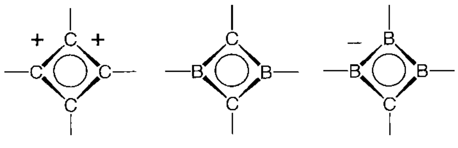
Fluctuating Skeletal Bonds

Triboracyclobutanides: Four-Membered Two-Electron Aromatic Compounds with Fluctuating Skeletal Bonds**

*Yüksel Sahin, Carsten Präsang, Peter Amseis, Matthias Hofmann, Gertraud Geiseler, Werner Massa, and Armin Berndt**

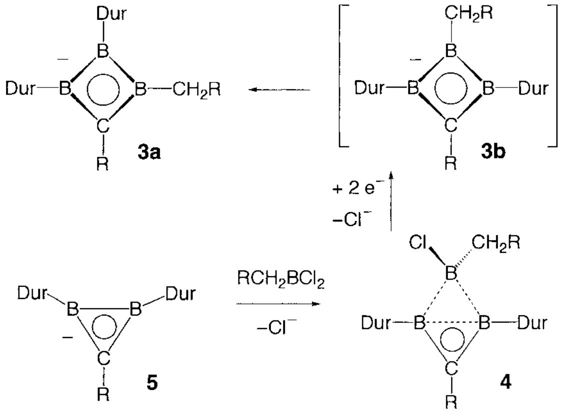
Among the series of isoelectronic four-membered, two-electron aromatic compounds **1**–**3** (Scheme 1), to date derivatives of the dicationic and uncharged skeletons **1**[1] and **2**,[2–4] respectively, have been realized experimentally. The barriers of their ring inversions, which are a measure of the stabilization of the folded over the planar rings, have not been determined experimentally for any example. We report herein the synthesis, crystal structure, and the ring inversion barrier of the anion **3a** (Scheme 2), and show, based on line shape analyses of its temperature-dependent NMR spectra, that its skeletal bonds fluctuate via a distorted triboratetrahedrane anion **6a** (see Scheme 3) as transition state. B3LYP computations[5] on model molecules support this proposal.

The unsymmetrically substituted triboracyclobutanide **3a** is obtained by reaction of lithium in diethyl ether with the symmetrically substituted derivative **4**, which is accessible from **5**[6] and dichloro(trimethylsilylmethyl)borane (Scheme 2). Attempts to detect the symmetrically substituted compound **3b** by NMR spectroscopic monitoring of the reaction of **4** with lithium naphthalenide in [D$_8$]THF at −80 °C proved unsuccessful. The constitutions of **3a** and **4** are in accord with their NMR data (Table 1) and are confirmed unambiguously by their crystal structure determinations[7] (Figure 1).



1 **2** **3**

Scheme 1. Frameworks of isoelectronic four-membered two-electron aromatic compounds **1**–**3**. Circles denote two cyclic delocalized electrons.



Scheme 2. Synthesis of the triboracyclobutanide **3a** by ring expansion of the diboracyclopropanide **5** via **4**. The compound **3b**, expected as the primary product of the reaction of **4** with lithium, was not detected. (R = SiMe$_3$, Dur = 2,3,5,6-tetramethylphenyl).

