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Thienoborepins: Conjugation Characteristics in Boron Heterocycles

Yoshikazu Sugihara,* Ryuta Miyatake, Toshiyasu Yagi, and Ichiro Murata

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka Osaka 560, Japan

Mamoru Jinguji and Tomoo Nakazawa

Department of Chemistry, Medical University of Yamanashi, Tamaho, Nakakoma, Yamanashi 408-38, Japan

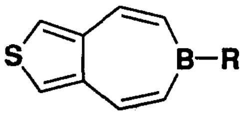
Akira Imamura

Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 724, Japan.

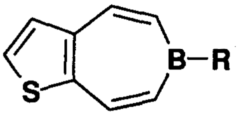
Abstract: Protonolysis, complex-formation with amines, ab initio molecular orbital calculations with 3-21G basis set, redox potentials, and spectroscopic features of 1-phenylthieno[3,4-*d*]borepin (**1**) and 1-phenylthieno[2,3-*d*]borepin (**2**) were examined. The compound **1** was shown to be more labile than **2**, which give us a guide for construction of stable heteroaromatics. Absorption and fluorescence spectra of **1** and **2** revealed the potential ability of boron heterocycles in the field of the organic optical materials.

Introduction

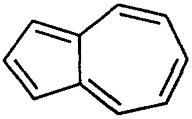
Thieno[3,4-*d*]borepin (**1a**) and thieno[2,3-*d*]borepin (**2a**)[1,2] are isoelectronic with azulene (**3**) and are regarded as the molecules which formally consist of electron-rich thiophene and electron-poor borepin rings. Recently, we have synthesized 1-phenyl derivatives (**1b** and **2b**) and revealed[2], on the basis of the ^{1}H, ^{13}C and ^{11}B chemical shifts of skeletal atoms, that each molecule is an aromatic compound possessing the dipole-moment vector whose negative end is toward the boron. These properties arise from a certain measure of π type overlap



1a: R = H
1b: R = Ph



2a: R = H
2b: R = Ph



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between the *p* orbitals of the boron and the carbon, by which the boron constitutes the cyclic conjugation and at the same time behaves as the π acceptor. In addition to these characteristics, the boron is more electropositive (electronegativity, 2.0) than the carbon (2.5). Hence, in Hückel molecular orbital calculations, the parameters are used as mentioned by Matteson[3] and Streitwieser[4]: $\alpha_B = \alpha - \beta$ and $\beta_{B-C} = 0.7\beta$. In these regards, **1b** and **2b** are the potential molecules to show the other novel features than those conjugated hydrocarbons have. Herein, we clarify the features of **1b** and **2b**.

Results and Discussion

Protonolysis.

On standing in a mixture of acetic acid and cyclohexane (1:30 v/v), **1b** and **2b** underwent the cleavage of boron–carbon bonds, forming the corresponding divinylthiophenes.[2] UV/VIS spectral change of each solution with time exhibited clear isosbestic points and could be analyzed with the first-order kinetics. As shown in Table I, protonolysis of **1b** is even more facile than that of 3-phenyl-3-benzoborepin (**4**),[5] and **4** is more sensitive to acid by 10 times than **2b**.

It has been established[6] that nucleophilic coordination of the oxy function of carboxylic acids to the boron promotes the protonolysis of usual alkenylboranes. However, it is unreasonable that the boron in **1b** is more positively charged than that of **4**, since an electron-rich thiophene ring is present in **1b**. Accordingly, instead of the nucleophilic coordination to the boron, protonation to the α carbons of the boron, which are secondly determinant in the case of usual alkenylboranes, seems to become an important factor discriminating between **1b** and **2b** and **4**.

That is, it is generally considered that the negative charge due to donation of the π-electron to the boron is decreased by polarization of the σ bond[7] composed of the electropositive boron and the electronegative carbon (B–C bond), and the fact evidently plays a role in thermodynamic stabilization of the system. However, when the strong electron donor, such as a thiophene ring, is conjugated, the σ polarization consequently gives rise to an unfavarable excess of the negative charge on an α carbon and lead to the kinetic instability. This would be the case of **1b**.

Table I. Protonolysis Rates, Redox Potentials, and Equilibrium Constants for the Complex Formation with Amine of **1b** and **2b**.

