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# Benzazole-N–$BH_3$ Adducts. Reductive Transposition of 2-Benzimidazole, 2-Benzothiazole, and 2-Benzoxazole N–$BH_3$ Adducts to 1,3,2-Benzimidazaborole, 1,3,2-Benzoxaborole, and 1,3,2-Benzothiazaborole

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## ABSTRACT

*1,3,2-Benzimidazaborole, 1,3,2-benzoxaborole, and 1,3,2-benzothiazaborole were synthesized from the corresponding 2-benzazole N–$BH_3$ and 2-benzazole S–$BH_3$ adducts through a reductive transposition from the isolobal fragment X–C($sp^2$) = N($sp^2$) – B($sp^3$) (X = N, O, S) to the fragment X–B($sp^2$) = N($sp^2$) – C($sp^3$). N–$BH_3$ substitution shifts to lower frequencies 4-H, C-3a, and C-7a resonances. The X-ray diffraction analysis of 2-(o-methoxyphenyl)benzothiazole N–$BH_3$ adduct is reported. Two new tetracyclic boron-bridged compounds were observed as by-products (6,9-(ethyl)-diaza-2-oxa-1-bora[3,4,7,8]-dibenzobycyclo[4.3.0]-nona-3,7-diene,* **6d**, *and 8-aza-9-oxa-2-thia-1-bora-[3,4,7,8]dibenzobycyclo[3.4.0]nona-3,7-diene,* **15d**, *when 2-(o-methoxyphenyl)-1-ethylbenzimidazole-$BH_3$* **6b** *and 2-(o-methoxyphenyl)-benzothiazole-$BH_3$* **15b** *adducts were heated.* © *1996 John Wiley & Sons, Inc.*

Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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## *INTRODUCTION*

In this work, a novel, clean reaction to obtain 1,3,2-benzazaborole derivatives **A** (Scheme 1) from the corresponding benzazole-N–$BH_3$ and S–$BH_3$ adducts is reported. The boron–nitrogen dative bond in imidazole derivatives is a very stable bond [1]. However, recent studies have been shown that imidazole



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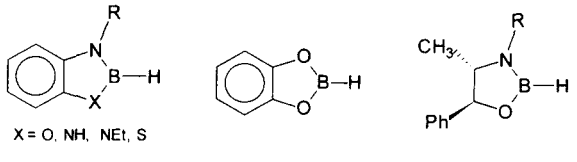
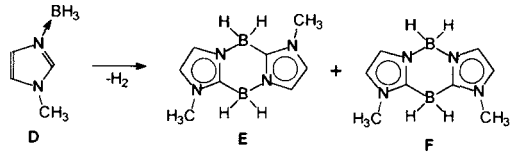


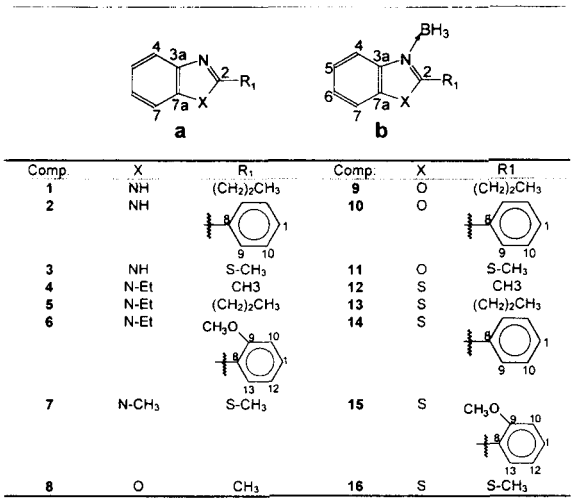

**SCHEME 1**




**SCHEME 2**

adducts **D** react at a high temperature with themselves to form the imidazabole compounds **E** and **F** [2] (Scheme 2). Herein, similar reactions for benzene-fused derivatives—benzimidazole, benzoxazole, and benzothiazole borane adducts—were studied.

The importance of benzoborolane as a reducing agent has been increased by the report of Männig and Nöth [3] that rhodium complexes catalyze hydroboration of alkenes with 1,3,2-benzodioxaborolane **B** [4,5]. These reagents are added regioselectively to C = C bonds in the presence of more reactive groups such as ketone or nitrile. Oxazaborolidine derived from pseudoephedrine **C** in the presence of rhodium complexes asymmetrically hydroborates styrenes [6]. The 1,3,2-benzazaboroles **A** studied here are potential reducing agents under the mentioned conditions [5].




**SCHEME 3** 1,3-Benzazaborole compounds (**a**) and their N-$BH_3$ adducts (**b**).

## *RESULTS AND DISCUSSION*

### *Synthesis of N→$BH_3$ Adducts*

The N–$BH_3$ adducts (**1b–16b**) were synthesized in quantitative yield by reaction of one equivalent of borane-THF complex with each of the 2-substituted-1,3-benzazoles (**1a–16a**, Scheme 3). The $^{11}B$ chemical shifts and the $^1J$(B,H) coupling constants of benzazole-N–$BH_3$ adducts are in the typical range for tetracoordinated N–B compounds [7] (Table 1). The general trend in $^{13}C$-NMR spectra is that C7a and C3a are shifted to lower frequencies because of the decreased electron-attracting effect of X (X = N, O, S) and loss of the deshielding effect of the nitrogen lone pair upon coordination [2] (Tables 2 and 3). The latter effect is similar to that produced by protonation [8]. $^1H$-NMR spectra are also sensitive to borane coordination, as shown by the shift to higher frequencies of 4-H (Table 4). Borane coordination produces only a local effect on the chemical shifts of the heterocycle, contrary to that found by protonation, which shifts all $^1H$ resonances to higher frequencies [8a].

The structure of **15b** has been obtained by X-ray diffraction analysis (Figure 1, Table 5). It shows that the N–B length [1.601(7) Å] is in the typical range

**TABLE 1** B-NMR Data ($\delta$, $J$ Hz) of [(N–B)-1,3-benzazole]$BH_3$ Adducts **1b–16b** in $CDCl_3$ with $Et_2O$–$BF_3$ as an External Reference

| *Comp.* | $\delta$ $^{11}B$ | $^1J$(B, H) | *Comp.* | $\delta$ $^{11}B$ | $^1J$(B, H) |
|---|---|---|---|---|---|
| **1b** | −22.9 | b | **9b** | −22.7 | 97 |
| **2b** | −22.0 | b | **10b** | −20.6 | 88 |
| **3b**[a] | −23.9 | b | **11b**[a] | −22.6 | b |
| **4b** | −23.3 | 90 | **12b** | −20.9 | 97 |
| **5b** | −22.6 | 81 | **13b** | −20.8 | 92 |
| **6b** | −21.6 | b | **14b** | −18.9 | 89 |
| **7b**[a] | −21.0 | b | **15b** | −19.2 | 73 |
| **8b** | −21.5 | b | **16b**[a] | −20.1 | b |

[a]In [$^2H_6$] DMSO.
[b]Broad signal.

for an N($sp^2$)–B($sp^3$) dative bond. The structure of the benzazole five-membered ring changes significantly through borane coordination, in comparison with the free base [9]. The N–C(7) bond length is enlarged 1.318(5) Å [1.280(9) Å (free base)] as well as the C(1)–C(2) bond, 1.397(6) Å [1.372(10) Å], while the S–C(7) is shortened 1.711(4) Å [1.749(8) Å (free base)]. The angle centered on sulfur becomes wider, 90.6(2)° [88.6(4)° (free base)]. These changes as a whole suggest the increase in electronic delo-

**TABLE 2** $^{13}$C-NMR Chemical Shifts of Benzazole Free Bases **1a–16a** in $CDCl_3$ with TMS as an External Reference

| *Comp.* | *C2* | *C3a* | *C4* | *C5* | *C6* | *C7* | *C7a* | *$R_1$* |
|---|---|---|---|---|---|---|---|---|
| **1a** | 155.5 | 138.5 | 114.5 | 121.4 | 121.4 | 114.5 | 138.5 | 31.1 ($CH_2$), 21.5 ($CH_2$), 13.8 ($CH_3$) |
| **2a** | 150.9 | 129.4 | 114.2 | 121.3 | 121.3 | 114.2 | 129.4 | 128.8 (C-11), 127.8 (C-10), 125.8 (C-9) |
| **3a**[a,b] | 151.2 | 139.7 | 113.6 | 121.2 | 121.2 | 113.6 | 139.7 | 13.8 (S–$CH_3$) |
| **3a**[b,c] | 152.3 | 136.4 | 110.9 | 121.9 | 121.9 | 117.8 | 144.5 | 13.8 (S–$CH_3$) |
| **4a** | 150.3 | 141.6 | 117.8 | 120.7 | 121.0 | 108.2 | 133.7 | 37.4 (N–$CH_2$), 13.9 ($CH_3$), 12.5 (N–$CH_2CH_3$) |
| **5a** | 154.3 | 142.4 | 118.7 | 121.3 | 121.6 | 108.8 | 134.3 | 37.9 (N–$CH_2$), 29.0 ($CH_2$), 20.9 ($CH_2$), 14.8 (N–$CH_2CH_3$), 13.7 ($CH_3$) |
| **6a** | 151.4 | 143.4 | 119.9 | 121.8 | 122.3 | 109.9 | 134.8 | 157.5 (C-9), 134.8 (C-8), 132.1 (C-13), 131.5 (C-11), 120.8 (C-12), 110.0 (C-10), 55.4 ($CH_3O$), 39.4 (N–$CH_2$), 14.7 ($CH_3$), C-8 n.o.[d] |
| **7a**[a,b] | 152.6 | 142.9 | 117.4 | 121.2 | 121.2 | 109.2 | 136.9 | 29.6 (N–$CH_3$), 14.1 (S–$CH_3$) |
| **8a** | 163.7 | 141.5 | 119.4 | 124.4 | 124.1 | 110.2 | 151.0 | 14.4 ($CH_3$) |
| **9a** | 167.1 | 141.5 | 119.5 | 125.1 | 124.4 | 110.2 | 150.8 | 30.5 ($CH_2$), 20.2 ($CH_2$), 13.7 ($CH_3$) |
| **10a** | 162.8 | 142.1 | 119.9 | 124.9 | 124.4 | 110.4 | 152.6 | 131.3 (C-11), 128.7 (C-10), 127.4 (C-9), C-8 n.o.[d] |
| **11a**[a,b] | 165.2 | 141.4 | 118.1 | 124.5 | 124.0 | 110.0 | 151.4 | 14.1 (S–$CH_3$) |
| **12a** | 165.5 | 153.1 | 122.1 | 125.6 | 124.4 | 121.1 | 135.4 | 19.8 ($CH_3$) |
| **13a** | 171.9 | 153.1 | 122.3 | 125.7 | 124.5 | 121.3 | 135.0 | 36.0 ($CH_2$), 22.9 ($CH_2$), 13.5 ($CH_3$) |
| **14a** | 167.8 | 154.0 | 123.0 | 126.1 | 125.0 | 121.4 | 134.9 | 133.4 (C-8), 130.8 (C-11), 128.8 (C-10), 127.4 (C-9) |
| **15a** | 163.0 | 152.1 | 122.7 | 125.8 | 124.5 | 121.1 | 136.1 | 157.1 (C-9), 131.7 (C-11), 129.4 (C-13), 121.0 (C-12), 110.6 (C-10), 55.5 ($CH_3O$), C-8 n.o.[d] |
| **16a**[a] | 167.7 | 152.8 | 121.5 | 126.1 | 124.0 | 120.9 | 134.6 | 15.4 (S–$CH_3$) |

