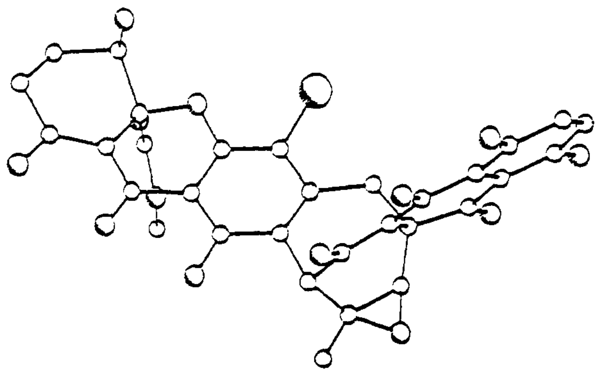
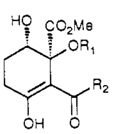


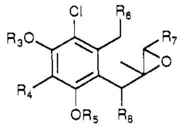
Figure 1. ORTEP structure of becticolin 2 (**2**) (relative configuration).

of the relative abundances of the isotopic peaks[10] of the molecular ion, the formula $C_{31}H_{23}ClO_{13}$ was deduced for both **1** and **2**. The ^1H NMR spectrum (CD_3COCD_3) of **1**[7] exhibits resonances for five phenolic protons, two aromatic protons, two methyl groups, an isolated benzylic methylene unit, and two isolated spin systems. These latter were identified as a system of six coupled protons corresponding to a CH_2CH_2CHOH substructure and a second spin system of two weakly coupled protons (δ = 4.04 ppm, 4.95 ppm, ^4J = 1.4 Hz). The ^{13}C spectrum of **1** exhibits signals for three quaternary sp^3, 18 nonprotonated sp^2, five methine, three methylene, and two methyl carbons.

Determination of the beticolin skeleton was partially achieved by analysis of a long-range ^1H–^{13}C 2D NMR chemical shift correlation experiment.[11] This experiment permitted assignment of partial structures A, B, and C, but no further connectivity could be surmised from these data, and the substitution of the aromatic ring of B was not clearly established. Analysis of data for **2** indicated the presence of the same structural features.

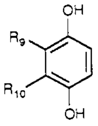


A



R_5 or R_3 = H

B



C

The structures of these compounds were ultimately obtained through X-ray analysis of **2**,[12] which was the only one to form suitable crystals (Figure 1). The phenol/quinone oxygen atoms were distinguished on the basis of bond lengths and on location of the hydrogen atoms, which were all observed in the last Fourier difference maps (except the resonant hydrogen atom of the planar β-keto/phenol system[13] C-8′, C-9′, C12′). All of the phenol hydrogens are intramolecularly H bonded to the phenol/quinone oxygen of the adjacent ring.

Because of the very similar spectroscopic data of both compounds, the diastereoisomeric structure **1** was assigned for beticolin 1 on the basis of NMR data, which show that the hydroxy group of partial structure A is axial in **2** and equatorial in **1**.[14] The presence of cis stereochemistry at positions 2 and 3 of beticolin 1 was supported by mass spectrometric determination of the proton affinity order (PA) of these compounds. Proton transfer was performed in a collision cell[15] between the MH^+ ion (generated in the source) and NMe_3 as nucleophilic reagent (PA value 942 kJ mol^{-1}),[16] giving rise to the $[Me_3NH]^+$ ion. The MH^+/$[Me_3NH]^+$ ratio is higher for **1** than for **2** (2.79 vs 0.94), indicating a higher PA value for **1**. This result could be explained by hydrogen bonding, which is only possible in a cis isomer. However, the relative stereochemistry between the C-11′–C-12′–C-13′–C-14′ substructure and the C-15 ester is not clearly inferred since no significant NOE effects were detected in either **1** or **2**.

Further attempts to obtain suitable crystals of **1** which would allow X-ray investigations in order to confirm the proposed structure are in progress.