	$k_{(rel)}$ $(t_{1/2})^a$	$E_1^{ox\,b}$	$E_2^{ox\,b}$	$E^{red\,b}$	K_m^c	K_p^d
1b	210 (10.7 min)	1.14^e	1.56^e	-1.70^e	2.9×10^2	3×10^4
2b	1 (2250 min)	0.90^f	1.25^f	-1.66^f	3.3×10	1×10^4

[a] Protonolysis rates in a mixture of acetic acid and cyclohexane (1: 30 v/v). 3-Phenyl-3-benzoborepin (**4**) was more sensitive than **2b** by 10 times.

[b] Measured against SCE in DMF with 0.1M *n*-Bu_4NClO_4 as supporting electrolyte at −35°C, Pt working electrode.

[c] Equilibrium constants with 2-methylpiperidine; 12–719 and 91–364 times excess of amine were used for **1b** and **2b**, respectively.

[d] Equilibrium constants with piperidine; 0.14–35 and 1.7–81 times excess of amine were used for **1b** and **2b**, respectively.

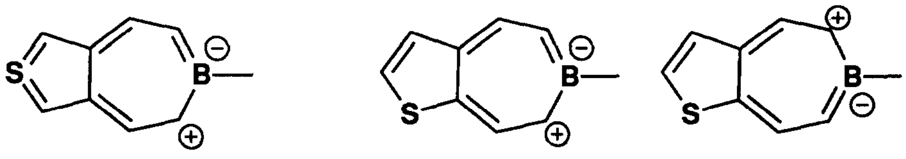
[e] The peak separations are 0.12, 0.14, and 0.06V for the first and second oxidation, and first reduction waves, respectively, n = $50mVsec^{-1}$.

[f] The peak separations are 0.11, 0.09, and 0.11V for the first and second oxidation, and first reduction waves, respectively, n = $20mVsec^{-1}$.

In order to rationalize the relative rates of **1b** and **2b**, it is convenient to refer to the crucial canonical structures **1A** and **2A** in Chart 1, which were for the first time adopted in our preceding reports[2] to interpret the chemical shift difference between α and β carbons of annelated borepins. As already noted, because of the unstable partial structure, tetravalent sulfur, the degree of contribution of this canonical structure **1A** to the actual one **1b** is considered smaller than that of **2A** to **2b**.[2b] In each canonical structure, the α carbon bears a positive charge. Hence, the α carbon in **2b** is less negatively charged as compared with that in **1b**, which retards the protonation at the α carbon of **2b**. Likewise, the negative charge of the boron in the canonical structure is closely related to the depression of coordination ability of this atom.

In the case of **4**, coordination of acetic acid to the boron is expected more facile as compared with both thienoborepins and the electron density of the α carbon would be no more than those in **1b** and **2b**, since the electron-rich heterole is absent in **4**.

Here we would like to put forward an further consideration. It should be noticed that the canonical structure A is closely associated with cyclic delocalization of the π electron through the boron. Furthermore, it is expected that positive charge on the α carbon depicted in the canonical structure enhances σ polarization. The σ polarization enhanced in this manner would increase the π-accepting ability of the boron, which leads to the further aromatic stabilization of the system. Thus the degree of contribution of these canonical structures are relevant not only



1A **2A**

Chart 1. Canonical Structures in which α carbons of the borons bear positive charges.

to the kinetic stabilization, but also to the thermodynamic stabilization of annelated borepins. We think that the consideration provides a useful guide to construct both the thermodynamically and kinetically stable heteroaromatics.