[a] In [$^2H_6$]DMSO.
[b] At 22.5 MHz.
[c] In [$^2H_7$]DMF at −65°C.
[d] n.o.: not observed.

calization of the five-membered ring due to N–$BH_3$ coordination [10]. The electron-attracting effect of borane decreases the electron density in the ring, which is compensated by more sulfur participation in the bonding scheme.

### *Synthesis of S→$BH_3$ Adducts*

2-Mercaptobenzazoles (**17a–19a**) exist in an equilibrium involving the iminothiol and thioamide forms (Scheme 4). It has been demonstrated that the thioamide tautomer predominates in solution [11]. For **17a**, an additional imidazole intermolecular tautomeric equilibrium also exists.

The reaction of 2-mercaptobenzimidazole (**17a**), 2-mercaptobenzoxazole (**18a**), and 2-mercaptobenzothiazole (**19a**) with $BH_3$-THF afforded the S→$BH_3$ adducts ($^{11}$B $\delta$ = −22.8, broad, **17b**; $^{11}$B $\delta$ = −21.9, $^1J$ = 86 Hz, **18b**; and $\delta$ = −22.9, broad, **19b**) as the only products. Compound **19b** decomposes in solution to the aminoborane **19c** [$^{11}$B $\delta$ = 25, $J$ (B,H) = 157 Hz]. The 2-mercaptobenzoxazole-S→$BH_3$ adduct (**18b**) proved to be an unusually stable adduct. The shift to low frequency of **C3a**, which was characteristic for nitrogen coordination or protonation (Table 6), suggests that it could be stabilized by an intermolecular hydric-protic interaction between the boron hydride moiety and the acidic H–N group [10,12]. The N–$BH_3$ adduct **18c** is discarded from consideration because the C-2 chemical shift remains in the region of the thioamide form ($\delta$ 183.2 for **18b** in contrast with 167.9 of **11b** of the iminothiol form, Scheme 5).

### *Synthesis of Benzoborole Heterocycles*

When the 1,3-benzazole-N→$BH_3$ adducts (**1b–16b**) and the S→$BH_3$ adducts (**17b–19b**) were heated in a nitrogen atmosphere, different products were found. For **1b–3b**, which bear an N–H acidic proton, nonidentified polymeric material was obtained. Compounds **4b–6b**, **8b–10b**, **12b–15b**, and **17b–19b** afforded the boron heterocycles (**4c–6c**, **8c–10c**, **12c–15c**, and **17c–19c**) in quantitative yield (Schemes 6 and 7). The $^{11}$B-NMR spectra present signals in the typical range for N–BH–N ($\delta \approx 25$), N–BH–O (≈28), and N–BH–S (≈38) fragments [7] (Table 7). $^{13}$C-NMR data of 1,3,2-benzazaborole compounds **4c–16c** and **20c–27c** are summarized in Table 8.

Heating of 1-(ethyl)-2-(*o*-methoxyphenyl)benzimidazole-$BH_3$ **6b** and 2-(*o*-methoxyphenyl)-benzothiazole-$BH_3$ **15b** at a high temperature af-

**TABLE 3** $^{13}$C-NMR Chemical Shifts of Benzazole-$BH_3$ Adducts **1b–16b** in $CDCl_3$ with TMS as an External Reference

| *Comp.* | *C2* | *C3a* | *C4* | *C5* | *C6* | *C7* | *C7a* | *$R_1$* |
|---|---|---|---|---|---|---|---|---|
| **1b** | 154.3 | 136.0 | 116.6 | 122.9 | 123.7 | 112.0 | 130.6 | 29.1 ($CH_2$), 20.3 ($CH_2$), 13.8 ($CH_3$) |
| **2b** | 149.7 | 137.3 | 116.3 | 122.8 | 123.6 | 111.2 | 131.0 | 127.16 (C-9), 129.50 (C-10), 130.50 (C-11), C-8 n.o.[d] |
| **3b**[a,b,c] | 154.7 | 138.9 | 119.4 | 123.9 | 123.9 | 112.1 | 133.7 | 13.9 (S–$CH_3$) |
| **4b** | 150.4 | 137.0 | 117.2 | 124.0 | 124.2 | 109.7 | 131.6 | 39.3 (N–$CH_2$), 14.7 ($CH_3$), 11.3 (N–$CH_2CH_3$) |
| **5b** | 153.5 | 137.3 | 117.6 | 124.1 | 124.3 | 109.8 | 131.7 | 39.3 (N–$CH_2$), 26.7 ($CH_2$), 15.1 (N–$CH_2\underline{CH_3}$), 14.1 ($CH_3$) |
| **6b** | 148.9 | 136.9 | 116.8 | 123.4 | 124.0 | 110.2 | 131.3 | 156.9 (C-9), 132.2 (C-11), 131.3 (C-13), 120.0 (C-12), 110.9 (C-10), 55.1 ($CH_3O$), 39.5 (N–$\underline{CH_2}$), 13.9 ($CH_3$) |
| **7b**[a,b] | 149.9 | 136.9 | 116.1 | 124.3 | 124.7 | 111.6 | 133.4 | 32.0 (N–$\underline{CH_3}$), 17.0 (S–$CH_3$) |
| **8b** | 166.4 | 135.4 | 116.8 | 126.8 | 126.1 | 111.5 | 148.2 | 28.5 ($CH_3$) |
| **9b** | 168.0 | 135.4 | 118.0 | 126.7 | 126.1 | 110.9 | 148.6 | 28.5 ($CH_2$), 19.4 ($CH_2$), 13.7 ($CH_3$) |
| **10b** | 162.2 | 137.0 | 118.9 | 127.2 | 126.3 | 111.0 | 148.4 | 133.3 (C-11), 131.1 (C-9), 128.6 (C-10), C-8 n.o.[d] |
| **11b**[a,b] | 167.9 | 135.8 | 115.2 | 126.0 | 125.3 | 110.8 | 149.6 | 13.3 (S–$CH_3$) |
| **12b** | 170.8 | 147.5 | 121.7 | 127.6 | 126.8 | 121.4 | 129.9 | 18.9 ($CH_3$) |
| **13b** | 176.1 | 147.6 | 121.7 | 127.5 | 126.7 | 121.5 | 130.0 | 34.2 ($CH_2$), 22.0 ($CH_2$), 13.8 ($CH_3$) |
| **14b** | 171.3 | 148.5 | 122.9 | 128.0 | 127.1 | 121.4 | 131.1 | 130.7 (C-9), 131.8 (C-11), 129.9 (C-8), 128.4 (C-10) |
| **15b** | 168.4 | 147.5 | 122.6 | 127.6 | 126.9 | 121.3 | 131.8 | 157.4 (C-9), 133.1 (C-11), 131.9 (C-13), 120.2 (C-12), 111.5 (C-10), 55.9 ($CH_3O$), C-8 n.o.[d] |
| **16b**[a,b] | 176.9 | 147.2 | 118.5 | 127.6 | 125.3 | 122.3 | 129.9 | 17.0 (S–$CH_3$) |

[a]In [$^2H_6$]DMSO.
[b]At 22.5 MHz.
[c]In [$^2H_7$]DMF at −20°C.
[d]n.o.: not observed.

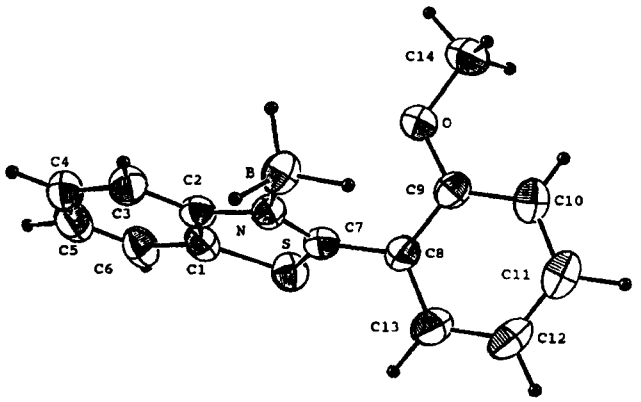
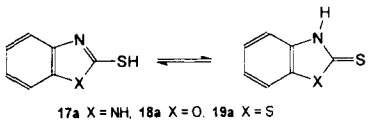
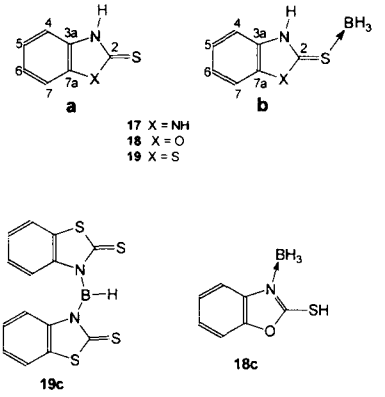



**FIGURE 1** Structure of **15b** obtained by X-ray diffraction analysis.

forded not only **6c** (40%) and **15c** (60%), respectively, but also the tetracyclic compounds **6d** (60%) and



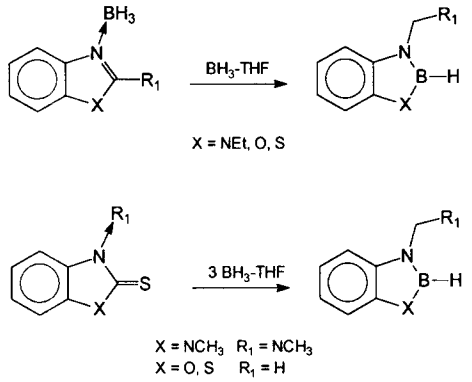

**SCHEME 4**



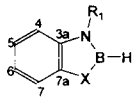

**SCHEME 5**

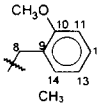
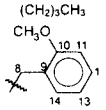
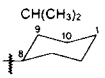
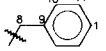
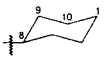
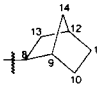
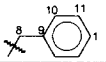
**15d** (40%), which result from incorporation of boron into the ring system and $CH_4$ evolution. A possible mechanism is depicted (Scheme 8).

