5-Methyl-1-phenylpyrrolo[3,4-*d*]borepin: a Polarized Aromatic Molecule

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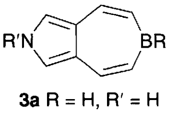
Spectroscopic data together with molecular orbital calculations show that 5-methyl-1-phenylpyrrolo[3,4-*d*]borepin is a polar aromatic system, whose stability confirms our guide for construction of stable heteroaromatic compounds.

Borepin[1] annelated with a heterole is isoelectronic to azulene, and is regarded as a polarized molecule since a heterole ring is electron donating and a borepin ring is electron accepting. Our previous papers[2] have described how the 1-phenyl derivatives **1b**, **2b** of thieno[3,4-*d*]borepin **1a** and thieno[2,3-*d*]borepin **2a** are aromatic 10π systems, each possessing a dipole moment vector the negative end of which is towards the boron. Compound **1b**, however, was more labile toward proton acids and formed an adduct with amines more readily than **2b**. Solvatochromism of fluorescent emissions of **1b** and **2b** indicated that the dipole moment vector in the electronically excited state (μ_e) of each molecule was larger than that in the ground state (μ_g).[3] These facts suggested a guide for the construction of polarized and stable heteroaromatic compounds.[2b,c]

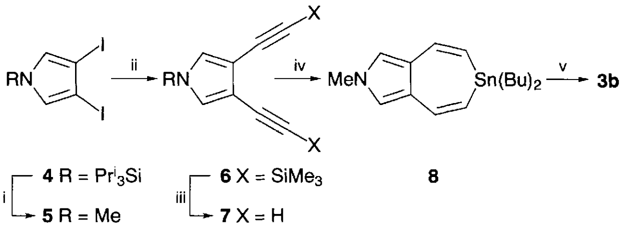
The negative end of the dipole moment vector of thiophene[4] is towards the heteroatom, and that of pyrrole is towards the opposite side.[5] Hence, we have examined 5-methyl-1-phenylpyrrolo[3,4-*d*]borepin **3b** for the construction of a more polarized heteroaromatic compound.

The synthetic method starting with 1-tris(isopropyl)silyl-3,4-diiodopyrrole **4**,[6] followed by a coupling reaction[7] and hydrostannation,[8] resembles that of **1b** and **2b**. Though **3b** decomposed in benzene at 30 °C, recrystallization was achieved in toluene at −50 °C to yield pale-yellow, flaky crystals (mp 120–122 °C).†

Table 1 shows chemical shifts of skeletal atoms in **3b** together with those of **1b**, **2b** and 1-phenylborepin.[1a] Downfield shifts for all skeletal protons of **3b** are indicative of the diamagnetic ring current induced over two rings in **3b**. Skeletal carbons as well as the boron in the borepin moiety are shielded and both the nitrogen and carbons in the pyrrole moiety are deshielded, when compared to corresponding atoms in a divinylborane moiety of 1-phenyl-4,5-dihydroborepin **10**[9] and those in a pyrrole moiety of 1-methyl-3,4-divinylpyrrole, respectively. Hence, it is indicated that π-electrons in **3b** are donated from the pyrrole ring to the borepin ring.[10] The pronounced shielding in the borepin ring in **3b** shows that **3b** possesses a larger dipole moment vector than **1b**. The chemical shifts of α-carbons to the boron indicate that these atoms in **3b** are more negatively charged compared to those in **1b** and **2b**. Interestingly, the chemical shift of the boron in **3b** is between those of **1b** and **2b**. Since the annelation modes in **1b** and **3b** are similar, the difference in the π electron-donating abilities between the thiophene and pyrrole rings rationalizes the ^{11}B chemical shifts of these two molecules. The upfield shift, *i.e.* the highest degree of delocalization of the π-electron onto the boron in **2b**, however, should be ascribed to the annelation mode of the two rings in this molecule, as suggested previously.[2c] These