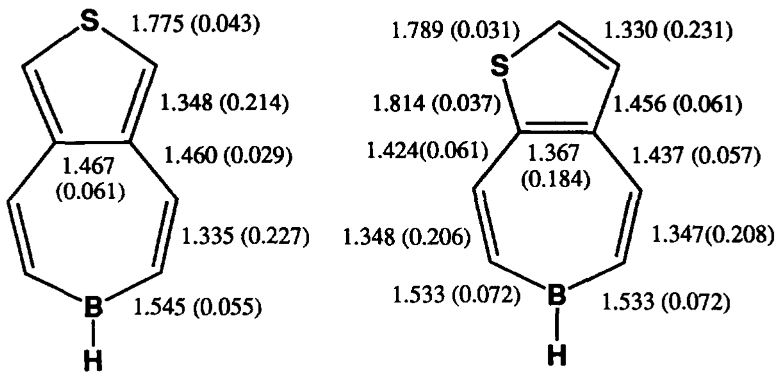
Adduct Formation with Amine

Though, upon addition of pyrrole, thiophene and acetonitrile to the solution of **1b** and **2b**, UV/VIS spectra did not reveal any change, the longer wavelength bands disappeared with piperidine or pyridine, indicating the complex-formation at the borons. The ^{1}H NMR spectra of **1b** and **2b** with a slight excess of piperidine displayed the upfield shifts for all skeletal protons. Since these chemical shifts of the adducts (**5**, **6**) are comparable with those of 3,4- or 2,3-divinylthiophene,[2] respectively, diamagnetic ring currents are shown to be induced over the two rings both in **1b** and **2b**. To apply the Benesi–Hildebrand equation[8] for determination of the equilibrium constants, weakly basic 2-methylpiperidine was employed, since a large excess of the amine was required. As for equilibrium constants with piperidine we followed the decrease of **1b** and **2b** upon addition of piperidine solutions of various concentrations and estimated equilibrium constants were averaged. From the constants shown in Table I, it emerges that, regardless of the high electron-donating thiophene rings, borons in **1b** and **2b** still possess the high coordination abilities to strongly Lewis-basic amines. That is, σ polarization of the boron–carbon bond would more than compensate for the π-accepting character of the boron, holding this atom Lewis-acidic. Furthermore, since it is conceivable that the equilibrium constant is relevant to the positive charge of the boron, the larger values for **1b** with both amines lead to the conclusion that the boron in **1b** is more positively charged than the same atom in **2b**.

Molecular Orbital Calculations

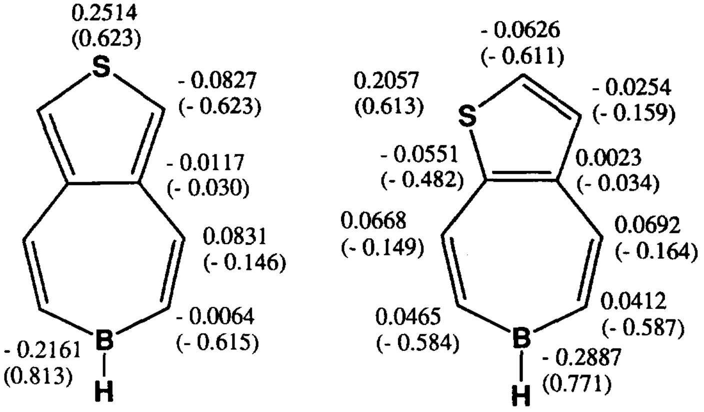
Ab initio molecular orbital calculations were performed for **1a** and **2a** with 3-21G basis set. The most stable geometry were found to be planar, since the vibrational analysis after the optimization of the planar geometry indicated all of the calculated frequencies are positive.

As shown in Chart II, bond alternation in the borepin ring is diminished for **2a**. In particular,



1a **2a**

Chart 2. Calculated Bond Lengths(Å) and π Atomic Orbital bond Populations (in parentheses) of **1a** and **2a** by Means of Ab Initio Molecular Orbital Calculations with the 3-21G Basis Set



1a **2a**

μ : **1.192 D** **2.112 D**

Chart 3. Calculated Net π Charges, Net Atomic Charges (in parentheses) of Skeletal Atoms, and Dipole Moments of **1a** and **2a** by Means of Ab Initio Molecular Orbital Calculations with the 3-21G Basis Set the length of the B–C bond is shortened by 0.012Å as compared with those of **1a**, indicating the increase of the π bond order. The calculated net atomic charge of the boron in **2a** is smaller and π electron is found to be responsible for this value. Though the α carbons in **1a** and **2a** totally bear negative charges, those of **1a** are more negatively charged. Furthermore, as for π charges of these atoms, while those for **1a** are slightly negative, those for **2a** are essentially positive. These tendencies are obviously consistent with the difference between the degrees of contribution of the canonical structures **1A** and **2A**. Calculated dipole moments for **1a** and **2a** are 1.192 D and 2.112 D, respectively, and the directions are reverse to that of azulene[9] with respect to the rings. Since it is known that the negative end of the dipole moment in thiophene[10] is toward the sulfur, donation of the π electron onto the boron play a decisive role for the dipole moments of **1a** and **2a**.

