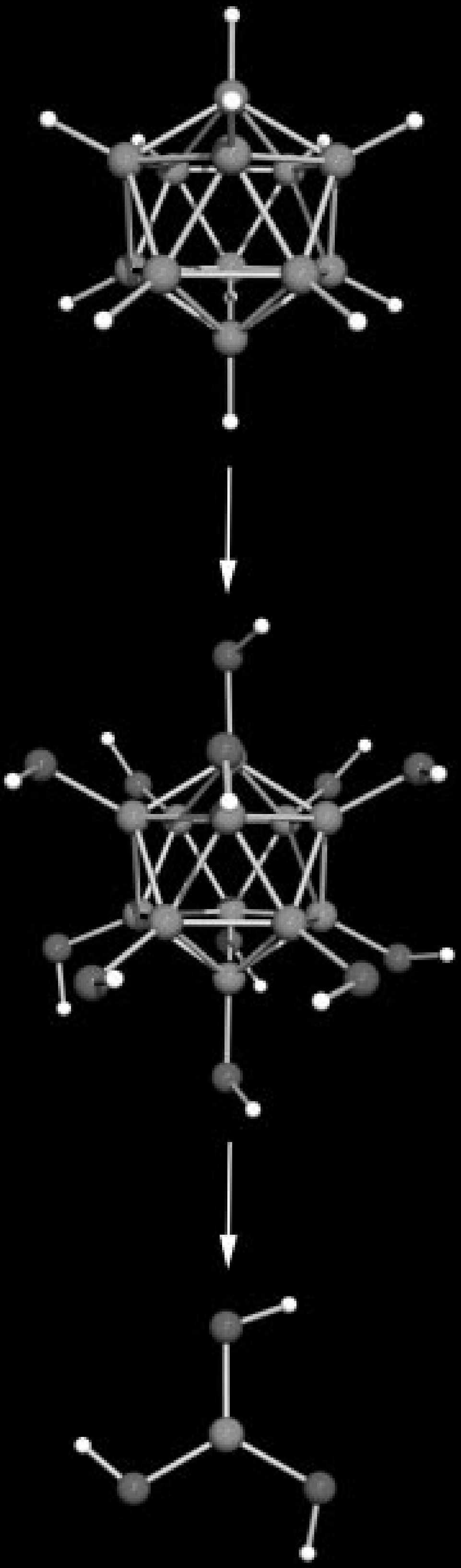
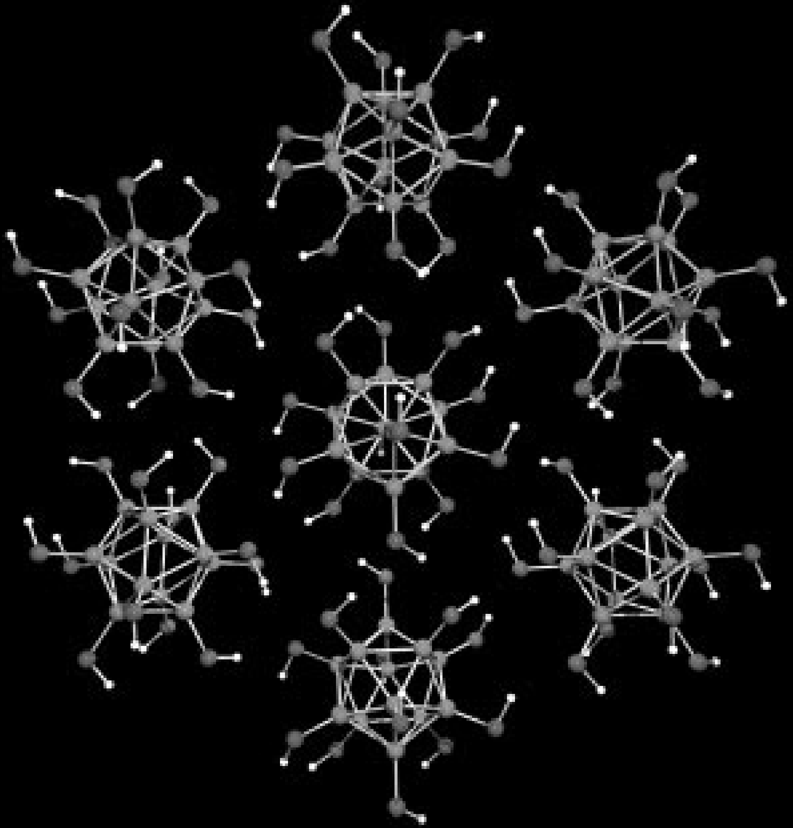
Oxidation of icosahedral boranes such as $[B_{12}H_{12}]^{2-}$ by hydrogen peroxide leads to a fascinating group of per-B-hydroxylated borane clusters.