The direct conversion of 1,3-benzazole by reaction with diborane in diglyme to 1,3,2-benzazaborole has been reported [13]. A similar reaction was observed in the reduction of benzothiazolium cations with $NaBH_3CN$ [14]. This conversion implies the reductive transposition of the boron and C-2 atoms, instead of the dimerization and $H_2$ evolution



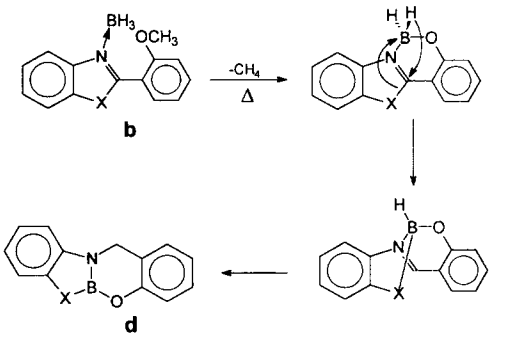

**SCHEME 6**



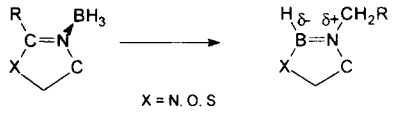
| Comp | X | $R_1$ | Comp. | X | $R_1$ |
|---|---|---|---|---|---|
| **4c** | N-Et | $CH_2CH_3$ | **15c** | S |  |
| **5c** | N-Et | $(CH_2)_3CH_3$ | **16c** | S | $CH_3$ |
| **6c** | N-Et |  | **20c** | NH | H |
| **7c** | N-$CH_3$ | $CH_3$ | **21c** | N-$CH(CH_3)_2$ | $CH(CH_3)_2$ |
| **8c** | O | $CH_2CH_3$ | **22c** | N-cyclohexyl |  |
| **9c** | O | $(CH_2)_3CH_3$ | **23c** | O | H |
| **10c** | O |  | **24c** | O | $CH(CH_3)_2$ |
| **11c** | O | $CH_3$ | **25c** | O |  |
| **12c** | S | $CH_2CH_3$ | **26c** | O |  |
| **13c** | S | $(CH_2)_3CH_3$ | **27c** | S | H |
| **14c** | S |  | | | |

**SCHEME 7** 1,3,2-Benzazaborole compounds synthesized.

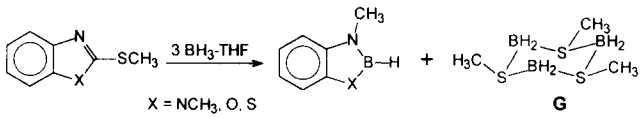
observed in imidazabole formation. The difference in reactivity should be based in electronic effects. In this work, similar transposition reactions were found for several amine borane adducts with a common structure involving the fragment X-C($sp^2$) = N($sp^2$)-B($sp^3$) (X = N, O, S) inserted in a five-membered heterocycle [15]. This fragment, after reductive transposition, becomes the fragment X-B($sp^2$) = N($sp^2$)–C($sp^3$) also inserted in a five-membered ring in which the boron atom substitutes the carbon atom in the heterocycle (Scheme 9). This reaction is an example of a chemical reaction in which



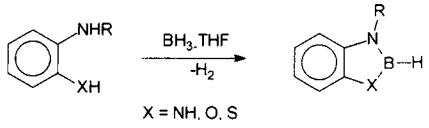

**SCHEME 8** Tetracyclic compounds **6d** and **15d** obtained from N-$BH_3$ adducts **6b** and **15b**, respectively.



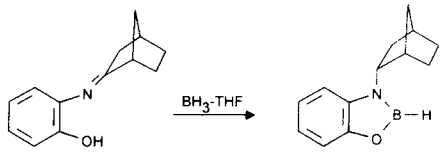

**SCHEME 9** Reductive transposition of the N-$BH_3$ adducts to the corresponding isolobal boraneimine fragment.




**SCHEME 10**




**SCHEME 11**




**SCHEME 12**

the product formed is isolobal [16] with the starting material and appears to be a general reaction for N–$BH_3$ adducts with the characteristics cited earlier. Similar reactions may be involved in reductions with $MBH_4$ (M = Na, Zn) [17].

The 2-(methylmercapto)benzazole N→$BH_3$ adducts (**7b**, **11b**, **16b**) were treated under less severe conditions, with an excess of $BH_3$-THF in refluxing THF. The methylmercapto function was lost, form-

**TABLE 4** $^1$H-NMR Chemical Shifts of Free Bases **1a–16a** and Benzazole-$BH_3$ Adducts **1b–16b** in $CDCl_3$ with TMS as an External Reference ($\delta$, $J$ in Hz)

| *Free Bases* | | | | | *Benzazole-$BH_3$ Adducts* | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Comp.* | *4-H* | *5-H* | *6-H* | *7-H* | *Comp.* | *4-H* | *5-H* | *6-H* | *7-H* |
| **1a**[d] | 7.51 | 7.15 | 7.15 | 7.51 | **1b**[t] | 7.85 | 7.31 | 7.31 | 7.47 |
| **2a**[e] | 7.61 | 7.21 | 7.21 | 7.61 | **2b**[u] | 8.03 | 7.40 | 7.40 | 7.60 |
| **3a**[a,f] | 7.40 | 7.10 | 7.10 | 7.40 | **3b**[b,c,v] | 7.6 | 7.4 | 7.4 | 7.4 |
| **4a**[g] | 7.72 | 7.18 | 7.18 | 7.18 | **4b**[w] | 7.98 | 7.37 | 7.37 | 7.37 |
| **5a**[h] | 7.71 | 7.18 | 7.18 | 7.18 | **5b**[x] | 8.03 | 7.39 | 7.39 | 7.40 |
| **6a**[i] | 7.83 | 7.27 | 7.27 | 7.29 | **6b**[y] | 8.08 | 7.34 | 7.34 | 7.65 |
| **7a**[a,b,j] | 6.10 | 6.40 | 6.40 | 6.40 | **7b**[a,b,z] | 7.8 | 7.4 | 7.4 | 7.4 |
| **8a**[k] | 7.63 | 7.25 | 7.25 | 7.42 | **8b**[aa] | 7.93 | 7.52 | 7.49 | 7.57 |
| **9a**[l] | 7.66 | 7.25 | 7.21 | 7.42 | **9b**[bb] | 7.92 | 7.48 | 7.48 | 7.58 |
| **10a**[m] | 7.78 | 7.31 | 7.31 | 7.51 | **10b**[cc] | 8.10 | 7.49 | 7.51 | 7.62 |
| **11a**[a,n] | 7.60 | 7.30 | 7.30 | 7.60 | **11b**[a,b,dd] | 7.3 | 7.3 | 7.3 | 7.3 |
| **12a**[o] | 7.95 | 7.45 | 7.34 | 7.82 | **12b**[ee] | 8.42 | 7.62 | 7.52 | 7.82 |
| **13a**[p] | 7.94 | 7.92 | 7.30 | 7.80 | **13b**[ff] | 8.41 | 7.63 | 7.53 | 7.88 |
| **14a**[q] | 8.06 | 7.42 | 7.29 | 7.79 | **14b**[gg] | 8.60 | 7.69 | 7.55 | 7.89 |
| **15a**[r] | 8.05 | 7.44 | 7.30 | 7.86 | **15b**[hh] | 8.56 | 7.69 | 7.57 | 7.89 |
| **16a**[a,s] | 7.9 | 7.3 | 7.3 | 7.9 | **16b**[a,b,ii] | 8.1 | 7.6 | 7.6 | 8.1 |