Redox Properties

In spite of the conjugation of trivalent borons with the electron-rich thiophene ring through ethylenic π bonds, the formation of the complex with amines simultaneously suggests that these two molecules (**1b** and **2b**) retain the low reduction potentials as well as the low oxidation potentials intrinsic of triarylborane and thiophene moieties, respectively. The redox properties of **1b** and **2b** were born out by cyclic voltammetry and are characterized, respectively, by one reduction wave around –1.7 V together with two oxidation waves around 1.0 and 1.4 V against SCE. Two different values, –2.12 V or –1.63 V, were reported as the first reduction potential of triphenylborane.[11] The values of 1.03 V and >1.5 V were reported for the oxidation potentials of 3,4':4,3'-bis(benzo[*b*]thiophene) and thieno[2,3-*b*]thiophene, respectively, as relatively low and high values for thiophene derivatives[12]. Thus, the first redox potentials of **1b** and **2b** are comparable with those of triarylborane and thiophenes, respectively, showing that these molecules have inherent redox properties of the thiophene and alkenylborane moieties. The fact should be ascribable to the insufficient conjugation between p-orbitals of the carbon and the boron as well as polarization of B–C σ bond.

Absorption and fluorescence Spectra

The longest wavelength absorption bands of **1b**, **2b**, and **4** essentially appear in the same position. In contrast to the fact that the corresponding band (^1L_b) of azulene(**3**) shows the distinct bathochromic shift with increasing solvent polarity,[13] these absorption bands of **1b**, **2b**, and **4** display slight solvatochromism.

Compounds **1b**, **2b**, and **4** are moderately fluorescent. While the quantum yield of fluorescent emission of **1b** in cyclohexane at ambient temperature is similar to that of **4**, the value of **2b** is much smaller. Upon cooling the solutions of **1b** and **2b** in methylcyclohexane to –123 °C, only the intensity of fluorescent emission of **2b** markedly increased by 56 times. Hence, the smaller quantum yield of **2b** would mainly be rationalized in terms of the intersystem crossing from the first singlet excited state to the thermally accessible upper triplet state lying slightly over the former.[14]

The wavelengths of fluorescent emission maximums of **1b** and **2b** shifted to longer wavelengths with increasing solvent polarity, whereas **4** showed such propensity only very slightly. For example, fluorescent emission maximums of **1b**, **2b**, and **4** in acetonitrile showed 41-, 14-, and 1-nm bathochromic shifts as compared with those in cyclohexane, respectively. The facts demonstrate that the first two compounds **1b** and **2b** have larger dipole moments in their electronically excited states. Plotting the Stokes shifts in various solvents against a measure for solvent polarity[15] defined by the dielectric constant ε and the refractive index n as $(\varepsilon-1)/(2\varepsilon+1)-(n^2-1)/(2n^2+1)$ gives the good linear relationships for **1b** and **2b**. If we take 4Å, which was estimated for azulene(**3**),[16] as the lower limit for the Onsager's effective cavity radii[17] of both molecules, the calculated differences between the dipole moments in the excited and in the ground states ($\mu_e-\mu_g$) are 7.7 D and 3.1 D for **1b** and **2b**, respectively. Since the actually effective cavity radii of **1b** and **2b** are considered larger than 4Å, the even larger values would be estimated for both molecules. Though the directions of the dipole moments in both the states were not determined experimentally, molecular orbital calculations show that the negative ends in both states of **1b** and **2b** are toward the borons.

It is well known that the dipole moments of azulene in its ground and excited state are of similar magnitude, but of inverse direction.[13a,18] Hence, both the direction and the magnitude of the dipole moments characterize **1b** and **2b**.

Table II. Selected Parameters for the Excited States of **1b** and **2b**

	$\Phi_f{}^a$	$\tau_f{}^b$	$\mu_e - \mu_g$
1b	7.2×10^{-2}	1.1 ns	7.7 D
2b	2×10^{-3}	< 0.1ns	3.1D
4	1.5×10^{-1}		0 D

[a] Quantum yields for fluorescent emission in cyclohexane were determined by reference to 9,10-diphenylanthracene ($\Phi_f = 0.86$).

[b] Fluorescence lifetimes were measured by the time-correlated single-photon counting technique using a Spectra Physics cavity-dumped dye laser, synchronously pumped by a mode-locked argon-ion laser. Samples were excited by the second harmonic of the dye laser (λ_{ex}= 300nm).