Acknowledgment. We thank S. Wiedemann for the gift of *C. beticola* strains, P. H. Lambert, Institut de recherches Servier, for HREIMS measurements, and C. Descoins for initiation and coordination of this work.

Registry No. 1, 137516-40-6; **2**, 137622-91-4.

Supplementary Material Available: Listings of crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic thermal factors, and hydrogen coordinates for **2** (5 pages); tables of observed and calculated structure factors for **2** (13 pages). Ordering information is given on any current masthead page.

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(9) Exact mass measurements are as follows. **1**: $M^{\bullet+}$ calcd for $C_{31}H_{23}O_{13}{}^{35}Cl$ *m/z* 638.0827 and for $C_{31}H_{23}O_{13}{}^{37}Cl$ *m/z* 640.0797, found 638.0775 and 640.0846, respectively; $[M - CO_2CH_3]^+$ calcd for $C_{29}H_{20}O_{11}{}^{35}Cl$ *m/z* 579.0694 and for $C_{29}H_{20}O_{11}{}^{37}Cl$ *m/z* 581.0664, found 579.0655 and 581.0682, respectively. **2**: $M^{\bullet+}$ calcd for $C_{31}H_{23}O_{13}{}^{35}Cl$ *m/z* 638.0827 and for $C_{31}H_{23}O_{13}{}^{37}Cl$ *m/z* 640.0797, found 638.0820 and 640.0868, respectively; $[M - CO_2CH_3]^+$ calcd for $C_{29}H_{20}O_{11}{}^{35}Cl$ *m/z* 579.0694 and for $C_{29}H_{20}O_{11}{}^{37}Cl$ *m/z* 581.0664, found 579.0685 and 581.0690, respectively.

(10) Found and calculated relative isotopic abundances for **2** (found, calcd): *m/z* 638 (100, 100), 639 (32.3, 35.6), 640 (39.4, 40.7), 641 (12.1, 12.9), 642 (2.8, 2.9), and 643 (0.5, 0.5) for $C_{31}H_{23}O_{13}Cl$.

(11) COLOC pulse sequence for $J_{C\text{-}H}$ = 8 Hz; see: Kessler, et al. *J. Magn. Reson.* **1984**, *57*, 331.

(12) X-ray analysis of **2**: Philips PW-1100 automatic four-circle diffractometer, equipped with Cu Kα radiation (λ = 1/5418 Å) and graphite monochromator. The system is orthorhombic, space group $P2_12_12_1$ with a = 20.231 (6) Å, b = 18.921 (5), Å, c = 8.223 (3) Å, and Z = 4. The structure was solved by direct methods and refined with anisotropic thermal factors to $R = \sum w_i||F_o| - |F_c||/\sum w_i|F_0| = 6.0\%$ for 2480 structure factors (unitary weights). No absorption corrections were made.

(13) The least-squares mean plane for the five atoms of the tautomeric system has a c^2 value of 40.5, and maximum deviations out of plane are +0.067(5) and −0.021(5) Å for the C-8′ and C-9′ atoms, respectively.

(14) Any other change relative to structure **2** is unlikely (the collision-activated dissociation spectra of the MH^+ ion from **1** and **2** are qualitatively identical).

(15) (a) Kentamaa, H. I.; Cooks, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 4122. (b) Meyerhoffer, W. J.; Bursey, M. M. *Org. Mass Spectrom.* **1989**, *24*, 169. (c) Cole, R. B.; Prevost, C.; Tabet, J. C. *Adv. Mass Spectrom.* **1989**, *11B*, 1054. (d) Orlando, R.; Murphy, C.; Fenselau, C.; Hansen, G.; Cotter, R. J. *Anal. Chem.* **1990**, *62*, 125.