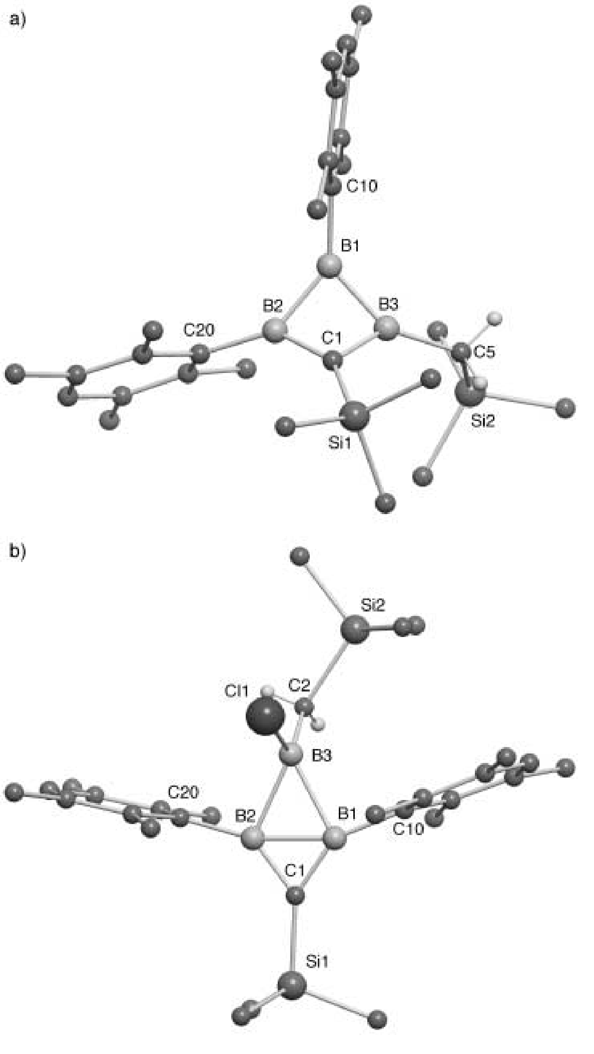


Figure 1. Structures of the anion **3a** (a) and of **4** (b) in the crystal. Hydrogen atoms were omitted for clarity, except those of the methylene groups. Selected bond lengths [pm] and angles [°]. **3a**: C1-B2 150.6(5), B2-B1 162.7(5), B1-B3 162.8(5), B3-C1 152.2(5), C1-B1 199.8(4), B2-B3 214.0(5), C1-Si1 182.7(3); C1,B2,B3/B3,B2,B1 59.3(3)°. **4**: C1-B1 142.8(8), C1-B2 145.4(7), B2-B1 169.5(9), B1-B3 192.6(8), B2-B3 189.0(9), C1-Si1 183.7(5), B1-C10 156.9(8), B2-C20 156.8(8), B3-C2 153.9(8), B3-Cl1 179.0(6); C1,B1,B2/B3,B2,B1 0.8(6)°.

---

[*] Prof. Dr. A. Berndt, Dr. Y. Sahin, Dr. C. Präsang, Dr. P. Amseis, G. Geiseler, Prof. Dr. W. Massa
Fachbereich Chemie
Universität Marburg
35032 Marburg (Germany)
Fax: (+49) 6421-282-8917
E-mail: berndt@chemie.uni-marburg.de
Dr. M. Hofmann
Anorganisch-Chemisches Institut
Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

The anion **3a** forms a solvent-separated ion pair with a lithium ion, which is coordinated by three molecules of diethyl ether. The four-membered ring of the triboracyclobutanide **3a** is strongly (by 59°) folded, as expected for an isoster of the 1,3-dihydro-1,3-diborete[2–4] **2** and the cyclobutadienyl dication[1] **1**. The substitution pattern of the boron atoms of **3a** does not correspond to the symmetric substitution pattern of its precursor **4**. Evidently, the initially formed, symmetrically substituted triboracyclobutanide **3b** rapidly isomerizes to **3a**. Line width phenomena in the NMR spectra of **3a** provide a hint for the mechanism of this isomerization. At low temperature there are ^{1}H and ^{13}C NMR signals for two different Duryl substituents, at higher temperatures their broadenings and coalescences are observed. The ^{11}B NMR spectrum of **3a** in [D$_8$]THF at 27 °C shows three signals at $\delta = 16$, 38, and 42 ppm, of which that at $\delta = 42$ ppm remains unchanged at higher temperatures, whereas the other two signals broaden. This shows that not only the Duryl substituents but also the boron atoms to which they are attached participate in the exchange. The barrier for the exchange of the environments of the Duryl substituents, that is the topomerization in **3a**, was determined to be 19.9 kcal mol^{-1} based on the line shape analysis of the signals of the *o*-Me, *m*-Me, and *p*-H atoms.[8] For the diastereotopic methylene protons of the Me$_3$SiCH$_2$ substituents, which reveal the planar chirality of **3a**, a more rapid exchange than for the Duryl substituents is determined from the line shape analysis of their signals. This is plausible, if one considers, that two pathways are available for the enantiomerization of **3a**: one by ring inversion via the planar transition state **7a** (Scheme 3b) and a second by rearrangement of the framework via a distorted triboratetrahedrane anion **6a**,[9,10] which *also* leads to an enantiomerization, however, without ring inversion (see Scheme 3a). The barrier of the enantiomerization by ring inversion is calculated to be 13.2 kcal mol^{-1}.[8]