[a]In [$^2H_6$]DMSO; [b]at 89.6 MHz; [c]in [$^2H_7$]DMF at −20°C; [d]$J$(4, 5) = 9.4, $J$(4, 6) = 2.6, $J$(5, 6) = 9.2, $J$(5, 7) = 3.3, 2.90 ($CH_2$), 1.88 ($CH_2$), 1.00 ($CH_3$); [e]$J$(4, 5) = $J$(6, 7) = 5.9, $J$(4, 6) = 2.7, $\delta$ = 8.20 (9-H), 7.48 (10-H), 7.48 (11-H); [f]2.7 (S–$CH_3$); [g]3.88 (N–$CH_2$), 2.46 ($CH_3$), 1.24 (N–$CH_2CH_3$); [h]4.08 (N–$CH_2$), 2.79 ($CH_2$), 1.90 ($CH_2$), 1.34 (N–$CH_2CH_3$), 1.04 ($CH_3$); [i]7.49 (13-H), 7.46 (11-H), 7.06 (12-H), 6.98 (10-H), 3.73 ($CH_3O$), 4.04 (N–$CH_2$), 1.29 ($CH_3$), [j]3.6 (N–$CH_3$), 2.8 (S–$CH_3$); [k]2.58 ($CH_3$); [l]2.85 ($CH_2$), 1.88 ($CH_2$), 1.01 ($CH_3$); [m]$\delta$ 8.22 (9-H), 7.50 (10, 11-H); [n]2.8 (S–$CH_3$); [o]2.84 ($CH_3$); [p]$J$(4, 5) = 8.1 $J$(4, 6) = 0.7, $J$(5, 6) = 8.0, $J$(5, 7) = 1.3, $J$(6, 7) = 7.8, 3.06 ($CH_2$), 1.89 ($CH_2$), 1.04 ($CH_3$); [q]$J$(4, 5) = 7.9, $J$(4, 6) = 1.2, $J$(4, 7) = 0.7, $J$(5, 6) = 8.1, $J$(5, 7) = 1.3, $J$(6, 7) = 8.0, 8.04 (9-H), 7.40 (10-H), 7.41 (11-H); [r]$J$(4, 5) = 8.2, $J$(4, 6) = 1.2, $J$(4, 7) = 0.6, $J$(5, 6) = 8.0, $J$(5, 7) = 8.0, 8.50 (13-H), 7.34 (11-H), 7.06 (12-H), 6.91 (10-H); [s]$J$(4, 5) = 8.1, $J$(5, 6) = 7.6, $J$(6, 7) = 8.1, 2.8 (S–$CH_3$); [t]12.9 (NH), 3.70 ($CH_2$), 1.83 ($CH_2$), 1.03 ($CH_3$); [u]$J$(4, 5) = 8.0, $J$(4, 6) = 1.0, 13.4 (NH), 8.02 (9-H), $J$(9, 10) = 8.6, 7.6 (10-H), 7.6 (11-H), 2.4 (BH); [v]2.8 (S–$CH_3$); [w]4.21 (N–$CH_2$), 2.73 ($CH_3$), 1.41 (N–$CH_2CH_3$); [x]4.27 (N–$CH_2$), 3.16 ($CH_2$), 1.84 ($CH_2$), 1.48 (N–$CH_2CH_3$), 1.10 ($CH_3$); [y]$J$(4, 5) = 6.8, $J$(4, 6) = 2.0, $J$(6, 7) = 7.5, 7.44 [11-H, $J$(H, H) = 6.3], 7.3 [13-H, $J$(12, 13) = 7.4], 7.04 [12-H, $J$(H, H) = 7.0], 6.9 [10-H, $J$(11, 12) = 8.5], 5.4 ($CH_3O$), 4.0 ($CH_2$), 1.2 ($CH_3$); [z]3.9 (N–$CH_3$), 2.7 (S–$CH_3$); [aa]2.89 ($CH_3$), 2.28 (H–B); [bb]3.25 ($CH_2$), 2.30 [H–B], 1.96 ($CH_2$), 1.08 ($CH_3$); [cc]8.50 (9-H), 7.62 (11-H), 7.58 (10-H); [dd]2.6 (S–$CH_3$); [ee]3.02 ($CH_2$); [ff]$J$(4, 5) = 8.1, $J$(4, 6) = 1.3, $J$(4, 7) = 0.6, $J$(5, 6) = 8.0, $J$(5, 7) = 1.4, $J$(6, 7) = 8.0, 3.40 ($CH_2$), 1.94 ($CH_3$), 1.04 ($CH_3$); [gg]$J$(4, 5) = 8.5, $J$(4, 6) = 1.2, $J$(4, 7) = 0.6, $J$(5, 6) = 8.4, $J$(5, 7) = 1.3, $J$(6, 7) = 6.6, 7.89 (9-H), 7.69 (11-H), 7.54 (10-H), 2.5 (H–B); [hh]$J$(4, 5) = 8.4, $J$(4, 6) = 1.4, $J$(5, 6) = 8.0, $J$(5, 7) = 1.4, $J$(6, 7) = 7.8, 7.57 (11, 13-H), 7.12 (12-H), 7.08 (10-H), 3.9 ($CH_3O$), 2.4 (H–B); [ii]2.8 (S–$CH_3$).

ing the $BH_2$–S trimer **G** [$^{11}$B $\delta$ = −13.7, $J$(B,H) = 123 Hz, $^{13}$C $\delta$ = 18.8, $^1$H $\delta$ = 2.2] and the N-methyl-1,3,2-benzazaborole (**7c**, **11c**, **16c**) compounds (Scheme 10).

The 1,3,2-benzazaborole compounds, **20c–25c** and **27c**, were prepared by the direct reaction of each of the 1,2-dialkylphenylenediamines, *o*-alkyl-aminophenols, and *o*-alkyl-aminothiophenols, respectively, with one equivalent of $BH_3$-THF [18] (Scheme 11). The benzazaborole **26c** was obtained by reacting an excess of $BH_3$-THF with the imine derived from *o*-aminophenol and 2-norbornanone (Scheme 12). The latter method provides a symmetrical N,N′-$R_1$-1,3,2-benzimidazaborole, in contrast with the reaction starting with benzimidazoles, which affords N-$R_1$, N′-$R_2$ 1,3,2-benzimidazaboroles.

## *EXPERIMENTAL*

### *Materials and Methods*

All new compounds were characterized by $^{11}$B, $^1$H, $^{13}$C, heteronuclear correlation experiments. 2-Substituted-1,3-benzimidazoles (**1a–2a**), 2-substituted-N-alkyl-1,3-benzimidazoles (**4a–6a**), 2-substituted-1,3-benzoxazoles (**8a–10a**), and 2-substituted-1,3-benzothiazoles (**12a–15a**) were synthesized by condensation of *o*-phenylenediamine, N-alkyl-*o*-phenylenediamines, *o*-aminophenol, and *o*-aminothiophenol, respectively, with the appropriate aldehyde or carboxylic acid, according to established procedures [19]. With regard to the preparation of the benzimidazoles (**4–6**), *o*-nitroacetanilide was reduced with borane to give the monosubstituted phenylenediamine. Reduction of the nitro group [20] was enabled because of the close proximity of the $BH_3$ to the nitro group in the intermediate amine-borane adduct. Condensation of *o*-phenylenediamine, *o*-aminophenol, and *o*-aminothiophenol with carbon disulfide in alkaline medium afforded the benzazole-2-thione compounds (**17a–19a**) [21]. After isolation, **17a–19a** were treated with one equivalent of metallic sodium and one equivalent of $CH_3I$ to yield **3a**, **11a**, and **16a**, respectively. The synthesis of **7a** was also performed by reaction of **3a** with sodium followed by methyl iodide [22].

**TABLE 5** Selected Bond Lengths (Å) and Angles (°) for **15b**

| Atoms | Bond Lengths (Å) | Atoms | Bond Lengths (Å) |
|---|---|---|---|
| S–C(1) | 1.731(5) | S–C(7) | 1.711(4) |
| O–C(9) | 1.351(5) | O–C(14) | 1.446(6) |
| N–C(2) | 1.400(6) | N–C(7) | 1.318(5) |
| N–B | 1.601(6) | C(1)–C(2) | 1.397(6) |
| C(1)–C(6) | 1.397(7) | C(2)–C(3) | 1.392(7) |
| C(3)–C(4) | 1.381(7) | C(4)–C(5) | 1.394(8) |
| C(5)–C(6) | 1.369(7) | C(7)–C(8) | 1.471(6) |
| C(8)–C(9) | 1.399(6) | C(8)–C(13) | 1.395(7) |
| C(9)–C(10) | 1.383(7) | C(10)–C(11) | 1.392(7) |
| C(11)–C(12) | 1.386(8) | C(12)–C(13) | 1.368(7) |
| **Atoms** | **Bond Angles (°)** | **Atoms** | **Bond Angles (°)** |
| C(1)–S–C(7) | 90.6(2) | C(9)–O–C(14) | 117.5(4) |
| C(2)–N–C(7) | 111.8(3) | C(2)–N–B | 121.6(3) |
| C(7)–N–B | 126.6(4) | S–C(1)–C(2) | 109.5(3) |
| S–C(1)–C(6) | 129.5(4) | C(2)–C(1)–C(6) | 121.0(4) |
| N–C(2)–C(1) | 113.4(4) | N–C(2)–C(3) | 126.0(4) |
| C(1)–C(2)–C(3) | 120.5(4) | C(2)–C(3)–C(4) | 117.8(5) |
| C(3)–C(4)–C(5) | 121.6(5) | C(4)–C(5)–C(6) | 121.0(5) |
| C(1)–C(6)–C(5) | 118.1(5) | S–C(7)–N | 114.6(3) |
| S–C(7)–C(8) | 119.7(3) | N–C(7)–C(8) | 125.7(4) |
| C(7)–C(8)–C(9) | 120.4(4) | C(7)–C(8)–C(13) | 120.1(4) |
| C(9)–C(8)–C(13) | 119.4(4) | O–C(9)–C(8) | 114.9(4) |
| O–C(9)–C(10) | 125.8(4) | C(8)–C(9)–C(10) | 119.4(4) |
| C(9)–C(10)–C(11) | 120.3(4) | C(10)–C(11)–C(12) | 120.2(5) |
| C(11)–C(12)–C(13) | 119.7(5) | C(8)–C(13)–C(12) | 121.0(5) |

**TABLE 6** $^{13}C$ Chemical Shifts for 2-Mercaptobenzazole Compounds (**17a–19a**) and Their Boron Derivatives (**17b–19d**) in [$^2H_6$]DMSO, Relative to TMS

| Comp. | C-2 | C-3a | C-4 | C-5 | C-6 | C-7 | C7a |
|---|---|---|---|---|---|---|---|
| **17a**[a] | 168.1 | 132.4 | 109.6 | 122.3 | 122.3 | 109.6 | 132.4 |
| **17b**[b,c,d] | 169.2 | 132.9 | 109.8 | 122.6 | 122.6 | 109.8 | 132.9 |
| **18a**[a] | 181.8 | 145.4 | 113.7 | 121.6 | 119.2 | 106.7 | 151.0 |
| **18b**[b,c,d] | 183.2 | 138.8 | 114.0 | 123.7 | 122.2 | 108.6 | 149.2 |
| **19a**[a] | 189.7 | 141.2 | 112.3 | 127.0 | 124.0 | 121.6 | 129.3 |
| **19b**[a,d,e] | 192.5 | 142.0 | 114.6 | 128.6 | 125.7 | 123.3 | n.o.[f] |
| **19c**[b,c,d] | 191.1 | 142.1 | 113.1 | 127.8 | 124.8 | 122.4 | 130.4 |
| **19d**[a,c,d] | 191.5 | 142.2 | 112.6 | 127.8 | 124.9 | 122.4 | 130.9 |

[a]At 67.8 MHz; [b] at 22.49 MHz; [c]at 0°C; [d]in [$^2H_8$] THF; [e]at −30°C; [f]not observed.