Since the relaxed excited states of both **1b** and **2b** were found to have the fairly large dipole moments, the Franck–Condon excited states would be polarized in the same order. Accordingly, within a series of compounds **1b**, **2b**, and **4**, increase of polarity of the Franck–Condon excited states does not accompany the bathochromic shift of the longest wavelength absorption band, that is, the blue light transparency is maintained. As for the difference between the dipole moments (μ_e–μ_g), the intriguing value of **1b** is essentially due to the fact that the boron possesses the π-accepting ability and this ability is enhanced in the electronically excited state. The large value of (μ_e–μ_g) should similarly be ascribable to the the small value of μ_g. This arises from the insufficient overlap between the *p* orbitals of the boron and the carbon in the ground state, since the insufficient overlap prevents the donation of π electron from the donor part to the acceptor one, causing the small value of μ_g. On the whole, the large value of (μ_e–μ_g),[19] the small value of μ_g, and the tendency to maintain the blue light transparency observed in a series of the boron heterocycles meet the requirement for the organic nonlinear optical material.[20]

To conclude, though **1b** and **2b** are aromatic molecules isoelectronic with azulene (**3**), they possess the novel properties which do not show up in azulene (**3**). The electronic structures of **1b** and **2b** are fairly divergent and this difference gives the information as to a molecular design of the stable heteroaromatic compounds. Furthermore, the present studies provide the general features as to the conjugated systems involving the trivalent boron, which are worthy of note in the field of organic optical materials.

Experimental Section

Protonolysis. Protonolysis was carried out in a mixture of acetic acid and cyclohexane (1:30 v/v) at room temperature. UV/VIS spectral change was followed by means of HITACHI 340 Spectrophotometer.

Adduct-formation with Amine. To apply the Benesi–Hildebrand equation for determination of the equilibrium constants with 2-methylpiperidine, 12–718 and 91–3640 times excess of the amine were used for **1b** and **2b**. The decrease of the longest wavelength band were monitored. The Benesi–Hildebrand plotting gave a good linear relationship. With piperidine, 0.07–35 and 1.7–81 times excess of the amine were used for **1b** and **2b**, respectively, and at the respective times the equilibrium constants were estimated supposing that all the borepin and amine are in equilibrium with 1:1 complex. The values thus obtained were averaged.

The ^{1}H NMR spectrum of a mixture of **1b** and piperidine (1:1.3 molar ratio) exhibited signals due to skeletal protons of **5** at δ 5.98 (H_2, H_8), 7.02 (H_4, H_6), and 7.09 (H_3, H_7) at room temperature. The spectrum of a mixture of **2b** and piperidine (1:2 molar ratio) revealed signals assigned to skeletal protons of **6** at δ 6.25 (H_2), 7.25 (H_3), 7.02 (H_5), 7.08 (H_6), 7.23 (H_7), and 6.26 (H_8) at room temperature. Both the spectra showed negligible change upon addition of further amount of piperidine to the mixtures.

Molecular Orbital Calculations. Ab initio molecular orbital calculations were performed with 3-21G basis set. The optimization of the planar geometry followed by the vibrational analysis indicates that the planar structure is stable since all of the calculated frequencies are positive.

Cyclic Voltammetry. Redox potentials were measured at –35 °C against SCE in DMF with 0.1M *n*-Bu_4NClO_4 as supporting electrolyte and with Pt working electrode by Yanaco polarographic analyzer P-1100. The peak separations are 0.12, 0.14, and 0.06 V for the first and second oxidation and the first reduction waves for **1b**, respectively, n = 50 $mVsec^{-1}$. Those values for **2b** are 0.11, and 0.09, and 0.11 V, respectively, n = 20 $mVsec^{-1}$.

Measurement of Fluorescence Lifetimes and Quantum Yields. The fluorescence lifetimes were measured by the time-correlated single-photon counting technique using a Spectra Physics argon-ion laser synchronously pumped, cavity-dumped dye laser as the excitation source. Samples were excited with the second harmonic of the dye (rhodamine 6G) laser at a repetition rate of 1 MHz. The fluorescence was dispersed with a Jobin Yvon H20 monochromator and detected by a Hamamatsu R106 photomultiplier. The fluorescence decay curves were processed and analyzed by a Sharp MZ80C personal computer. Quantum yields were determined by reference to that ($\phi_f = 0.86$)[21] of 9,10-diphenylanthracene.

Solvent Effect on Fluorescent Maximums. Stationary state spectrometry was carried out by HITACHI 650-60 Fluorescence Spectrophotometer. We employed cyclohexane, carbon tetrachloride, tetrahydrofuran, dichloromethane, acetonitrile, and methanol as common solvents for **1b** and **2b**. *n*-Hexane, diethyl ether, dimethylformamide, and ethanol were also examined.

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