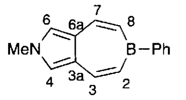


3a R = H, R′ = H
b R = Ph, R′ = Me

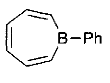


Scheme 1 *Reagents and conditions*: i, MeI (5 equiv.), $(Bu)_4NF$ (1 equiv.), THF, room temp., 30 min, 96%; ii, $HC{\equiv}CSiMe_3$ (2.1 equiv.), CuI (0.1 equiv.), $PdCl_2(Ph_3P)_2$ (0.1 equiv.), piperidine, 40–45 °C, 20 h, 78%; iii, K_2CO_3 (1 equiv.), MeOH, 2.5 h, 30 °C, quant.; iv, $SnH_2(Bu)_2$ (1 equiv.), AIBN (cat. amount), benzene, reflux, 2 h, 50%; v, $PhBCl_2$ (2 equiv.), degassed hexane, ice cooling, 10 min, 45%

Table 1 δ^{1}H, ^{13}C, ^{11}B and ^{14}N of **3b**, **1b**, **2b** and **9** compared with those of a corresponding divinylheterole and 1-phenyl-4,5-dihydroborepin[a,b]



3b



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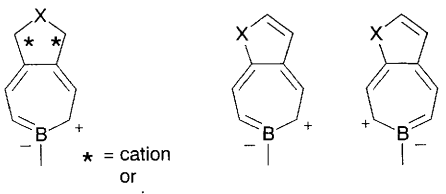
	3b[j]	**1b**[k]		**2b**[l]	**9**[m]
H-2,8[c,d]	7.19 (2.21)	7.31 (2.07)	7.88 (2.62)	7.81 (2.63)	8.10 (1.35)
H-3,7	8.04 (1.37)	8.09 (1.36)	8.43 (1.61)	8.44 (1.53)	7.62 (0.44)
H-4,6	7.06 (0.43)	7.75 (0.48)		7.40–7.50 (0.32–0.42)	
H-5			7.56 (0.41)		
C-2,8[d,e]	132.3 (−3.6)	134.7 (−1.2)	140.8 (4.9)	139.3 (3.4)	149.5 (13.6)
C-3,7	145.1 (−11.6)	145.7 (−11.0)	145.9 (−10.8)	143.6 (−13.1)	148.2 (−6.8)
C-3a,6a[d,g]	127.1 (5.6)	141.8 (3.0)	142.9 (4.4)	146.1 (9.3)	135.4
C-4,6	123.7 (3.9)	129.8 (8.4)		132.4 (8.8)	
C-5			127.6 (2.0)		
B[e,h]	50.0 (−4.6)	50.8 (−3.8)	48.5 (−6.1)		48.8 (−5.8)
N[g,i]	−217 (11)				

[a] Chemical shifts in $CDCl_3$. [b] The numbering shown was chosen for its consistency with that of **3b**. Plus and minus symbols in parentheses indicate deshielding and shielding, respectively. [c] Compared with those of a corresponding divinylheterole. [d] $SiMe_4$ as standard. [e] Compared with those of 1-phenyl-4,5-dihydroborepin. (see [f]). [f] Ref. 9. [g] Compared with those of a heterole moiety of a correspon-ding divinylheterole. [h] BF_3OEt_2 as standard. [i] aq. $NaNO_2$ as standard. [j] This work. [k] Ref. 2*a*. [l] Ref. 2*b*. [m] Ref. 1*a*.

trends in chemical shift of the boron and α-carbons are interpretable as a result of a lower degree of contribution of the canonical structure **1A**[2c] or **3A**, in which an unstable 1,3 dipole is involved in the heterole moiety. The canonical structure **2A** would contribute to a greater extent since it does not possess such an unstable partial structure.