**TABLE 7** $^{11}B$-NMR data ($\delta$, $J$ Hz) of 1,3,2-benzazaborole Compounds **4c–16c** and **20c–27c** in $CDCl_3$ with $Et_2O$–$BF_3$ as an External Reference

| Comp. | $\delta$ $^{11}B$ | $^1J(B,H)$ | Comp. | $\delta$ $^{11}B$ | $^1J(B,H)$ |
|---|---|---|---|---|---|
| **4c** | 24.4 | 143 | **15c** | 38.4 | 137 |
| **5c** | 24.5 | 167 | **16c** | 38.0 | 123 |
| **6c** | 25.1 | b[a] | **20c** | 23 | 134 |
| **7c** | 25.4 | 149 | **21c** | 23 | 145 |
| **8c** | 27.5 | b[a] | **22c** | 23 | b[a] |
| **9c** | 27.8 | 158 | **23c** | 28 | 168 |
| **10c** | 28.5 | b[a] | **24c** | 28 | 126 |
| **11c** | 28.1 | 170 | **25c** | 28 | 167 |
| **12c** | 37.3 | b[a] | **26c** | 28 | 161 |
| **13c** | 37.5 | 147 | **27c** | 37 | 156 |
| **14c** | 38.6 | 178 | | | |

[a]Broad signal.

Benzazole-$BH_3$ adducts and benzazaborole compounds were handled under a nitrogen atmosphere using carefully dried glassware and dried solvents. Starting materials such as *o*-phenylenediamine, *o*-aminothiophenol, *o*-aminophenol, and 2-methylbenzoxazole were commercial products. $BH_3$-THF was prepared according to reported methods [18]. N-ethyl-1,2-phenylenediamine was synthesized as reported in Ref. [23]. Compounds **1a**, **2a**, **4a**, **5a**, **8a–10a**, and **12a–14a** were prepared as described in Ref. [19a] and **6a** and **15a** as in Ref. [19b]. Borane adducts **1b–16b** were prepared in quantitative yield from **1a–16a** [2]. Compounds **20c–27c** were prepared as reported for 1,3,2-benzodioxaborole [18,24], from the 2-(substituted)-1,2-phenylenediamines [25]. Melting points were measured on a Gallenkamp apparatus and are uncorrected. 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 $^1H$- and $^{13}C$-NMR spectra were obtained on a JEOL GSX 270 (270.67/67.94 MHz) or on a JEOL FX-90Q (28.69/90 MHz) spectrometer, TMS was used as an external standard. Direct $^1H$–$^{13}C$ chemical shifts correlation experiments (HETCOR) were obtained using a 1024 × 512 data point matrix and a 4566 × 523 Hz or 1000 × 310 Hz frequency matrix with pulse intervals 1 and 2 set at 3.145 and 0.957 ms or 3.125 and 1.613 ms, respectively, and a relaxation delay of 2 seconds. The $^{11}B$ NMR spectra were taken on a JEOL GSX 270 (86.84 MHz) or JEOL FX-90Q (89.55 MHz) instrument, and $Et_2O$–$BF_3$ was used as an external standard ($^{11}B$ = 32.083971 MHz). Elemental analyses were performed by Oneida Research Services, Whitesboro, New York.

*2-Propyl-1H-benzimidazole* (**1a**). A 1.22 g (13 mmol) portion of *o*-phenylenediamine, 1 g (13 mmol) of butyric acid, and 10 g of polyphosphoric acid were heated under vigorous stirring to 140°C. After 4 hours, the mixture was poured into 300 mL of cold water, and then the solution was neutralized with ammonium hydroxide. The precipitate was filtered off, and the solution was concentrated to dry-

**TABLE 8** $^{13}$C-NMR $\delta$ of 1,3,2-benzazaborole Compounds **5c–16c** and **20c–27c** in $CDCl_3$ with TMS as an External Reference

| *Comp.* | *C3a* | *C4* | *C5* | *C6* | *C7* | *C7a* | *$R_1$ and/or $R_2$* |
|---|---|---|---|---|---|---|---|
| **4c**[b] | 133.6 | 108.5 | 118.4 | 118.4 | 108.5 | 133.6 | 38.7 ($N–CH_2$), 16.0 ($CH_3$) |
| **5c**[b] | n.o.[a] | 108.5 | 118.4 | 118.3 | 108.6 | 135.0 | 44.0 ($N–\underline{CH_2}CH_3$), 38.7 ($CH_2$), 32.3 ($CH_2$), 20.3 ($\underline{CH_2}$), 16.0 ($N–CH_2\underline{CH_3}$), 13.8 ($CH_3$) |
| **6c**[b] | 132.2 | 109.9 | 119.5 | 118.6 | 108.1 | 131.5 | 128.2 (C-12), 127.8 (C-14), 120.4 (C-13), 55.5 ($N–CH_2Ar$), 42.3 ($CH_3O$), 37.8 ($N–CH_2$), 16.0 ($CH_3$), C-9 n.o.[a] |
| **7c**[b] | 138.5 | 108.1 | 118.6 | 118.6 | 108.1 | 135.8 | 30.6 ($CH_3$) |
| **8c**[b] | 137.2 | 112.4 | 121.8 | 120.6 | 109.3 | 150.3 | 37.8 ($CH_2$), 15.4 ($CH_3$) |
| **9c**[b] | 137.2 | 112.4 | 121.8 | 120.0 | 109.4 | 150.3 | 42.8 ($N–CH_2$), 31.7 ($CH_2$), 20.1 ($CH_2$), 13.7 ($CH_3$) |
| **10c**[b] | 137.6 | 112.4 | 121.9 | 120.3 | 110.2 | 146.9 | 128.6 (C-11), 127.4 (C-12), 127.0 (C-10), 47.1 ($N–CH_2$), C-9 n.o.[a] |
| **11c**[b] | 137.9 | 112.4 | 121.9 | 120.0 | 108.9 | 150.1 | 29.2 ($CH_3$) |
| **12c**[b] | 145.6 | 112.0 | 124.5 | 120.8 | 126.0 | 130.1 | 42.1 ($CH_2$), 16.7 ($CH_3$) |
| **13c**[b] | 145.9 | 111.7 | 124.5 | 120.6 | 126.0 | 127.4 | 47.3 ($CH_2$), 34.2 ($CH_2$), 22.0 ($CH_2$), 13.7 ($CH_3$) |
| **14c**[b] | 145.6 | 112.7 | 124.6 | 121.0 | 125.9 | 137.4 | 128.5 (C-12), 127.2 (C-11), 126.4 (C-10), 51.4 ($CH_2$) |
| **15c**[b] | 145.6 | 113.1 | 125.0 | 121.6 | 126.4 | 130.0 | 157.1 (C-10), 128.5 (C-12), 127.6 (C-14), 121.4 (C-13), 110.2 (C-11), 54.8 ($CH_2$), 46.7 ($CH_3O$), C-9 n.o.[a] |
| **16c**[b] | 146.8 | 111.3 | 125.8 | 124.7 | 120.8 | 129.7 | 34.6 ($CH_3$) |
| **20c**[c] | 135.6 | 111.2 | 119.3 | 119.3 | 111.2 | 135.6 | |
| **21c**[c] | 137.6 | 109.0 | 118.6 | 118.6 | 109.0 | 137.6 | 45.0 (CH), 24.0 ($CH_3$) |
| **22c**[c] | 137.2 | 108.7 | 118.2 | 118.2 | 108.7 | 137.2 | 53.2 (CH), 34.9 ($CH_2$), 26.1 ($CH_2$), 26.1 ($CH_2$) |
| **23c**[c] | 136.4 | 112.6 | 120.3 | 120.3 | 112.0 | 150.4 | |
| **24c**[c] | 137.8 | 112.4 | 121.6 | 119.9 | 109.7 | 150.2 | 44.8 (CH), 23.4 ($CH_3$) |
| **25c**[c] | 136.7 | 112.4 | 121.6 | 119.8 | 109.6 | 150.1 | 52.8 (CH), 34.3 ($CH_2$), 25.7 ($CH_2$), 25.7 ($CH_2$) |
| **26c**[b] | 137.8 | 112.3 | 121.7 | 120.1 | 110.3 | 150.5 | 55.2, 39.5, 38.3, 36.8, 35.0, 29.5, 21.4 |
| **27c**[c] | 145.6 | 113.4 | 124.5 | 120.4 | 124.9 | 133.6 | |

[a]Not observed; [b]at 67.9 MHz; [c]at 22.5 MHz.

ness, then redissolved in hot water and crystallized from ethanol to give 1.87 g (11.7 mmol, 90%) of the desired product; mp 145–147°C. MS (70 eV); *m/z* (%): 160 (22) [$M^+$].

*2-Phenyl-1H-benzimidazole* (**2a**). As described for **1a**, **2a** was prepared from *o*-phenylenediamine and benzoic acid. The reaction afforded a white powder; mp 249.5–251°C. IR (KBr), $\nu$ ($cm^{-1}$): 294 (NH).

*2-(Methylmercapto)benzimidazole* (**3a**). A 2 g (13.3 mmol) portion of **17a** was dissolved in 50 mL of tetrahydrofuran (THF) and mixed with 0.3 g (13.3 mmol) of metallic sodium. The mixture was refluxed for 6 hours. After addition of 5.8 mL (13.3 mmol) of $CH_3I$ and heating for 2 hours, the solvent was eliminated in vacuum. The residue was washed with a mixture of 25 mL of $CH_2Cl_2$ and 75 mL of $H_2O$ (1:3). A white solid was obtained, 1.12 g (56.0%). Mp 196°C (194–200°C [26]). IR (KBr), $\nu$ ($cm^{-1}$): 3448 (N–H), 1636, 1498 (C=C), 740 (C–S). MS (70 eV), *m/z* (%): 164.2 (100%).

*1-Ethyl-2-methylbenzimidazole* (**4a**). As described for **1a**, **4a** was prepared from N-ethyl-1,2-phenylenediamine and acetic acid. The reaction afforded the product as a brown oil in 90% yield.