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1-Phenylthieno[3,4-*d*]borepine: A New 10 π Electron System Isoelectronic with Azulene

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Much attention has recently been focused on the chemistry of borepines.[1] The interest in this ring system stems from its isoelectronic relationship to the carbon species tropylium ion, since a neutral sp^2-hybridized boron atom is regarded as equivalent to a carbocation.[2] Ashe et al.[1f] and Nakadaira et al.[1g] have claimed

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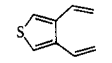
(1) (a) Leusink, A. J.; Drenth, W.; Noltes, J. G.; van der Kerk, G. J. M. *Tetrahedron Lett.* **1967**, 1263–1266. (b) Axelrad, G.; Halpern, D. *J. Chem. Soc. D* **1971**, 291. (c) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436–4437. (d) van Tamelen, E. E.; Brieger, G.; Untch, K. G. *Tetrahedron Lett.* **1960**, No. 8, 14–15. (e) Jeffries, A. T., III; Gronowitz, S. *Chem. Scr.* **1973**, *4*, 183–187. (f) Ashe, A. J., III; Frederick, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 1897–1880. (g) Nakadaira, Y.; Sato, R.; Sakurai, H. *Chem. Lett.* **1987**, 1451–1452.

Table I. ^{1}H, ^{13}C, and ^{11}B NMR Chemical Shifts of **3** Compared with Those of **1**, **2**, **8**, **9**, **10**, **11**, and **12**[a]



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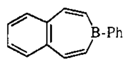

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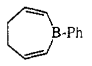

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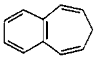
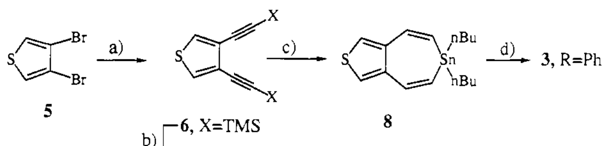


12

	3[b]	**1**[c]	**2**[d]	**8**[b]	**9**[b]	**10**[b,e]	**11**[e,f]	**12**[b]
H-2,8	7.31[g]	7.49	7.76	6.16	5.24[h]	7.74	6.75	5.84
H-3,7	8.09[g]	7.76	7.69	7.65	6.73	8.23	7.18	6.59
H-4,6	7.75			7.25	7.27			
C-2,8	134.3	148.5	150.5	129.1	115.6	140.2	135.9	128.3
C-3,7	145.7	145.3	146.3	143.1	130.1	154.0	156.7	130.5
C-3a,6a	141.8	147.6	134.7	141.4	138.8	138.4		
C-4,6	129.8			129.9	121.4			
B	50.8	53.6				49.5	54.6	

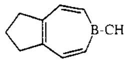
[a] Numbering shown was chosen for consistency with that for **3**. [b] This work. [c] Reference 1f. [d] Reference 1g. [e] Reference 1a. [f] Reference 7. [g] $J_{2,3} = J_{7,8} = 13.74$ Hz. [h] Only the chemical shift for (*E*)-H is shown. (*Z*)-H: δ 5.57.

Scheme I[a]



[a] Synthesis of **3** (R = Ph); reagents and conditions: (a) HC≡C-Si$(CH_3)_3$ (2.4 equiv), $PdCl_2(Ph_3P)_2$ (0.04 equiv), CuI (0.04 equiv), piperidine, reflux, 15 h, 85%; (b) K_2CO_3 (0.4 equiv), MeOH, room temperature, 3.5 h, 71%; (c) $SnH_2(nBu)_2$ (1.1 equiv), KOH (0.5 equiv), 18-crown-6 (0.005 equiv), degassed benzene, room temperature, 2 h, 85%; (d) $PhBCl_2$ (3 equiv), degassed hexane, ice-cooling, 10 min, 40%.

cyclic conjugation through a boron atom on the basis of spectroscopic examinations of 1-methyl-4,5-propanoborepine (**1**) and 1-methylborepine (**2**), respectively.



