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Insight into the Electronic State of 1-Phenylthieno [2,3-*d*]borepin by Means of Nuclear Magnetic Resonance Spectroscopy

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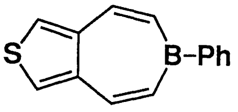
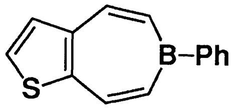
In order to obtain an insight into the electronic states in connection with the condensation modes of thiophene and borepin rings, we examined 1-phenylthieno[2,3-*d*]borepin (**2**). While 1-phenylthieno[3,4-*d*]borepin is a peripherally conjugated compound, **2** was shown to be an aromatic compound which maintains characteristics in conjugation of individual rings.

In the preceding paper,[1)] we have claimed that 1-phenylthieno[3,4-*d*]borepin (**1**) is a peripherally conjugated compound with a dipole moment whose negative end is toward a borepin ring. In order to obtain a further insight into electronic states in connection with the condensation modes of thiophene and borepin rings, we examined 1-phenylthieno[2,3-*d*]borepin (**2**). Herein we show a synthetic method and an insight into the electronic state of **2** on the basis of the ^{1}H, ^{13}C, and ^{11}B NMR spectroscopic data.

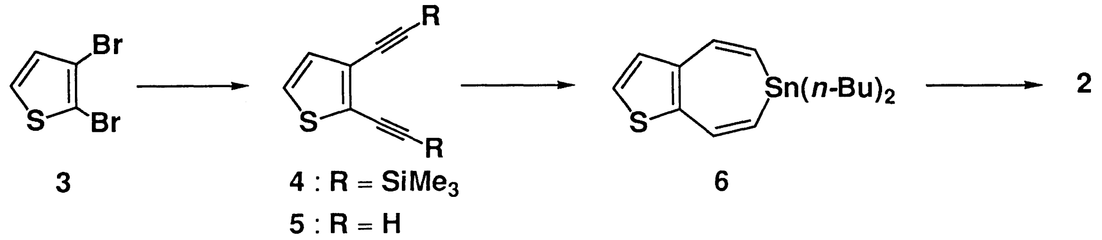


1



2

The synthetic method for **2** closely resembles that for **1**. Thus, commercially available 2,3-dibromothiophene (**3**) (10 g, 41 mmol) was treated with (trimethylsilyl)acetylene (8.9 g, 91 mmol) in the presence of cuprous iodide (0.3 g, 1.6 mmol) and dichlorobis(triphenylphosphine)palladium (II) (1.2 g, 1.7 mmol) in refluxing piperidine for 4 h to give 2,3-bis[(trimethylsilyl)ethynyl]thiophene (**4**) in 28% yield, together with 3-(trimethylsilyl)ethynylthiophene in 28% yield. After desilylation of **4** with potassium carbonate in



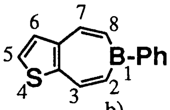
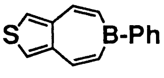
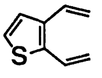
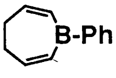
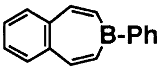
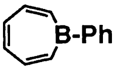
Scheme 1.

methanol, hydrostannation with an equimolar amount of di-*n*-butylstannane (1.5 g, 6.4 mmol) catalyzed by powdered potassium hydroxide (0.26 g, 6.5 mmol)/18-crown-6 (30 mg, 0.1 mmol) afforded 1,1-di-*n*-butylthieno[2,3-*d*]stannepin (**6**) in 51% yield. The reaction of the stannepin (**6**) (0.71 g, 1.9 mmol) in *n*-hexane (13 ml) with phenylboron dichloride (0.65 g, 4.1 mmol) gave the desired thienoborepin (**2**) in 43% yield as a solid, which was isolated by filtration followed by recrystallization with benzene as pale yellow flaky crystals (mp 165 − 166 °C).[2]