*1-Ethyl-2-propylbenzimidazole* (**5a**). As described for **1a**, **5a** was prepared from N-ethyl-1,2-phenylenediamine and butyric acid. The reaction afforded the product as a brown oil in 75% yield.

*1-Ethyl-2-(o-methoxyphenyl)benzimidazole* (**6a**). As described for **15a**, **6a** was prepared from N-ethyl-1,2-phenylenediamine and *o*-anisaldehyde. The reaction afforded the product as a brown oil in 80% yield.

*2-(Methylmercapto)-1-methylbenzimidazole* (**7a**). A 0.5 g (3.0 mmol) portion of **3a** was dissolved in 15 mL of THF, and 0.14 g (3.0 mmol) of Na was added. The mixture was refluxed for 6 hours, then 2.67 mL (3.0 mmol) of $CH_3I$ were added and heated for 2 hours. Extraction with 50 mL of $CH_2Cl_2$ and 10 mL of $H_2O$ afforded a brown liquid, 0.45 g (>90%). IR ($CH_2Cl_2$), $\nu$ ($cm^{-1}$): 1702, 1612 (C=C), 750 (C–S). MS (70 eV), *m/z* (%): 178.2 (100%).

*2-Propylbenzoxazole* (**9a**). As described for **1a**, **9a** was prepared from *o*-aminophenol and butyric acid. The reaction afforded the product as a brown oil in 80% yield. MS (70 eV), *m/z* (%): 162 (100) [$M^+$].

*2-Phenylbenzoxazole* (**10a**). As described for **1a**, **10a** was prepared from *o*-aminophenol and benzoic acid. The product was an orange crystalline powder, mp 92–93°C, yield 94%.

*2-(Methylmercapto)benzoxazole* (**11a**). This compound was synthesized from **18a** as described for **3a**. The reaction afforded a brown oil in 40% yield. IR ($CH_2Cl_2$), $\nu$ ($cm^{-1}$): 1600, 1500 (C=C), 742 (C–S). MS (70 eV), *m/z* (%): 165.0 (100%).

*2-Methylbenzothiazole* (**12a**). As described for **1a**, **12a** was prepared from *o*-aminothiophenol and acetic acid. The reaction afforded a clear oil in 80% yield.

*2-Propylbenzothiazole* (**13a**). As described for **1a**, **13a** was prepared from *o*-aminothiophenol and butyric acid. The reaction afforded a brown oil in 85% yield. MS (70 eV), *m/z* (%): 177 (18) [$M^+$].

*2-Phenylbenzothiazole* (**14a**). As described for **1a**, this compound was prepared from *o*-aminothiophenol and benzoic acid. The product was a white crystalline powder (85% yield), mp 89–92°C.

*2-(o-Methoxyphenyl)benzothiazole* (**15a**). A 2 g (16 mmol) amount of *o*-aminothiophenol, 1.98 g (16 mmol) of *o*-anisaldehyde, and 5 mL of nitrobenzene were refluxed (200°C) during 12 hours, then the mixture was cooled for 12 hours. Crystals were filtered off and recrystallized several times from acetone to give 3 g of product as a pale yellow crystalline powder; mp 108°C, 74% yield.

*2-(Methylmercapto)benzothiazole* (**16a**). This compound was synthesized as described for **3a** from **19a**. The reaction afforded a brown liquid in 90% yield. IR ($CH_2Cl_2$), $\nu$ ($cm^{-1}$): 3054 (C–H), 1462, 1468 (C=C), 1266 (C–N). MS (70 eV), *m/z* (%): 181.0 (100%).

*Benzimidazole-2-thione* (**17a**). A solution of 2 g (18.5 mmol) of *o*-phenylenediamine in 8 mL of N,N'-dimethylformamide and 0.7 g of NaOH (18.5 mmol) was cooled to 0°C. After the addition of 1.1 mL of $CS_2$ (18.5 mmol), the mixture was stirred for 20 minutes and heated to reflux for 8 hours. The excess of solvent was removed in vacuum, to give a brown solid that was washed with $CHCl_3$. A beige solid (1.27 g, 63.5% yield) was obtained; mp 305°C (303–304°C [27]). IR (KBr), $\nu$ ($cm^{-1}$): 3238 (N–H), 1626, 1518 (C=C), 1190 (C=S), 702 (C–S). MS (70 eV), *m/z* (%): 150.1 (100%). $^1H$ NMR ([$^2H_6$]DMSO, 270 MHz), $\delta$ = 11.7 (s, 2H, 1,3-H–N), 7.2 (m, 2H, 4,7-H), 7.1 (m, 2H, 5,6-H).

*Benzoxazolidine-2-thione* (**18a**). This compound was obtained as **17a** from 2 g (18.34 mmol) of *o*-aminophenol, 8 mL N,N'-dimethylformamide, 0.69 g of NaOH (18.34 mmol), and 1.4 mL of $CS_2$ (18.34 mmol). A beige solid was obtained (1.9 g, 94.6%). Mp 312°C (193–195°C [27]). IR (KBr), $\nu$ ($cm^{-1}$): 3442 (N–H), 1594, 1414 (C=C), 1070 (C=S), 738 (C–S). MS (70 eV), *m/z* (%): 151.1 (76%). $^1H$ NMR ([$^2H_6$]DMSO, 270 MHz): $\delta$ = 7.1 (m, 2H, 4,7-H), 6.9 (m, 1H, $J$(HH) = 7.6 Hz, $J$(HH) = 7.2 Hz, $J$(HH) = 1.3 Hz, 5-H), 6.8 (m, 1H, $J$(HH) = 7.9 Hz, $J$(HH) = 7.6 Hz, $J$(HH) = 1.3 Hz, 6-H).

*Benzothiazolidine-2-thione* (**19a**). A solution of 6 g (48 mmol) of the *o*-aminothiophenol in 15 mL of dry ethanol and 4.31 mL of $CS_2$ (48 mmol) was cooled to 0°C and stirred for 10 minutes, then the mixture was heated to reflux for 8 hours. The product was purified with activated carbon, filtered, and the solvent was removed in vacuum. The solid was purified by crystallization from a saturated methanolic solution. Brown crystals (5.7 g, 96.2% yield). Mp 175–177°C (170–180°C [27]). IR (KBr), $\nu$ ($cm^{-1}$): 3108 (N–H), 1684, 1558 (C=C), 1034 (C=S), 752 (C–S). MS (70 eV), *m/z* (%): 167.1 (100%). $^1H$ NMR ([$^2H_6$]DMSO, 270 MHz]): $\delta$ = 13.8 (s, v.b., 1H, H–N), 7.7 [m, 1H, $J$(HH) = 8.5 Hz, 7-H], 7.4 [m, 1H, $J$(HH) = 8.2 Hz, $J$(HH) = 7.3, 6-H], 7.3 [m, 2H, 4,5-H].

*2-Propyl-1H-benzimidazole-borane Adduct* (**1b**). This adduct was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 3285 (NH) 2318, 2260 (BH), 1164 (BN).

*2-Phenyl-1H-benzimidazole-borane Adduct* (**2b**). This adduct was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 3294 (NH), 2364, 2308, 2256 (BH), 1194 (BN). MS (70 eV), *m/z* (%): 207.3 (24) [$M^+$], 194.3 (100) [$M^+ - BH_2$], 193.3 (26) [$M^+ - BH_3$].

*[(N–B)-2-(Methylmercapto)benzimidazole]borane Adduct* (**3b**). A solution of 0.2 g (1.21 mmol) of **3a** in 2 mL of THF, maintained under a nitrogen atmosphere, was added to 0.4 mL of $BH_3$-THF (3.0 M) at 0°C. The solvent was removed in vacuum at 0°C. An unstable beige solid was obtained in quantitative yield. IR (THF), $\nu$ ($cm^{-1}$): 2360 (B–H), 1436, 1420 (C=C), 1068, 1158 (N–B), 748 (C–S).

*1-Ethyl-2-methylbenzimidazole-borane Adduct* (**4b**). This adduct was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2388 (BH). MS (70 eV), *m/z* (%): 174 (10) [$M^+$], 173 (100) [$M^+$-H], 160 (8) [$M^+ - BH_3$].

*1-Ethyl-2-propylbenzimidazole-borane Adduct* (**5b**). This adduct was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2412, 2350, 2300, 2275 (BH), 1174 (BN). MS (70 eV), *m/z* (%): 201 (48) [$M^+$], 199 (100) [$M^+ - H_2$].

*1-Ethyl-2-(o-methoxyphenyl)benzimidazole-borane Adduct* (**6b**). **6b** was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2397, 2358, 2307. 2256 (BH), 1163 (BN).

*[(N–B)-2-(Methylmercapto)-1-methylbenzimidazole]borane Adduct* (**7b**). This adduct was prepared as described for **1b** from **7a** and obtained in quantitative yield. Unstable brown solid. IR (THF), $\nu$ ($cm^{-1}$): 2368 (B–H), 1476, 1402 (C=C), 1158, 1124 (N–B), 748 (C–S).

*2-Methylbenzoxazole-borane Adduct* (**8b**). **8b** was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2336, 2286 (BH), 1150 (BN).

*2-Propylbenzoxazole-borane Adduct* (**9b**). **9b** was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2380, 2274 (BH), 1158 (BN). MS (70 eV), *m/z* (%): 174 (3) [$M^+$– H], 133 (4) [$M^+ - C_3H_8$].

*2-Phenylbenzoxazole-borane Adduct* (**10b**). This adduct was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2398, 2362, 2270 (BH), 1142 (BN). MS (70 eV), *m/z* (%): 209 (2) [$M^+$], 195 (100) [$M^+ - BH_3$], 160 (8) [$M^+ - BH_3$].

*[(N–B)-2(Methylmercapto)benzoxazole]borane* (**11b**). This compound was prepared as described for **1b** from **11a** in quantitative yield. Unstable brown solid. IR (THF), $\nu$ ($cm^{-1}$): 2366 (B–H), 1506, 1452 (C=C), 1160, 1132 (N–B), 750 (C–S).

*2-Methylbenzothiazole-borane Adduct* (**12b**). **12b** was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2398 (BH), 1158 (BN). MS (70 eV), *m/z* (%): 163 (11) [$M^+$], 162 (100) [$M^+$– H], 161 (39) [$M^+ - H_2$].