These “inorganic sugars” are crossbreeds of borate minerals and boron hydrides. More information is given on the following pages.

Aromatic Polyhedral Hydroxyborates: Bridging Boron Oxides and Boron Hydrides**

Toralf Peymann, Axel Herzog, Carolyn B. Knobler, and M. Frederick Hawthorne*

Polyhydroxylated molecules have fascinated scientists pursuing various disciplines. Carbohydrates are ubiquitous in nature and serve as a source for chemical energy (glucose), the backbone for genetic information (ribose), and the organic constituents of plants (cellulose) or insects (chitin).[1] The three-dimensional network of silica and its derived minerals[2] results from the condensation of polyhydroxylated silicates. The most prominent polyhydroxylated boron compound is boric acid $B(OH)_3$. Its alkaline solutions deposit $Na_2[B_4O_5(OH)_4] \cdot n H_2O$, found in two abundant boron minerals, kernite ($n = 2$) and borax ($n = 8$).[3] Except for the trigonal and tetrahedral boron–oxygen units common to borate minerals,[4] the recurring structural motif in boron chemistry is the icosahedron. The allotropes of elemental boron,[5] boron-rich solids,[6] and the parent anion of the polyhedral boranes, $[closo\text{-}B_{12}H_{12}]^{2-}$ (**1**),[7] all contain B_{12} icosahedra.

The charge-delocalized icosahedral ion **1** may be considered as the parent aromatic species that serves borane chemistry as benzene serves organic chemistry.[8] Isoelectronic substitution of one or two $:B-H$ vertices in **1** by $:C-H^+$ provides the aromatic derivatives $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ (**2**) and three isomeric dicarbaboranes (1,2- or *ortho*; 1,7- or *meta*; and 1,12- or *para*) *closo*-$C_2B_{10}H_{12}$.[9] Each of these isoelectronic derivatives of **1** undergoes characteristic hydrogen substitution reactions at the B–H vertices resulting in a huge number of known icosahedral species. Of special interest are derivatives in which every available B–H vertex has been substituted. Thus, hydrophobic derivatives of **1**, **2**, and the three isomeric dicarbaboranes, such as $[closo\text{-}B_{12}Cl_{12}]^{2-}$,[10] $[closo\text{-}CB_{11}(CH_3)_{12}]^-$,[11] and *closo*-1,12-$C_2B_{10}(CH_3)_{12}$,[12] have been synthesized. Similar highly substituted polyhedral borane derivatives with hydrophilic substituents such as hydroxyl are, until now, unknown. We here report the synthesis of per-*B*-hydroxylated icosahedral borane derivatives, which may be considered to be derivatives of a new type of polyhedral subboric acid. Described are the per-*B*-hydroxylated icosahedra $Cs_2[closo\text{-}B_{12}(OH)_{12}]$, Cs_2-**3**; $Cs[closo\text{-}1\text{-}H\text{-}1\text{-}CB_{11}(OH)_{11}]$, Cs-**4**; and *closo*-1,12-H_2-1,12-$C_2B_{10}(OH)_{10}$ (**5**); prepared by the oxidation of the icosahedral boranes Cs_2-**1**, Cs-**2**, and *closo*-1,12-$(CH_2OH)_2$-1,12-$C_2B_{10}H_{10}$ (**6**), respectively, with 30% hydrogen peroxide at the reflux temperature. The new compounds **3**–**5** were characterized by ^{11}B NMR spectroscopy, electrospray mass spectrometry, and, for Cs_2-**3** and **5**, single-crystal X-ray diffraction.

