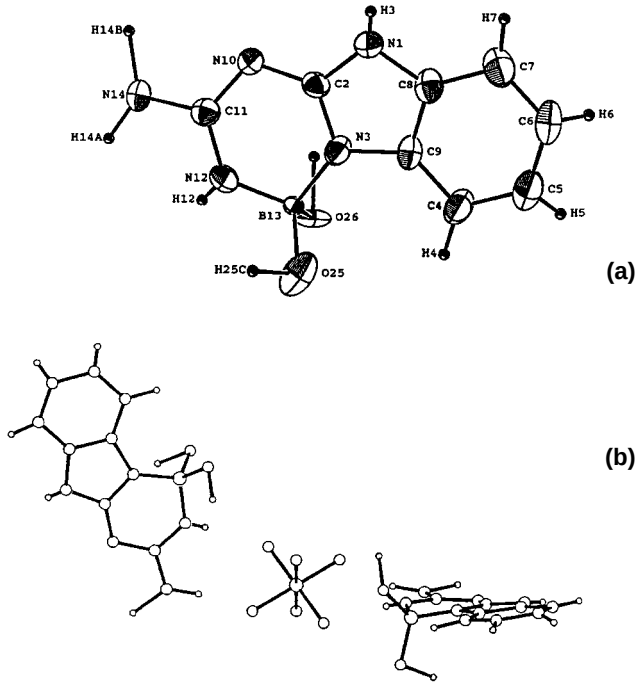

FIGURE 15 (a) Structure of **19** obtained by X-ray diffraction analysis. (b) View of the solvated potassium atom and two molecules of **19.**

compound **5** dissolved in 30 mL of dry methanol and 15 mL of dry toluene was refluxed for 7 hours with use of a Dean Stark trap, with molecular sieves present. The solvent was evaporated in vacuum, and a white solid was obtained (0.24 g, 83%). A mixture of compounds was detected by NMR spectroscopy, **7** (80%) and **5** (20%). The solid was recrystallized from methanol–THF (60/40) and then from dry methanol, and the crystals were suitable for the X-ray diffrac-

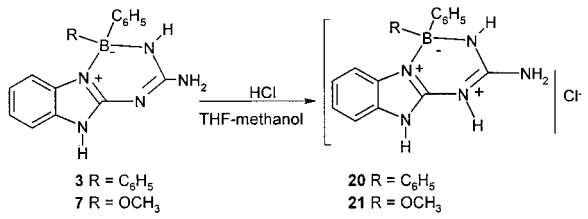

FIGURE 16 Protonation products of 3 and 7.

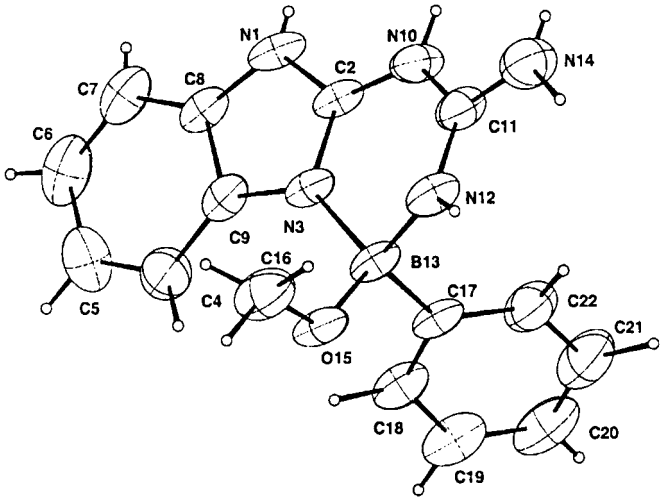

FIGURE 17 Structure of **21** obtained by X-ray diffraction analysis; the chloride anion is not shown.