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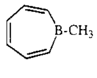

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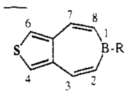

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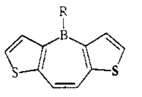


4

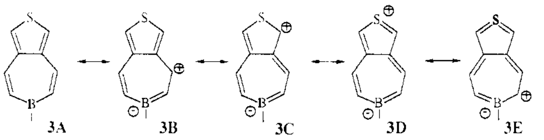
On the basis of these precedents, as well as the well-known fact that a divalent sulfur is electronically equivalent with an ethylenic double bond, replacement of two sp^2-carbon atoms of azulene by a trivalent boron and a divalent sulfur forms a new family of molecules, such as thieno[3,4-*d*]borepine (**3**), which would likewise be expected to enjoy 10 π electron delocalization to some extent. Although such a system is involved in a part of the borepino[3,2-*b*:6,7-*b*′]dithiophenes (**4**) synthesized by Jeffries and Gronowitz,[1e] the intrinsic properties of the thienoborepine system would be substantially perturbed by an additional thieno annelation. The synthesis and examination of the chemical and physical properties of 1-phenylthieno[3,4-*d*]borepine (**3**, R = Ph) will provide insight into this assumption.

Our synthesis of **3**, starting from 3,4-dibromothiophene (**5**),[3] is essentially the same as that described for **1**[1f] (Scheme I).[4] Thus, 1-phenylthieno[3,4-*d*]borepine (**3**, R = Ph)[4] is obtained as stable pale yellow flaky crystals, mp 165 °C (recrystallized from benzene), in 20.5% overall yield.

On standing in chloroform at room temperature for 1 week, **3** was converted into 3,4-divinylthiophene (**9**)[4] quantitatively. This transformation presumably occured by a trace of acid in the chloroform, since the formation of **9** from **3** was accelerated (completed within 12 h) by the addition of a catalytic amount of acetic acid.[5]

Unlike azulene, the electronic spectrum of **3** (R = Ph) in cyclohexane exhibits absorption bands only in the UV region (226 (log ϵ 4.35), 254 (4.30), 264 (4.31), 275 (4.49), 316 (sh, 4.17), 331 (4.39), 348 nm (4.33)) which are quite similar to those of 1-phenylbenzo[*d*]borepine (**10**).[1a] The longer wavelength bands with vibrational fine structure disappeared immediately on addition of piperidine, suggesting that the boron atom participates effectively in a cyclic conjugation.

The ^{1}H, ^{13}C, and ^{11}B NMR chemical shifts[6] are summarized in Table I together with those of some pertinent reference compounds. From the comparison some intriguing features emerged. All of the ring protons of **3** resonate at lower magnetic field than those of the corresponding protons of **8**, **9**, **11**,[7] and **12**,[8] in which cyclic conjugations are lacking and are comparable to those of **1**,[1f] **2**,[1g] and **10**.[1a] This strongly suggests the existence of a diatropic ring current associated with the 10 π electron system of **3**. In sharp contrast to borepine **1**, in which both the α- and β-carbons are almost equally deshielded in its ^{13}C NMR spectrum, the thienoborepine **3** shows that the α-carbons are not deshielded as in the normal vinylborane **11**. This is also true for the benzoborepine **10**. This trend is presumably due to the fact that, unlike **1** in which a canonical structure having a positive charge at the α-carbon atom is the principal contributor, a contribution of such a canonical form **3E** for **3** is unfavorable, since it contains a high-energy tetravalent sulfur atom. In the case of **10**, the corresponding canonical structures also contain an unfavorable *o*-quinoid structure. Furthermore, the chemical shifts of the α- and β-carbons of **3** are found to be much higher field than those of **10** and **11**. This can reasonably be interpreted in terms of the charge donation from the thiophene moiety toward these carbon atoms in **3** (due to the contribution of **3C** and **3D**).



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(2) Schulman, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 3785–3788; **1984**, *106*, 7696–7700. *Tetrahedron Lett.* **1983**, *24*, 1863–1866. Allinger, N. L.; Siefert, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 752–760.