The ^{11}B NMR spectra of species **3**–**5** are consistent with their structures in that **3** (point group I_h) gave a singlet at $\delta = -17.1$, **4** (C_{5v}) exhibited three singlets at $\delta = -7.3$, -15.3, and -17.1, and **5** (D_{5d}) displayed a singlet at $\delta = -17.0$. Electrospray mass spectrometry confirmed the *m*/*z* values expected for the assigned polyhydroxylated structures **3** and **4**. The water-soluble salts Cs_2-**1** and Cs-**2** served as precursors to ions **3** and **4**, whereas the synthesis of **5** employed the slightly water-soluble precursor **6**, because *closo*-1,12-$C_2B_{10}H_{12}$ is water-insoluble and hence not available to the hydrogen peroxide reagent. During this reaction sequence, the diol **6** is most likely oxidized to the corresponding dicarboxylic acid, which subsequently decarboxylates during *B*-hydroxylation to afford species **5**.

Because the per-*B*-hydroxylated species are thermodynamically unstable with respect to boric acid, continued degradation to this product under experimental conditions is expected and observed. The yields of the syntheses reported here are: **5** (80%), **3** (65%), and **4** (31%). This distribution reflects the higher kinetic stabilities of the two centrosymmetric cage structures **1** and *closo*-1,12-$C_2B_{10}H_{10}$ relative to that of the polarized cluster **2**.

One unexpected feature of the anion **3** is the low solubility of its alkali metal salts in water even though its surface is covered with hydroxyl groups. Thus, Cs_2-**3** can be recrystallized from water, whereas Li_2-**3**, Na_2-**3**, and K_2-**3** precipitate quantitatively upon addition of the corresponding alkali metal chloride to warm aqueous solutions of Cs_2-**3**. The anion **3** probably functions as a strong multihapto ligand for the smaller alkali metal ions and displaces their water of hydration, cross-linking and precipitating the aggregated alkali metal salts. The per-*B*-hydroxylated *closo*-1,12-carborane **5** is insoluble in water as well as in organic solvents. This property of **5** can be attributed to the absence of a dipole moment and the strong network of the hydrogen bonding involving every pendant hydroxy group and C–H as well as water in the crystal lattice. The close packing of this network is reflected by the density of **5** ($\rho = 1.73\ g\,cm^{-3}$), which is unusually high for a covalent organic compound (for comparison: the density of *closo*-1,12-H_2-1,12-$C_2B_{10}(CH_3)_{10}$ is $0.97\ g\,cm^{-3}$).[12] The overall geometry of the icosahedral framework in both **3** and **5** is not affected by per-*B*-hydroxylation.

In the solid-state structure of **5** (Figure 1),[13] the B–B (177.6(5)–183.7(5) pm) and B–C (171.6(5)–173.4(5) pm) bond lengths are similar to those of unsubstituted *closo*-1,12-$C_2B_{10}H_{12}$ determined by electron diffraction (B–B 177.2(13)-179.2(7) pm, B–C 171.0(11) pm).[14] Similarly, the B–B distances[15] of anion **3** (Figure 2) (177.5(9)–181.4(9) pm) do not deviate significantly from those present in **1** (175.5(7)–178.0(7) pm).[7] The B–O bond lengths of the anion **3** are elongated by about 5 pm compared with those of **5** (**3** 143.3(7)–145.9(9) pm; **5**: 138.6(4)–140.3(4) pm), which may be due to the interaction of the delocalized negative charge in **3** and the B–O dipoles.

The dianion **3** is only the second derivative of **1** to be described that is saturated with twelve chalcogen substituents. The first to be synthesized was the selenoborate Cs_8[*closo*-

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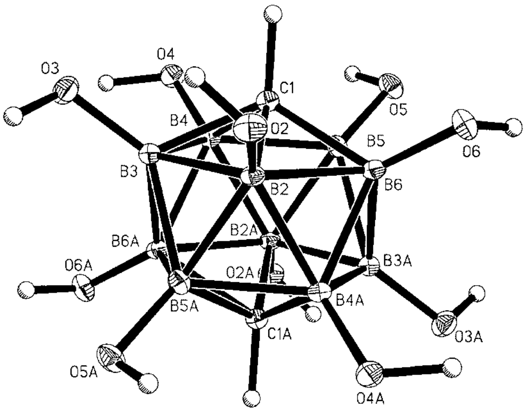

Figure 1. ORTEP diagram of **5**. The ellipsoids represent a 30 % probability level. Selected bond lengths [pm]: B–B 177.6(5)–183.7(5), B–O 138.6(4)–140.3(4), B–C 171.6(5)–173.4(5).