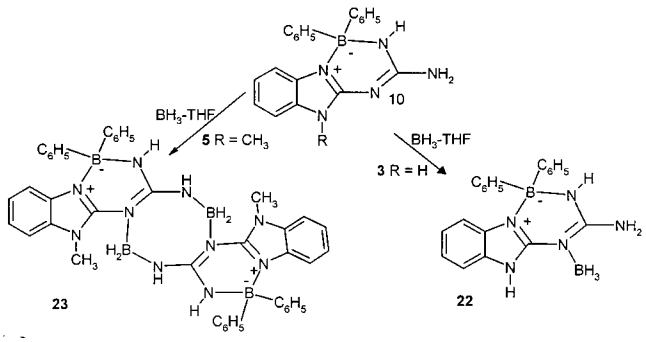

FIGURE 18 An eight-membered ring dimer.

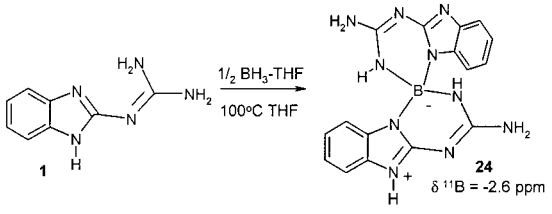

FIGURE 19 Spiranic compound **24.**

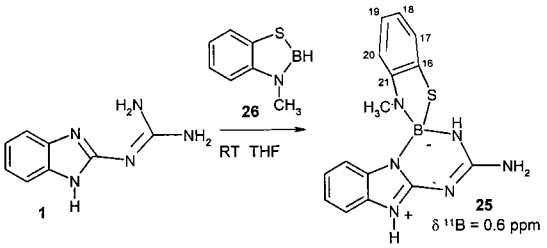

FIGURE 20 Spiranic compound **25** identified by NMR spectroscopy.

tion analysis. Dec. 280°C, IR ν cm^{-1}: 3080 (N–H), 1672 (C=N), 1506 (C=C), 1368 (B–O), 1198 (B–N).

Isopropoxy-phenyl-(2-guanidinobenzimidazole-N,N′)borate **8.** A solution of 0.25 g (0.78 mmol) of compound **5** in 30 mL of dry isopropyl alcohol and 25 mL of toluene was refluxed for 6 hours. The solution was evaporated partially, and a solid was precipitated by addition of 10 mL of hexane. A white solid was obtained (0.18 g, 73%). Dec. 279°C, IR ν cm^{-1}: 3390 (N–H), 1628, 1608 (C=N), 1584, 1550 (C=C), 1312, 1286 (B–O), 1170, 1126 (O–C), 1036, 1022 (B–N).

Acetoxy-phenyl-(2-guanidinobenzimidazole-N,N′) borate **9.** A solution of 100 mg (0.36 mmol) of **5** in 50 mL of dry THF and 15 mL of dry toluene was treated with 0.02 mL of glacial acetic acid, and the mixture was refluxed for 7 hours. The solvents were evaporated in vacuum to give a white solid (80 mg, 69%). Dec. 250°C, IR ν cm^{-1}: 3388 (N–H), 1680 (C=N), 1610, 1592 (C=C), 1292 (B–O), and (O–C), 1196, 1018 (B–N).

Methoxy-phenyl-(2-guanidino-1-methyl-benzimidazole-N,N′)borate **10.** Compound **10** was prepared following the same procedure as for compound **7.** A white powder was obtained (80%). Dec. 260°C, IR ν cm^{-1}: 3070 (N–H), 1646, 1626 (C=N), 1580, 1542 (C=C), 1332 (B–O), 1196 (B–N).

Dihydroxy-(2-guanidino-1-methyl-benzimidazole-N,N′)borate **16.** A solution of 80 mg (0.42 mmol) of **2** in 20 mL of dry THF was treated with 2 mL of BH_3 DMS (2.1 M, 0.42 mmol), and the reaction mixture was kept at 0°C for 30 minutes. The solvent was evaporated in vacuum to give a white solid, which was dissolved in acetone. After 10 hours, the solvent was evaporated in vacuum, a pink solid being obtained (0.06 g, 60%). Dec. 220°C, IR ν cm^{-1}: 3386 (N–H, OH), 1650 (C=N), 1546, 1468 (C=C), 1342 (B–O), 1016 (B–N). Formation of compound **15** was followed only by ^{11}B NMR spectroscopy.