(3) Steinkopf, W.; Jacob, H.; Penz, H. *Justus Liebigs Ann. Chem.* **1934**, *512*, 136–164.

(4) All new compounds have been characterized spectroscopically and by elemental analysis and/or mass spectrometry. **6**: ^{1}H NMR ($CDCl_3$, 100 MHz) δ 0.23 (s, 18 H), 7.36 (s, 2 H); EI–MS *m/z* 276 (M^+, 80), 261 ($M^+ - CH_3$, 100). **7**: colorless oil; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.22 (s, 2 H), 7.47 (s, 2 H); EI-MS *m/z* 132 (M^+, 100). **8**: colorless oil; ^{1}H NMR•($CDCl_3$, 90 MHz) δ 0.62–1.71 (m, 18 H), 6.23 (d, $J = 14$ Hz, H-2,8), 7.25 (s, 2 H, H-4,6), 7.73 (d, $J = 14$ Hz, H-3,7). **9**: colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.24 (dd, $J = 17.6$, 1.5 Hz, 2 H), 5.57 (dd, $J = 11.0$, 1.5 Hz, 2 H), 6.73 (dd, $J = 17.6$, 11.0 Hz, 2 H), 7.27 (s, 2 H); EI-MS *m/z* 136 (M^+, 60), 135 ($M^+ - H$, 100).

(5) A similar reaction was also observed for 1-phenyl-1,4-dihydroborabenzene: Ashe, A. J., III; Paul, S. *J. Am. Chem. Soc.* **1971**, *93*, 1804–1805.

(6) 400 MHz and 100 MHz for ^{1}H and ^{13}C NMR measurements, respectively, with TMS as an internal reference. ^{11}B NMR were measured at 128.15 MHz with $(C_2H_5)_2OBF_3$ as an external reference.

(7) Herberich, G. E.; Bauer, E.; Hengesbach, J.; Kölle, U.; Huttner, G.; Lorenz, H. *Chem. Ber.* **1977**, *110*, 760–772. Sheehan, D. Ph.D. Thesis, Yale University, New Haven, CT, 1964.

(8) Wittig, G.; Eggers, H.; Duffner, P. *Chem. Ber.* **1958**, *619*, 10. Burdett, K. A.; Shenton, F. L.; Yates, D. H.; Swenton, J. S. *Tetrahedron* **1974**, *30*, 2057–2065. Hanafusa, T.; Imai, S.; Ohkata, K.; Suzuki, H.; Suzuki, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 73–74.

The ^{11}B chemical shift of **3** (50.8 ppm) is slightly upfield compared to that of **1** (53.6 ppm) and **11** (54.6 ppm) and is comparable to that of **10** (49.5 ppm). Although the π electrons are delocalized toward boron (**3D**), the observed ^{11}B chemical shift of **3** reveals a substantial σ polarization from boron toward the neighboring carbon atoms.[2,9]

In order to confirm the characteristic features of the electronic structure, ab initio molecular orbital calculations of **3** (R = H) were performed with the STO-3G 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. Charge densities and π electron densities (in parentheses) of skeletal atoms are as follows: 0.2674 (0.2144) for B; −0.1840 (0.9953) for C_2; −0.0295 (0.9285) for C_3; −0.0195 (1.0361) for C_{3a}; −0.1765 (1.0702) for C_4; and 0.2817 (1.7301 for $3p\pi$, and 1.9950 for $2p\pi$) for S. The HOMO–LUMO gap in **3** (0.409 au) is found to be larger than that in azulene (0.340 au). This corresponds well to the fact that **3** has no long wavelength absorption maxima in the visible region. These results clearly support the experimental data. As a whole, the thiophene moiety has positive charges and the borepine moiety has negative charges. The calculated dipole moment is 2.35 *D*, which has the reverse direction to that of azulene.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 03214103) from the Ministry of Education, Science and Culture, Japan.

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[9] Byum, Y.-G.; Saebo, S.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3689–3696.