B3LYP/6-311 + G** computations[5] reveal that the transition state **6c** (Scheme 4) lies 17.2 kcal mol^{-1} above **3c**, and planar **7c** is 9.6 kcal mol^{-1} higher in energy than **3c**. The distorted tetrahedral transition state of the isomerization of the 1,2-dihydro-1,2-diborete to the unsubstituted 1,3-dihydro-1,3-diborete **2u**, which is isoelectronic to the framework of **6**, lies 22.9 kcal mol^{-1} above **2u** according to computations by McKee; planarization of **2u** requires only

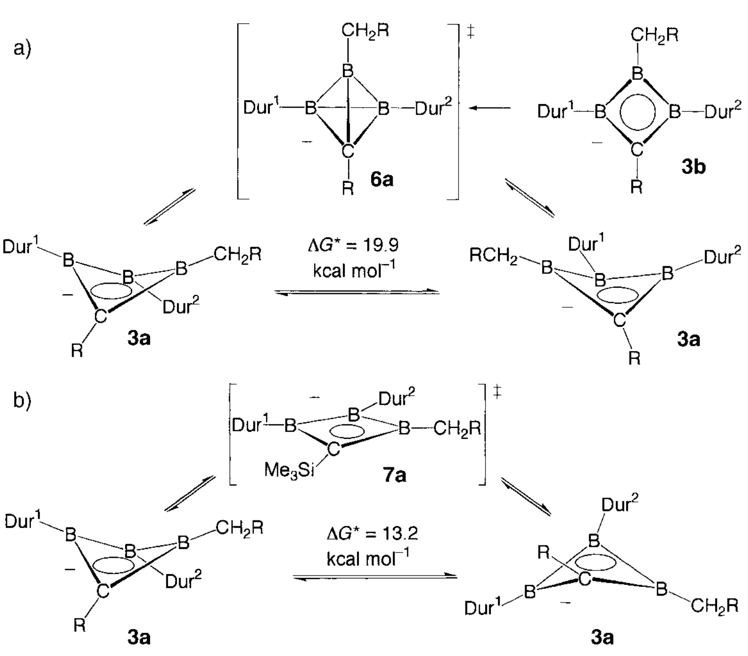
Table 1: Selected physical and spectroscopic properties of **3a**·Li(DME)$_2$ and **4**.[a]

3a·Li(DME)$_2$: pale yellow solid, m.p. 73–75 °C (without decomp), yield 90%. ^{1}H NMR (500 MHz, [D$_8$]THF, −23 °C): $\delta = 6.36$, 6.20 (each s, each 1 H, *p*-H, $T_{coal} = 40$ °C); 3.41, 3.26 (each DME); 2.04, 2.02 (each s, each 6 H, *o*- or *m*-CH$_3$, $T_{coal} = 17$ °C); 1.98, 1.94 (each s, each 6 H, *o*- or *m*-CH$_3$, $T_{coal} = 27$ °C); 0.92, 0.43 (each d, each 1 H, BCH$_2$, $T_{coal} = 37$ °C); −0.05, −0.08 ppm (each s, each 9 H, Me$_3$Si); ^{13}C NMR (75 MHz, [D$_8$]THF, 27 °C): $\delta = 156.4$, 155.6 (each br. s, each 1 C, *i*-C); 133.4, 131.9, 130.4, 130.0 (each s, each 2 C, *o*- and *m*-C); 129.0 (br. s, 1 C, CB$_2$); 126.6, 124.5 (each d, each 1 C, *p*-C); 20.7, 20.0 (each q, each 4 C, *o*- and *m*-CH$_3$); 9.7 (br. t, 1 C, BCH$_2$), 2.4, 1.8 ppm (each q, each 3 C, Me$_3$Si); ^{11}B NMR (160 MHz, [D$_8$]THF, 27 °C): $\delta = 42$, 38, 16 ppm