Difluoro-(2-guanidinobenzimidazole-N,N′)borate **17.** A solution of 500 mg (2.85 mmol) of **1** dissolved in 20 mL of dry THF was reacted with 3.0 mL (2.84 mmol) of BF_3-OEt_2 at O°C for 30 minutes. The reaction mixture afforded a brown solid. The solvent was evaporated in vacuum and the reaction mixture was separated in a chromatographic column made with florisil alkalinized with Na_2CO_3. Compound **17** was separated with ethanol–hexane (90/10) as eluent. After evaporation of the solvent, a yellow solid remained that was washed with a mixture of $CHCl_3$–hexane–water (20:20:10 mL) to give a yellow solid (375 mg, 75%). Mp 258–261°C. IR ν cm^{-1}: 3524 (N–H), 1686 (C=N), 1598, 1546 (C=C), 1350 (C–N), 1280 (B–N). ^{19}F δ (ppm): −135.2 (BF_2), −145.97 ($NaBF_4$). MS (70 eV), *m/z* (%): 223.25 (100), 206.25 (43). $C_8H_8N_5BF_2$ 1/10 $NaBF_4$ (233.97). Calcd: C, 41.42; N, 30.18; H, 3.90; found: C, 41.50; N, 29.41; H, 3.87.

Dihydroxy-(2-guanidino-1-benzimidazole-N,N′) borate, Potassium Salt **19.** A solution of 0.25 g (1.43 mmol) of **1** dissolved in 25 mL of THF was mixed at O°C with 0.1 g (4.3 mmol) of K_2CO_3 dissolved in 1 mL of H_2O and 1.5 mL of BF_3–OEt_2 (1.42 mmol), the mixture being maintained at 0°C for 30 minutes. The solvent was evaporated in vacuum. The reaction product was dissolved in a mixture of acetone/water (70/30), and after 45 days, crystals were formed (0.15 g, 60%). Mp, 229–235°C. IR ν cm^{-1}: 3354, 3340 (N–H, OH), 1654 (C=N), 1628, 1544 (C=C), 1374 (B–O), 1298, 1286 (B–N).

Diphenyl-(2-guanidinium-10H-benzimidazole-N,N′)borate Hydrochloride **20.** A solution of 10 g (0.29 mmol) of **3** in 20 mL of THF was reacted with 0.30 mL of HCl (37%) at room temperature for 2 hours. The solvent was evaporated in vacuum. A white solid was obtained (95 mg, 95%). Dec. 290°C, IR ν cm^{-1}: 3100 (N–H), 2980 (N^+–H), 1686, 1678 (C=N), 1588, 1580 (C=C). $C_{20}H_{19}N_5BCl\cdot 3/4H_2O$ (389.17). Calcd: C, 61.72; N, 17.99; H, 5.31; found: C, 61.68; N, 17.58; H, 5.22.

Phenylmethoxy-(2-guanidinobenzimidazole-N,N′)borate Hydrochloride **21.** To a suspension of 0.18 g (0.67 mmol) of compound **7** in 10 mL of dry THF was added 0.05 mL of aqueous HCl (37%). After 24 hours, colorless crystals sensitive to the air were obtained (0.1 g, 60%). Dec. 240°C. The crystals were analyzed by X-ray diffraction. IR ν cm^{-1}: 3322 (N–H), 1694 (C=N), 1586, 1468 (C=C), 1336 (B–O), 1198 (B–N).

N-Borane-(diphenyl-2-guanidinobenzimidazole-N,N′)borate **22.** A solution of 200 mg (5.8 mmol) of **3** solved in 25 mL of dry THF was reacted with 0.2 mL of BH_3 THF (3 M, 6 mmol) at 0°C for 30 minutes. The solvent was evaporated in vacuum to give a white solid in quantitative yield (2.05 g). IR ν cm^{-1}: 3334 (N–H), 2364 (B–H), 1648, 1612 (C=N), 1540 (C=C), 1176 (B–N).

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