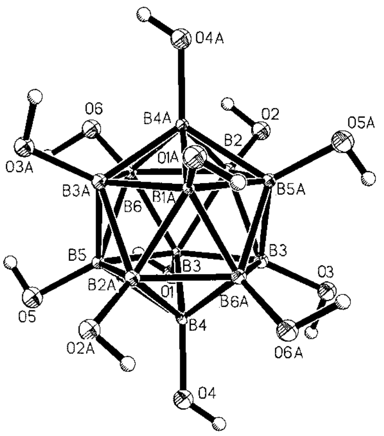

Figure 2. ORTEP diagram of **3**. The ellipsoids represent a 30 % probability level. Selected bond lengths [pm]: B–B 177.5(9)–181.4(9), B–O 143.3(7)–145.9(9).

$B_{12}(Se_2BSe)_6]$ obtained directly from elemental boron, Cs_2Se, and selenium at 700 °C in a sealed glass ampoule.[16] The structure of this species displays Se-B(Se)-Se bridges between neighboring boron vertices of the icosahedron. Related species, in which two or three neighboring B–O vertices of **3**–**5** are bridged by a trigonally or tetrahedrally surrounded boron atom, appear to be likely targets for synthesis ($Cs_2[\textit{closo}\text{-}B_{12}(O_2BOH)_6]$ as an example).

Species **3**–**5** suggest the potential existence of a new field of boron cluster chemistry, wherein the aromatic icosahedral cluster functions only as the scaffolding for reactions that would be performed on its oxygen sheathing, such as the use of **3** as the central core for dendrimeric chemistry.[17] Furthermore, it is conceivable that the high-temperature pyrolysis of a simple salt of **3** might form a very stable polymeric network of icosahedra connected by covalent B-O-B bonds. Species of this sort should be very robust due to strong B–O bonds, but their dianionic cages should serve as a source of electrons for chemical processes such as $B_{12}(OH)_{12}^{2-} + 24\,OH^- \rightarrow 12\,B(OH)_3 + 26\,e^-$ and perhaps provide some water solubility. In addition, the possibilities for the covalent incorporation of species such as **3** in metal oxide lattices are boundless. The organic chemistry of **4** and **5** and their derivatives similarly opens new areas of novel chemical cross-fertilization.

Experimental Section

Caution! On this scale and under these conditions no explosions occurred. Nevertheless, this does not preclude such an event when dealing with these species. Extreme precautions should be taken!

The ^{11}B NMR spectra were obtained with a Bruker AM-500 spectrometer at 160 MHz. ^{11}B NMR chemical shifts were externally referenced to $BF_3 \cdot Et_2O$; peaks upfield of the reference are designated as negative. ESI mass spectra were recorded by injecting the sample dissolved in water into an ionspray source. The mass spectrometer was operated in the negative-ion mode.

Cs_2-**3**: A suspension of Cs_2-**1** (1.00 g, 2.50 mmol) in 30 % hydrogen peroxide (40 mL) was refluxed for three days. The obtained solution was cooled overnight in a refrigerator to precipitate crude Cs_2-**3**, which was recrystallized from water. The product was collected by filtration and dried to yield pure Cs_2-**3** (0.97 g, 65 %) as a white powder. ^{11}B NMR (H_2O): $\delta = -17.1$ (s); ESI-MS: m/z: 335.1 $[\{[H][B_{12}(OH)_{12}]\}^-]$.

Cs-**4**: A suspension of Cs-**2** (0.10 g, 0.36 mmol) in 30 % hydrogen peroxide (10 mL) was refluxed for five hours. The obtained solution was cooled overnight in a refrigerator to precipitate crude Cs-**4**, which was recrystallized from water. The product was collected by filtration and dried to yield pure Cs-**4** (0.05 g, 31 %) as a white powder. ^{11}B NMR (H_2O): $\delta = -7.3$ (s, B12), -15.3 (s, B2-6), -17.1 (s, B7-11); ESI-MS: m/z: 319.0 ($[HCB_{11}(OH)_{11}]^-$).