1 A: X = S
3 A: X = NMe

2 A: X = S

In a mixture of acetic acid and cyclohexane (1 : 30 *v*/*v*) at room temp., **3b** underwent protonolysis faster (0.103 min^{-1}, relative rate: 330) than **1b** (0.065 min^{-1}, 210) and **2b** (3.08×10^{-4} min^{-1}, 1), quantitatively giving 1-methyl-3,4-divinylpyrrole. For usual alkenylboranes, the determinant factor in protonolysis with carboxylic acids is known to be coordination of the boron to an oxygen atom of carboxylic acids.[11] A highly π electron-donating pyrrole ring in **3b**, however, would diminish the coordination ability of the boron to a greater extent. Hence, protonation on the α-carbons of the boron is concluded to play a key role in the protonolysis of **3b**. Thus, donation of π electrons from a pyrrole ring toward the electropositive boron gives rise to an unfavourable negative charge on the α-carbons of the boron in **3b**, which accelerates protonation to these atoms causing the kinetic instability. Equilibrium constants for adduct formation[12] with piperidine were 1×10^3, 3×10^4, and 1×10^4, and the values with 2-methylpiperidine were 9, 2.9×10^2, and 3.3×10 for **3b**, **1b** and **2b**, respectively. This is partly interpretable in view of the higher electron density of the boron in **3b**. Thus, of these three compounds, **3b** is most labile toward acids and most stable toward amines.

The absorption spectrum of **3b** displays only slight solvatochromism. The longest wavelength band (cyclohexane, 356 nm, log ε: 3.99 sh)‡ shows a bathochromic shift of only 8 nm as compared with **1b**[2a,c] or 1-phenyl-3-benzoborepin.[9a,c] The fluorescence spectrum ($\Phi = 1.3 \times 10^{-1}$, cyclohexane) displays marked solvatochromism, *e.g*. 87 nm with a change of the solvent from cyclohexane to DMF. If we take 4 Å, which was estimated for azulene,[13] as the lower limit for the Onsager's effective cavity radius,[14] the difference between the dipole moment vector of the excited state and that of the ground state (μ_e–μ_g) is considered to be 9.2 D.[15] The value is larger than those of **1b** and **2b** (7.7 and 3.1 D, respectively).[2c] Comparison with that of 1-phenyl-3-benzoborepin (0 D)[2c] reveals the notable feature of borepin annelated with a heterole.

Ab initio MO calculations carried out for **3a** with a 3-21G set[2a,c] are consistent with the above-mentioned findings.[16] Both the calculated net atomic charge and the net π charge (0.792 and −0.2460, respectively) of the boron in **3a** are between those of **1a** (0.813, −0.2161) and **2a** (0.771, −0.2887).[2c] The values for the α-carbons are in the order of **3a** (−0.614, −0.0244), **1a** (−0.615, −0.0064), and **2a** (−0.587, 0.0412 and −0.584, 0.0465), respectively. The dipole moment (5.286 D) is much larger than that of **1a** (1.192 D) and **2a** (2.112 D). The distance between the boron and the α-carbon (1.543 Å), which is relevant to a double bond character, is comparable with that of **1a** (1.545 Å) and is definitely longer than that of **2a** (1.533 Å). Bond alternation in C$_2$–C$_3$ and C$_3$–C$_{3a}$ bonds (C$_8$–C$_7$, C$_7$–C$_{6a}$) (1.340, 1.443 Å) is between those of **1a** (1.335, 1.460 Å) and **2a** (1.347, 1.437 Å and 1.348, 1.424 Å).[2c]

On the whole, **3b** is a highly polarized and peripherally conjugated aromatic compound. It holds the optical features[2c,17] that were observed in a series of compounds **1b**, **2b**, and 1-phenyl-3-benzoborepin. Comparison of their structural properties and reactivities further supports our consideration of the construction of heteroaromatics.[2b,c]

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Footnotes

† All compounds were identified spectroscopically and by means of HRMS.