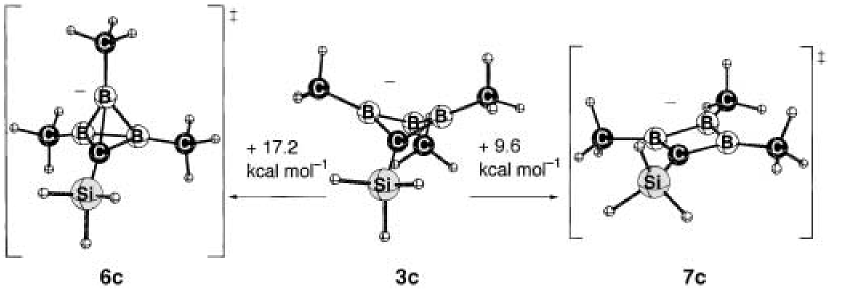
4: colorless solid, m.p. 133–134 °C (decomp), yield 55%. ^{1}H NMR (500 MHz, C$_6$D$_6$, 27 °C): $\delta = 7.04$ (s, 2 H, *p*-H); 2.54, 2.19 (each s, each 12 H, *o*- and *m*-CH$_3$); 1.49 (s, 2 H, BCH$_2$); 0.32, −0.21 ppm (each s, 9 H, Me$_3$Si); ^{13}C NMR (125 MHz, C$_6$D$_6$, 27 °C): $\delta = 137.2$, 134.6 (each s, each 4 C, *o*- and *m*-C); 134.0 (br. s, 2 C, *i*-C); 132.9 (d, 2 C, *p*-C); 22.0 (br. t, 1 C, BCH$_2$); 22.2, 19.7 (each q, each 4 C, *o*- and *m*-CH$_3$); 0.6, 0.3 ppm (each q, each 3 C, Me$_3$Si); ^{11}B NMR (160 MHz, C$_6$D$_6$, 27 °C): $\delta = 71$ (1B), 38 ppm (2B)

---

[a] DME = 1,2-dimethoxyethane.



Scheme 3. a) Distorted triboratetrahedrane anions of the type **6a**[9] as transition states of the isomerization **3b**→**3a** and of the enantiomerization of **3a** without ring inversion but with topomerization, that is exchange of the boron atoms with the Duryl substituents. There are only ten electrons available for the six skeletal bonds of the tetrahedron. b) Enantiomerization of **3a** with ring inversion the planar transition state **7a**.



Scheme 4. Computed[5] energy differences between **3c** and distorted tetrahedral **6c** and planar **7c**, respectively.

16.9 kcal mol^{-1}.[4] For the dianion of B_4Me_4[10] the distorted tetrahedral form according to our computations lies only 4.9 kcal mol^{-1} above the folded two-electron aromtic compound; its planarization requires 7.3 kcal mol^{-1}. Thus, an increasing number of boron atoms in four-membered two-electron aromatic compounds facilitates the planarization as well as the fluctuation of the skeletal bonds.

Received: August 6, 2002 [Z19899]

---

[1] M. Bremer, P. von R. Schleyer, U. Fleischer, *J. Am. Chem. Soc.* **1989**, *111*, 1147, and references therein.

[2] M. Hildenbrand, H. Pritzkow, W. Siebert, *Angew. Chem.* **1985**, *97*, 769; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 759, and references therein.

[3] P. H. M. Budzelaar, K. Krogh-Jespersen, T. Clark, P. von R. Schleyer, *J. Am. Chem. Soc.* **1985**, *107*, 2723.

[4] M. McKee, *Inorg. Chem.* **2000**, *39,* 4206, and references therein.

[5] All geometries were optimized by employing the B3LYP hybrid functional together with the 6-31G(d) basis set, and the nature of the stationary points was characterized by analytical frequency calculations. Relative energies are based on energy calculations with 6-311+G(d,p) and are corrected for zero-point energies. a) Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, und J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[6] The synthesis of **5** will be described elsewhere.