*2-Propylbenzothiazole-borane Adduct* (**13b**). **13b** was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2430, 2352 (BH), 1176 (BN). MS (70 eV), *m/z* (%): 190 (47) [$M^+$], 188 (100) [$M^+ - H_2$].

*2-Phenylbenzothiazole-borane Adduct* (**14b**). This adduct was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2352, 2256 (BH).

*2-(o-Methoxyphenyl)benzothiazole-borane Adduct* (**15b**). This adduct was obtained as a white powder in quantitative yield. IR (KBr), $\nu$ ($cm^{-1}$): 2414, 2360, 2262 (BH), 1146 (BN). MS (70 eV), *m/z* (%): 154 (4) [$M^+$– H], 241 (83) [$M^+ - BH_3$].

*[(N–B)-2-(Methylmercapto)benzothiazole]borane Adduct* (**16b**). **16b** was prepared from **16a** as described for **1b** and was obtained in quantitative yield as an unstable yellow solid. IR (THF), $\nu$ ($cm^{-1}$), 2364 (B–H), 1458, 1424 (C=C), 1174, 1074 (N–B), 760 (C–S).

*[(S–B)-2-(thione)benzimidazole]borane Adduct* (**17b**). A solution of 0.2 g (1.33 mmol) of **17a** in 2 mL of dry THF was cooled to −78°C under a nitrogen atmosphere. After the addition of 0.44 mL (1.33 mmol) of $BH_3$-THF (3.0 M), the mixture was stirred for 30 minutes. The solvent was removed in vacuum to 0°C. An unstable beige solid was obtained in quantitative yield. $^1H$ NMR ($CD_6CO$, 89.55 MHz, 0°C), $\delta$ = 7.0 (m, 4H, 4,5,6,7-H).

*[(S–B)-2-(Thione)benzoxazole]borane Adduct* (**18b**). This adduct was prepared as described for **17b** from **18a** and obtained in quantitative yield. Unstable beige solid. IR (THF), $\nu$ ($cm^{-1}$): 2368 (B–H), 1472, 1460 (C=C), 1292 (C–N), 1068 (C=S), 794 (C–S). $^1H$ NMR ($CD_6CO$, 89.55 MHz, 0°C), $\delta$ = 7.4 (m, 1H, 7-H), 7.1 (m, 3H, 4,5,6-H).

*[(S–B)-2-(Thione)benzothiazole]borane Adduct* (**19b**). This adduct was prepared *in situ*; 50 mg (0.3 mmol) of **19a** was dissolved in 0.4 mL of [$^2H_8$]THF, and 0.1 mL of $BH_3$-THF (3.0 M) was added at −78°C. $^1H$ NMR ([$^2H_8$] THF, 270 MHz, −30°C), $\delta$ = 7.2 (m, 4H, 4,5,6,7-H).

*1,3-Diethyl-1,3,2-benzimidazaborole* (**4c**). In a dried and nitrogen-evacuated glass ampoule was weighed 150 mg of **4b**. The ampoule was sealed under a nitrogen atmosphere and placed inside an aluminum capsule. This capsule was heated in an oil bath at 110–120°C for 1 hour to afford **4c** in quantitative yield as a colorless oil. $^1H$ NMR ($CDCl_3$, 270 MHz): $\delta$ = 7.03 (m, 4H, H–Ar), 3.77 (q, 2H, N–$CH_2$), 1.39 (t, 3H, N–$CH_2\underline{CH_3}$). $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 133.6 (C-3a,7a), 118.4 (C-5,6), 108.5 (C-4,7), 38.7

(N-$CH_2$), 16.0 ($CH_3$). MS (70 eV), *m/z* (%): 174 (79) [$M^+$].

*1-Butyl-3-ethyl-1,3,2-benzimidazaborole* (**5c**). Compound **5c** was obtained from **5b** as described for **4c** (colorless oil). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.03 (m, 4H, H-Ar), 3.76 (q, 2H, N-$CH_2CH_3$), 1.74 (m, 2H, N-$CH_2CH_2$), 1.40 (t, 3H, N-$CH_2CH_3$), 1.37 (sext, 2H, $CH_2$), 0.94 (t, 3H, $CH_3$).

*1-(o-Methoxybenzyl)-3-ethyl-1,3,2-benzimidazaborole* (**6c**). This compound was obtained from **6b** as described for **4c** (colorless oil). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ = 7.0 (m, 8H, H-Ar), 4.96 (s, 2H, N-$CH_2$-Ar), 4.84 (s, 3H, $CH_3O$), 1.42 (q, 2H, N-$CH_2CH_3$), 1.09 (t, 3H, N-$CH_2CH_3$). $^{13}$C NMR (67.9 MHz, $CDCl_3$) $\delta$ = 132.2, 131.5, 128.2, 127.8, 120.4, 119.5, 118.6, 110.4, 108.1, 55.5, 42.3, 16, C*i* were not observed.

*1,3-Dimethyl-1,3,2-benzodiazaborole* (**7c**). A 0.49 g (2.8 mmol) amount of **7a** was mixed with 5.0 mL of $BH_3$-THF (3.0 M, 2.8 mmol) and heated to reflux for 6 hours. The solvent was removed in vacuum; 0.34 g (69.7%) of an unstable colorless liquid was obtained after distillation in vacuum to 55–60°C (0.25 Torr). IR ($CH_2Cl_2$), $\nu$ ($cm^{-1}$): 2588 (B-H), 1488, 1606 (C=C). −MS (70 eV), *m/z* (%): 145.2 (1%) [$M^+$]. $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ = 7.0 (s, 4H, 4,5,6,7-H), 3.4 (s, 3H, N-$CH_3$).

*3-Ethyl-1,3,2-benzoxaborole* (**8c**). Compound **8c** (colorless oil) was obtained from **8b** as described for **4c**. $^1$H NMR (270 MHz, $CDCl_3$), $\delta$ = 7.26 (d, 1H, 4H), 7.07 (m, 3H, 5,6,7-H), 3.86 (q, 2H, $CH_2$), 1.41 (t, 3H, $CH_3$). IR ($CHCl_3$), $\nu$ ($cm^{-1}$): 2684 (BH), 1212 (BO), 1134 (BN).

*3-Butyl-1,3-benzoxaborole* (**9c**). Compound **9c** (yellow oil) was obtained from **9b** as described for **4c**. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ = 7.22 (m, 1H, 4-H), 7.04 (m, 1H, 5-H), 6.95 (m, 2H, 7-H), 6.94 (t, 1H, 6-H). IR ($CDCl_3$), $\nu$ ($cm^{-1}$): 2605, 2620 (BH), 1236 (BO).

*3-Benzyl-1,3,2-benzoxaborole* (**10c**). This compound (colorless oil) was obtained from **10b** as described for **4c**. $^1$H NMR ($CDCl_3$) $\delta$ = 7.24 (m, 1H, 4-H), 7.20 (m, 5H, H-Ar), 6.94 (m, 2H, 5,6-H), 6.81 (m, 1H, 7-H), (s, 2H, N-$CH_2$). IR ($CDCl_3$), $\nu$ ($cm^{-1}$): 2606 (BH).

*3-Methyl-1,3,2-benzoxazaborole* (**11c**). Compound **11c** was prepared as described for **7a** from **11a**. A colorless liquid was distilled (54°C, 0.25 Torr), 0.82 g (37.4%). IR ($CHCl_3$), $\nu$ ($cm^{-1}$): 2618 (B-H), 1706, 1616 (C=C), 1364 (B-O), 1436 (B-N). MS (70 eV), *m/z* (%): 132.2 (100%) [$M^+$]. $C_7H_8BNO$, calcd. 63.24 C, 10.53 N, 6.06 H; found 63.04 C, 10.27 N, 6.03 H. $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ = 7.2 (m, 1H, 4-H), 7.1 (m, 1H, 5-H), 7.0 (m, 2H, 7,6-H), 3.3 (s, 3H, N-$CH_3$).

*3-Ethyl-1,3,2-benzothiazaborole* (**12c**). This compound (colorless oil) was obtained from **12b** as described for **4c**. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ = 7.63 (d, 1H, 7-H), 7.27 (t, 1H, 5-H), 7.16 (d, 1H, 4-H), 7.07 (t, 1H, 6-H), 3.88 (q, 2H, N-$CH_2$), 1.40 (t, 3H, N-$CH_2CH_3$).

*3-Butyl-1,3,2-benzothiazaborole* (**13c**). This compound was obtained from **13b** as described for **4c** (colorless oil). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ = 7.66 (d, 1H, $J$(6,7) = 7.7, 7-H), 7.29 (t, 1H, $J$(5,6) = 7.1, 5-H), 7.17 (d, 1H, $J$(4,5) = 7.6, $J$(4,6) = 1.2, 4-H), 7.08 (t, 1H, 6-H), 3.89 (t, 2H, N-$CH_2$), 1.76 (tt, 2H, N-$CH_2CH_2$), 1.37(tq, 2H, $CH_2$), 0.95 (t, 3H, $CH_3$). IR ($CDCl_3$), $\nu$ ($cm^{-1}$): 2592 (BH), 1324 (BS), 1308 (BN).

*3-Benzyl-1,3,2-benzothiazaborole* (**14c**). Compound **14c** was obtained from **14b** as described for **4c** (colorless oil). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ = 7.68 (d, 2H, $J$(10,11) = 7.9, 10-H), 7.58 (d, 1H, $J$(6,7) = 7.6, $J$(5,7) = 1.9, 7-H), 7.15 (m, 3H, 11,12-H), 7.07 (t, 1H, 6-H), 6.96 (t, 1H, 5-H), 6.93 (d, 1H, $J$(4,5) = 7.2, 4-H), 4.97 (s, 2H, N-$CH_2$). IR ($CDCl_3$), $\nu$ ($cm^{-1}$): 2766 (BH). MS (70 eV), *m/z* (%): 225 (93) [$M^+$].