‡ UV–VIS of **3b** (cyclohexane): λ_{max}/nm = 220 (log ε, 4.29), 261 (4.29), 270 (4.56), 280 (4.77), 318 (4.19), 331 (4.33), 356 (3.99).

References

1 For monocyclic borepins, see: (*a*) A. J. Ashe, III, J. W. Kampf, Y. Nakadaira and J. M. Pace, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1255; (*b*) A. J. Ashe, III and F. J. Drone, *J. Am. Chem. Soc.*, 1987, **109**, 1879; (*c*) Y. Nakadaira, R. Sato and H. Sakurai, *Chem. Lett.*, 1987, 1451; (*d*) J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, 1975, **97**, 4436.

2 (*a*) Y. Sugihara, T. Yagi, I. Murata and A. Imamura, *J. Am. Chem. Soc.*, 1992, **114**, 1479; (*b*) Y. Sugihara, R. Miyatake and T. Yagi, *Chem. Lett.*, 1993, 933; (*c*) Y. Sugihara, R. Miyatake, T. Yagi, I. Murata, M. Jinguji, T. Nakazawa and A. Imamura, *Tetrahedron*, 1994, **50**, 6495.

3 For the importance of a value, μ_e–μ_g, in the field of nonlinear optical organic materials, see: J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664.

4 B. Harris, R. J. W. Le Fevre and E. P. A. Sullivan, *J. Chem. Soc.*, 1953, 1622; D. T. Clark, *Tetrahedron*, 1968, **24**, 2663.

5 T. J. Barton, R. W. Roth and J. G. Verkade, *J. Am. Chem. Soc.*, 1972, **94**, 8854.

6 A. Alvarez, A. Guzmán, A. Ruiz, E. Velarde and L. M. Muchowski, *J. Org. Chem.*, 1992, **57**, 1653; K.-P. Stefan, W. Schuhmann, H. Parlar and F. Korte, *Chem. Ber.*, 1989, **122**, 169.

7 S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627.

8 A. J. Leusink, H. A. Budding and J. G. Noltes, *J. Organomet. Chem.*, 1970, **24**, 375; A. J. Leusink, J. G. Noltes, H. A. Budding and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 1036.

9 (*a*) A. J. Leusink, W. Drenth, J. G. Noltes and G. J. M. van der Kerk, *Tetrahedron Lett.*, 1967, 1263; (*b*) G. E. Herberich, E. Bauer, J. Hengesbach, U. Kölle, G. Huttner and H. Lorenz, *Chem. Ber.*, 1977, **110**, 760; (*c*) D. Sheehan, PhD Thesis, Yale University, New Haven, CT, 1964.

10 H. Nöth and B. Wrackmeyer, *Chem. Ber.*, 1974, **107**, 3089; B. F. Spielvogel, W. R. Nutt and R. A. Izydore, *J. Am. Chem. Soc.*, 1975, **97**, 1609.

11 L. H. Toporcer, R. E. Dessy and S. I. E. Green, *J. Am. Chem. Soc.*, 1965, **87**, 1236.

12 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.

13 N. Mataga and T. Kubota, *Molecular Interactions and Electronic Spectra*, Marcel-Dekker, New York, 1970, ch. 13, p. 390; (*b*) E. Lippert, *Z. Electrochem.*, 1957, **61**, 962.

14 L. Onsager, *J. Am. Chem. Soc.*, 1936, **58**, 1486.

15 E. Lippert, *Z. Naturforsch. Teil A.*, 1955, **10**, 541; N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 1955, **28**, 690; 1956, **29**, 465.

16 For the molecular orbital calculations of the π electron density of the boron in borepins bearing a π electron-donating substituent, see: J. M. Schulman, R. L. Disch and M. L. Sabio, *J. Am. Chem. Soc.*, 1982, **104**, 3785.

17 *Nonlinear Optical Properties of Organic Molecules and Crystals*, vol. 1, 2. ed. D. S. Chemla and J. Zyss, Academic, Orlando, FL, 1987.