[7] Crystal structure analyses: **3a**$\cdot$Li$(Et_2O)_3$: A colorless crystal ($0.45\times0.35\times0.25$ mm^3) was measured at 193 K on an IPDS area detector system (Stoe) with $Mo_{K\alpha}$ radiation. $C_{40}H_{76}B_3LiO_3Si_2$, monoclinic, space group $P2_1/c$, $Z=4$, $a=1183.4(1)$, $b=2277.6(2)$, $c=1756.7(1)$ pm, $\beta=98.32(1)°$, $V=4685.0(6)\times10^{-30}$ m^3, $\rho_{calcd}=0.993$ Mg m^{-3}, 50384 reflections up to $\theta=25.84°$, 8557 independent ($R_{int}=0.1160$), 3910 with $I>2\sigma(I)$. The structure was solved with direct methods and refined against F^2 with full matrix. Hydrogen atoms were considered as riding at calculated positions, $wR_2=0.1527$ for all reflections, $R=0.0691$ for observed reflections. Limited accuracy due to the disorder of the diethyl ether in the $Li(Et_2O)_3$ cation. **4**: Pale yellow crystal ($0.30\times0.15\times0.05$ mm^3) $C_{28}H_{46}B_3ClSi_2$, monoclinic, space group $C2/c$, $Z=8$, $a=3031.1(2)$, $b=988.1(1)$, $c=2217.6(1)$ pm, $\beta=111.06(1)°$, $V=6198.1(8)\times10^{-30}$ m^3, $\rho_{ber}=1.086$ Mg m^{-3}, measurement as for **3a**$\cdot$Li$(Et_2O)_3$, 12475 reflections up to $\theta=24.0°$, 4627 independent ($R_{int}=0.1414$), 1857 with $I>2\sigma(I)$ (only very thin platelets available). The structure was solved analogously to that of **3a**, resulting in $wR_2=0.1144$ for all reflections, and $R=0.0539$ for the observed reflections. CCDC-187178 (**3a**$\cdot$Li-$(Et_2O)_3$) and CCDC-187179 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit @ccdc.cam.ac.uk).

[8] The line shape analysis was carried out with WIN-DYNA 32, Bruker Analytik GmbH, Version 1.01; the changes in the chemical shifts in the investigated temperature interval were considered to be linear and the line widths of the trimethylsilyl groups were used as the reference line widths. The rate constants of the ring inversion k_{RInv} were computed from the difference in rate constants of the enantiomerization without ring inversion k_{tet} (coalescence of the methyl groups and protons at the aromatic group) and the enantiomerization with ring inversion k_{total} (coalescence of the methylene protons) according to $k_{RInv}=k_{total}-k_{tet}$.

[9] Tetrahedra of CB_3 anions are, like those of the isoelectronic B_4 dianions, distorted.[10] There are three forms for distorted tetrahedra of the type **6a**: two enantiomers with short C–BDur edges (the transition state between **3b** and **3a**), and one with a short C–BCH_2R edge (the transition state of the degenerate rearrangement of **3a**).

[10] A. Neu, T. Mennekes, U. Englert, P. Paetzold, M. Hofmann, P. von R. Schleyer, Angew. Chem. **1997**, *109*, 2211; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2117.

Boron-Containing Rings

A Diboracyclopropane with a Planar-Tetracoordinate Carbon Atom and a Triborabicyclobutane**

*Yüksel Sahin, Carsten Präsang, Matthias Hofmann, Govindan Subramanian, Gertraud Geiseler, Werner Massa, and Armin Berndt**

Dedicated to Professor Paul von Ragué Schleyer

Known molecules with a planar-tetracoordinate carbon atom[1] contain metal centers.[2] According to computations[3] the prototype of such molecules *without* metal centers is the diboracyclopropane **1u** (Scheme 1). Derivatives of the lower energy isomer **2u** with planar-tetracoordinate *boron* atoms[4]

---

[*] Prof. Dr. A. Berndt, Dr. Y. Sahin, Dr. C. Präsang, Dr. G. Subramanian, G. Geiseler, Prof. Dr. W. Massa
Fachbereich Chemie
Universität Marburg
35032 Marburg (Germany)
Fax: (+49) 6421-282-8917
E-mail: berndt@chemie.uni-marburg.de
Dr. M. Hofmann
Anorganisch-Chemisches Institut
Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.