Like **1**, the UV/VIS spectrum of **2** in cyclohexane essentially consists of two bands centered at 282 nm (log ε, 4.60) and 331 nm (4.30), and the longer wavelength band has prominent vibrational fine structure (λmax 331 and 346 nm). The band, however, is broader[3] and the intensity is much larger as compared with 3-phenyl-3-benzoborepin (**7**),[3] suggesting more than two transitions are involved in the band.[4]

In Table 1, here summarized are ^{1}H, ^{13}C, and ^{11}B chemical shifts of **1**, **2** and some pertinent related compounds (**7**, **8**, **9**, and **10**). For the comparison of chemical shifts of skeletal protons, carbons, and the boron in the thiophene or borepin moiety in **2**, compounds **8** and **9** are regarded as good reference compounds, respectively. The protons attached to the borepin ring in **2** (H_2, H_3, H_7, and H_8) resonate downfield by ca. 1.1 − 1.3 ppm. Signals due to thiophene ring protons likewise appear downfield by ca. 0.4 ppm. The marked deshielding for all the skeletal protons obviously exhibits that the diamagnetic ring current is induced in **2**. In ^{13}C NMR spectra, thiophene ring carbons in **2** show distinct downfield shifts. As for skeletal atoms in the borepin ring, while α carbons of the boron are deshielded to some extent, β carbons and the boron are by far shielded, indicating that total π electron density on these atoms in **2** is higher than that of the corresponding

Table 1. ^{1}H, ^{13}C, and ^{11}B NMR Chemical Shifts of **2** Compared with Those of **1**, **7**, **8**, **9**, and **10** [a)]

	 **2** b)	 **1** c)	 **8** b, g)	 **9** d)	 **7** c, e)	 **10** f)
H - 2, 8	7.88 7.81	7.31	5.26 5.18	6.75	7.74	8.10
H - 3, 7	8.43 8.44	8.09	6.82 6.91	7.18	8.23	7.62
H - 5	7.56		7.15			
H - 6	7.40-7.50	7.75	7.08			
C - 2, 8	140.8 139.3	134.7	114.2 114.8	135.9	140.2	149.5
C - 3, 7	145.9 143.6	145.7	128.8 127.7	156.7	154.0	148.2
C - 3a, 6a	142.9 146.1	141.8	138.5 136.8		138.4	135.4
C - 5	127.6		125.6			
C - 6	132.4	129.8	123.6			
B	48.5	50.8		54.6	49.5	48.8

a) Numbering shown was chosen for consistency with that of **2**. b) This work. c) Ref. 1. d) Ref. 5. e) Ref. 3. f) Ref. 6. g) Only the chemical shift for (E) - H is shown.

atoms in **9**. These data convincingly manifest that **2** is an aromatic compound with a dipole moment.

Meanwhile we would like to put forward further considerations. From Table 1, it is found that protons attached to the borepin ring in **2** resonate downfield over those of **7**. Since the diamagnetic anisotropy due to the neighboring thiophene ring is definitely smaller for H_7 and H_8 in **2** than that of the benzene ring for the corresponding protons in **7**, downfield shifts for these protons of **2** should reasonably be ascribed to the predominant diamagnetic ring current induced in the borepin ring of **2** as compared with that in **7**. A consideration on relative shifts of α and β carbons of the boron advances this view. Thus, it has been stressed[7)] that both the α and β carbons of monocyclic borepins such as **10** are almost equivalently deshielded in contrast to vinyl boranes whose β carbons are highly deshielded. Actually, while the shift of the β carbon from the α carbon is -1.3 ppm for **10**, the value for **9** is 20.8 ppm. Though the chemical shift differences for **7** and **1** are diminished to some extent (13.8 and 11.0 ppm), the β carbons of both compounds are still highly deshielded than the α carbons like **9**. The trend holds in **2**. The decrease of the chemical shift difference, however, is by far pronounced. The characteristics in ^{13}C NMR spectra should successfully be interpreted in terms of the extent of contribution of the canonical forms **A** (Chart 1) in which α carbons bear positive charge to cause the downfield shifts of the carbons. In the case of **1** and **7**, the form **1A** and **7A** are considered not to be principal contributors, since each form possesses an unstable tetravalent sulfur or *o*-quinodimethane structure, respectively. The situation for **2A** is similar to **7A**. The form **2A** should, however, contribute to a larger extent because of a smaller aromatic resonance energy of a thiophene ring. The form **10A** does not bear any such moieties which cause the destabilization of the form. Thus, relative shifts of α and β carbons for **10**, **2**, **1**, **7**, and **9** are parallel with the contribution of the each canonical form **A**. Since the canonical forms **A** involve the conjugation of 6π electrons in the borepin ring (borepin conjugation), they should be associated with the above-mentioned diamagnetic ring current inferred from ^{1}H chemical shifts. Consequently, the consideration based on ^{13}C chemical shifts is consistent with that of ^{1}H chemical shifts.