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closo-Silaboranes and *closo*-Carboranes: Contrasting Relative Stabilities and Breakdown of the Rule of Topological Charge Stabilization

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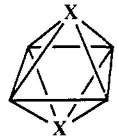
Despite their diagonal relationship in the periodic table and the many similarities between silicon and boron, studies of the chemistry of compounds involving both silicon and boron are only beginning to appear.[2,3] Since silicon is isoelectronic to carbon, a conceptually simple point of entry to the chemistry of boron and silicon is provided by the silaborane family of molecules, the silicon analogues of carboranes.[4] To our knowledge, there have been no reports to date of polyhedral boranes based on the octahedron and the pentagonal bipyramid in which one or more silicon atoms form a part of the polyhedra. In this paper, we use the concept of compatibility of orbitals in overlap[5] and ab initio molecular orbital calculations to predict the relative stabilities of positional isomers among the *closo*-silaboranes, **1c**–**6c**. The relative stabilities predicted by the orbital overlap model for the silaboranes emerge in the reverse order to those found in the corresponding *closo*-carboranes,[4,5a,6] and in the case of $Si_2B_4H_6$, the ordering is contrary to predictions based on the rule of topological charge stabilization.[6b] However, the ab initio calculations on the isomers of $Si_2B_4H_6$ and $Si_2B_5H_7$ support the qualitative orbital overlap predictions which now invite experimental verification.



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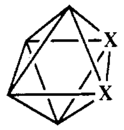

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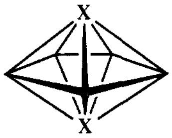

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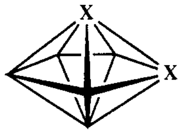

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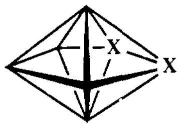

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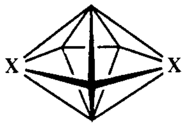

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(a) X = BH^- (b) X = CH (c) X = SiH

There are several qualitative approaches available to rationalize and to predict the relative stabilities of positional isomers within a given polyhedral system. Carboranes form a well-studied group of compounds on which these methods can be tried. In one approach, Williams[7] suggested that the carbon atoms in dicarbacarboranes prefer to be as far apart as possible so as to minimize the repulsion between the negatively charged CH groups. The greater stability of 1,6-*closo*-$C_2B_4H_6$ (**1b**) over the 1,2-isomer (**2b**) could be explained on this basis. Extrapolation of this rule to the $Si_2B_4H_6$ system leads to the prediction that in this case also the 1,6-isomer (**1c**) should be favored over the 1,2-isomer (**2c**). In a second approach, Gimarc has used the rule of topological charge stabilization to explain the relative stabilities of *closo*-carboranes.[6b,8] According to this model, more electronegative atoms prefer to be located at sites of higher electron density while more electropositive elements prefer sites of lower electron density. The pattern of relative electron densities has normally been determined by calculations on a model isoelectronic, isostructural, homoatomic system. To apply this rule to polyhedral molecules where all the vertices are identical, the procedure which has been used previously involves applying a perturbation to the homoatomic system. For example, the positional preference for electronegative substituents in $B_6H_6^{2-}$ (**1a**) was obtained by calculating the charges on the atoms in a C_5N^- octahedron by the extended Hückel method.[6b] Since the unique carbon was calculated to have the greater negative charge, the 1,6-isomer of $C_2B_4H_6$ (**1b**) was predicted to be favored over the 1,2-isomer (**2b**), as found experimentally. We have performed similar calculations on C_5B^{3-}

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[1] (a) Australian National University. (b) University of Hyderabad.

[2] Most of the experimental work has been directed toward the chemistry of the binary solids of silicon and boron: see, for example: Makarenko, G. N. In *Boron and Refractory Borides*; Matkovich, V. I., Ed.; Springer Verlag: Berlin, 1977. See also the introduction in ref 3c.

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