*3-(o-Methoxybenzyl)-1,3-benzothiazaborole* (**15c**). This compound was obtained from **15b** as described for **4c** (colorless oil). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ = 7.53 (d, 1H, $J$(6,7) = 7.5-H), 6.98 (t, 1H, 12-H), 6.95 (d, 1H, $J$(4,5) = 7.4, 4-H), 6.95 (t, 1H, $J$(5,6) = 7.4, 5-H), 6.86 (t, 1H, 13-H), 6.80 (d, 1H, 14-H), 6.59 (t, 1H, 6-H), 6.47 (d, 1H, 11-H), 5.01 (s, 2H, (N-$CH_2$), 3.29 (s, 3H, $CH_3O$). IR ($CDCl_3$), $\nu$ ($cm^{-1}$): (BH), 1348 (BS), 1304 (BN).

*3-Methyl-1,3,2-benzothiazaborole* (**16c**). Compound **16c** was obtained from **16b** as described for **4c**; it is a colorless liquid (distilled to 69°C, 0.25 Torr, 0.41 g, 42% yield). IR (THF), $\nu$ ($cm^{-1}$): 2618 (B-H), 1590, 1466 (C=C), 1178 (B-S). MS (70 eV), *m/z* (%): 149.2 (100%) [$M^+$]. $C_7H_8BNS$ (148.8), calcd 56.43 C, 9.30 N, 5.40 H; found 56.23 C, 8.93 N, 5.49 H. $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ = 7.6 (m, 1H, 7-H), 7.3 (m, 1H, 5-H), 7.1 (m, 2H, 4,6-H), 3.4 (s, 3H, N-$CH_3$).

*1,3-H-1,3,2-Benzimidazaborole* (**20c**). Com-

pound **20c** was prepared from 1,2-phenylenediamine and $BH_3$-THF, as described before [26]. Colorless liquid (distilled to 130°C, 0.25 Torr) (69%). $^1H$ NMR ($CDCl_3$, 89.55 MHz) $\delta$ = 6.9 (m, 4H, 4,5,6,7-H), −IR ($CCl_4$), $\nu$ ($cm^{-1}$) 2610 (B–H).

*1,3-Diisopropyl-1,3,2-benzimidazaborole* (**21c**). This compound was obtained from 1,2-(diisopropyl)phenylene diamine as **20c** in quantitative yield. IR ($CHCl_3$), $\nu$ ($cm^{-1}$): 2625 (B–H).

*1,3-Dicyclohexyl-1,3,2-benzimidazaborole* (**22c**). This compound was obtained as a white solid from 1,2-(dicyclohexyl)phenylenediamine in quantitative yield. $^1H$ NMR ($CDCl_3$, 89.55 MHz) $\delta$ = 6.9 (m, 4H, 4,5,5,7-H), 3.5 (m, 2H, CH), 2.4–1.0 (m, 20H, $CH_2$). IR ($CHCl_3$), $\nu$ ($cm^{-1}$): 2610 (B–H).

*3H-1,3,2-Benzoxaborole* (**23c**). Compound **23c** was obtained from 2-aminophenol as a colorless liquid (distilled at 107°C, 0.25 Torr, 44% yield). $^1H$ NMR ($CDCl_3$, 89.55 MHz) $\delta$ = 7.2 (d, 1H, 4-H), 7.0 (m, 3H, 4,5,6-H). IR (THF), $\nu$ ($cm^{-1}$): 2614 (B–H).

*3-Isopropyl-1,3,2-benzoxaborole* (**24c**). Compound **24c** was obtained as a colorless liquid from 2-(N-isopropyl)aminophenol in quantitative yield. IR ($CHCl_3$): $\nu$ ($cm^{-1}$) 2627 (B–H).

*3-Cyclohexyl-1,3,2-benzoxaborole* (**25c**). This compound was obtained as a white solid in quantitative yield from 2-(N-cyclohexyl)aminophenol. $^1H$ NMR ($CDCl_3$, 89.55 MHz) $\delta$ = 7.4 (d, 1H, 4-H), 7.1 (m, 3H, 4,5,6-H), 3.6 (m, 1H, CH), 2.4–0.9 (m, 10H, $CH_2$). IR ($CHCl_3$), $\nu$ ($cm^{-1}$): 2626 (B–H).

*3-Norbornyl-1,3,2-benzoxaborole (endo)* (**26c**). Compound **26c** was obtained as a colorless liquid (distilled at 170–190°C, 0.25 Torr) from N-[(2-hydroxy)phenyl]norbornaneimine. $^1H$ NMR ($CDCl_3$, 270 MHz) $\delta$ = 7.23 (d, 1H, $J$(4,5) = 7.7, 4-H), 7.05 (m, 1H, $J$(5,6) = 7.8, 5-H), 6.99 (m, 1H, 6-H), 6.94 (d, 1H, $J$(6–7) = 6.8, 7-H), 4.1 (m, 1H, 8-H), 2.52 (m, 1H, 12-H), 2.26 (m, 1H, 9-H), 2.03 (d, 1H, 14-H), 1.53 (d, 1H, 14-H), 1.5–1.6 (m, 2H, 10-H*a*, 11-H*a*), 1.42 (m, 1H, 13-H*e*), 1.33 (m, 1H, 13-H*a*), 1.28 (m, 1H, 11-H*e*), 1.25 (m, 1H, 10-H*e*). IR ($CHCl_3$), $\nu$ ($cm^{-1}$): 2624 (B–H).

*1H-1,3,2-Benzothiazaborole* (**27c**). Compound **27c** was obtained from 2-aminothiophenol and was purified by distillation (100°C, 0.250 Torr) to give a solid; mp 52°C (74% yield). $^1H$ NMR ($CDCl_3$, 270 MHz) $\delta$ = 7.6 (d, 1H, 7-H), 7.1 (m, 2H, 5,6-H), 6.9 (d, 1H, 4-H), 3.4 (b, 1H, BH), IR ($CCl_4$) $\nu$ ($cm^{-1}$) 2608 (B–H).

**TABLE 9** Crystallographic Experimental Details for **15b**

| *Crystal Data* | *2-(o-Methoxyphenyl)-benzothiazole-borane adduct* ***15b*** |
|---|---|
| Formula | $C_{14}H_{14}BNOS$ |
| Fw (g/mol) | 255.15 |
| Habit | yellow rectangular |
| Crystal size (mm) | 0.40 × 0.30 × 0.40 |
| F(000) | 536 |
| Crystal system | orthorombic |
| Space group | $Pna2_1$ |
| a (Å) = | 8.522 (2) |
| b (Å) = | 10.869(4) |
| c (Å) | 14.344 (6) |
| $\alpha$ (°) = | 90 |
| $\beta$ (°) = | 90 |
| $\gamma$ (°) = | 90 |
| V ($Å^3$) = | 1328.6(4) |
| Z | 4 |
| Systematic absences | *h*01: $h = 2n$; 0*k*1:$k + 1 = 2n$ |
| Diffractometer | CAD4-Enraf-Nonius |
| Radiation (Å) | MoK$\alpha$ (0.71073) |
| Linear abs coeff $cm^{-1}$ | 2.200 |
| D (calc) (g $cm^{-3}$) | 1.28 |
| Scan type | $\omega/2\theta$ |
| Scan width (deg) | 0.6 + 0.840 $tg\,\theta$ |
| Scan speed (deg/min) | 2–20 |
| $\theta$ limits (deg) | 0–25 |
| Temperature (°C) | −80 |
| Reflections collected | 2226 |
| Unique reflections collected | 2226 |
| Unique reflections used | 1360 $(Fo)^2 > 3\,\sigma(Fo)^2$ |
| R (int) | 0.01 |
| Decay % | <1 |
| $R = \Sigma\|\|Fol - |Fc|\|)/\Sigma|Fol$ | 0.047 |
| $Rw = [\Sigma\, w(|Fol - |Fc|-)^2/\Sigma\, wFo^2]^{1/2}$ | 0.058 |
| Goodness of fit | 1.08 |
| No. of variables | 212 |
| $\Delta\rho$min (e/$Å^3$) | −0.39 (0) |
| $\Delta\rho$max (e/$Å^3$) | 0.70 (16) |

*6,9-(Ethyl)-diaza-2-oxa-1-bora-[3,4,7,8]dibenzobycyclo[4.3.0]nona-3,7-diene* (**6d**). This compound was obtained as a colorless oil mixed with **6c** (40%). $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ = 7.0 (m, 8H, H–Ar), 4.96 (s, 2H, N–$\underline{CH_2}$Ar), 1.03 (t, 2H, N–$CH_2\underline{CH_3}$). $^{13}C$ NMR (67.9 MHz, $CDCl_3$) $\delta$ = 132.8, 132.2, 128.0, 120.8, 119.0, 118.5, 109.8, 107.4, 110.2, 55.8, 36.5, 15.4; C*i* signals were not observed. $^{11}B$ RMN (86.8 MHz, $CDCl_3$) $\delta$ = 22.8 (s, b).

*8-Aza-9-oxa-2-thia-1-bora-[3,4,7,8]dibenzobycyclo[3.4.0]nona-3,7-diene* (**15d**). Compound **15d**

was obtained as a colorless oil mixed with **15c** (60%). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ = 8.5 (s, 1H, H–Ar), 8.0 (d, 1H, $J$(H,H) = 7.9 Hz, H–Ar), 7.85 (d, 1H, $J$(H,H) = 7.9 Hz, H–Ar), 7.84 (d, 1H, $J$(H,H) = 7.9 Hz), 7.14 (m, 3H, H–Ar), 4.8 (s, 2H, $CH_2$). $-^{13}$C NMR (67.8 MHz, $CDCl_3$) $\delta$ = 150.0, 143.7, 128.7, 127.7, 126.0, 125.8, 125.7, 125.1, 123.3, 121.1, 119.0, 110.0, 43.2 ($^3J$(C,H) = 5.6 Hz). $^{11}$B NMR (86.8 MHz, $CDCl_3$) $\delta$ = 37.6 (s, b). MS (70 eV), *m/z* (%): 225 (100) [$M^+ - CH_2$].

*X-ray structure determination of* **15b**. Single crystals of **15b** were grown from a saturated THF solution at room temperature. Suitable single crystals were sealed in a glass capillary and mounted on the difractometer (ENRAF-NONIUS CAD4). The structure was solved by direct methods. H atoms were located and refined isotropically. All calculations were performed on a VAX computer using Molen. Crystallographic experimental data are summarized in Table 9.

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