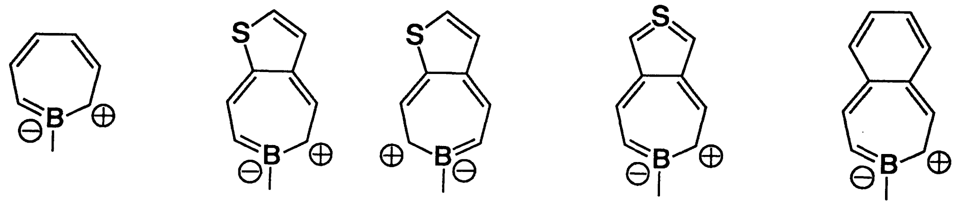


Chart 1.

Lastly, it is worthy to comment on ^{11}B chemical shifts. It is shown that the borons of **1**, **2**, and **10** are shielded than that of **9**. If we subtract the upfield shifts due to the increase of the electron densities by the annelation of the thiophene rings in **1** and **2**, ^{11}B chemical shift is found to be upfield with the increase of the borepin conjugation in each compound. Nöth[8)] has presented a linear relationship between chemical shifts of ^{11}B and ^{13}C as given by $\delta^{11}B = 0.393\ \delta^{13}C - 30.73$. In the equation, a proportionality constant is only 0.393. Hence, the observed upfield shift is meaningful than it looks. Furthermore, using CNDO/S method, Kroner[9)] has demonstrated that chemical shifts of the boron are not correlated with the total electron density but with π electron density at the boron. In each canonical structure A, σ polarization of B - C σ bond is considered to be enhanced due to the positive charge on the α carbon. The σ polarization enhanced in this manner increases the π electron accepting ability of the boron to bring about the upfield shift of the boron. Namely, ^{11}B chemical shift would be correlated with the extent of the borepin conjugation as well as ^{1}H and ^{13}C chemical shifts. Due to the optimum bond angle of a hexagon of the benzene ring, the borepin ring in **7** is thought to be endowed by other strain than those in **1**, **2**, and **10**, which causes the deviation of **7** from the relationship.

To conclude, while **1** is peripherally conjugated compound, **2** was shown to be an aromatic compound which maintains characteristics in conjugation of individual rings. Furthermore, it was revealed that chemical shifts of skeletal atoms clearly exhibit the bonding characteristics of the compound composed of a borepin ring.

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References

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2) Selected data of **2**. Found: C, 75.72; H, 5.11%. Calcd for $C_{14}H_{11}BS$: C, 75.70; H, 4.99%. ^{1}H NMR ($CDCl_3$) $\delta = 7.4 - 7.5$ (4H, m), 7.56 (1H, d, J =5.2 Hz), 7.81 (1H, dd, J =13.7 and 2.2 Hz), 7.88 (1H, dd, J =13.4 and 2.3 Hz), 8.05 - 8.15 (1H, m), 8.43 (1H, d, J =13.4 Hz), and 8.44 (1H, d, J =13.7 Hz). ^{13}C NMR $CDCl_3$) 127.6, 128.0, 129.9, 132.4, 139.3(br), 140.8(br), 142.9, 143.6, 144.6(br), 145.9, and 146.1. UV/VIS (cyclohexane) 220 (log ε, 4.12), 282 (4.60), 316 (4.12), and 331 (4.30) nm.
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