5: A suspension of **6** (1.00 g, 4.90 mmol) in 30 % hydrogen peroxide (75 mL) was refluxed for 12 hours. A colorless precipitate formed, which was filtered off and washed with water. After drying at 150 °C/5 × 10^{-5} Torr pure **5** (1.19 g, 80 %) was obtained as a white powder. ^{11}B NMR (H_2O): $\delta = -17.0$.

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[13] a) $\mathbf{5} \cdot 2\,H_2O$, monoclinic, space group $C2/c$, $a = 15.960(13)$, $b = 7.812(6)$, $c = 11.867(10)$ Å, $\beta = 118.28(2)°$, $V = 1303(2)$ Å^3, $\rho = 1.73$ g cm^{-3}, $2\theta_{max} = 60°$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, θ–2θ scan mode, 298 K. Of the 1902 unique reflections measured, 1013 were considered observed $[I > 2\sigma(I)]$. Data were corrected for Lorentz and polarization effects but not for absorption, $\mu = 1.5$ cm^{-1}. Atoms were located by use of

statistical methods (SHELX86), and 115 parameters were refined. Water hydrogen atoms were included as located. All other hydrogen atoms were included in calculated positions after they had been located. $R = 0.067$, $wR = 0.193$, refined against $|F^2|$. b) Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410414 (**5**) and CSD-410413 (**3**).

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[15] Cs_2-**3**·$2H_2O$, monoclinic, space group $P2_1/a$, $a = 13.135(9)$, $b = 7.342(6)$, $c = 8.304(6)$ Å, $\beta = 97.39(2)°$, $V = 794(1)$ Å^3, $\rho = 2.66$ g cm^{-3}, $2\theta_{\max} = 115°$, $\lambda(Cu_{K\alpha}) = 1.5418$ Å, $\theta - 2\theta$ scan mode, 298 K. Of the 1079 unique reflections measured, 1015 were considered observed $[I > 2\sigma(I)]$. Data were corrected for Lorentz and polarization effects and for absorption, $\mu = 3.6$ cm^{-1}. Atoms were located by use of statistical methods (SHELXS90), and 98 parameters were refined. Water hydrogen atoms were not located. All other hydrogen atoms were included as located. $R = 0.045$, $wR = 0.124$, refined against $|F^2|$.[13b]

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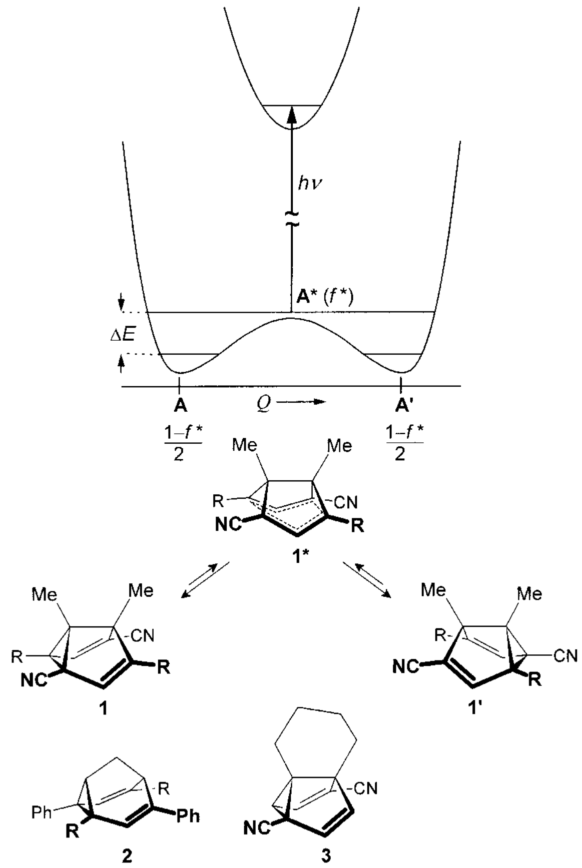
The Equilibrium between Localized and Delocalized States of Thermochromic Semibullvalenes and Barbaralanes—Direct Observation of Transition States of Degenerate Cope Rearrangements

Helmut Quast* and Maximilian Seefelder

Dedicated to Professor William von Eggers Doering on the occasion of his 80th birthday

The Möbius–Hückel concept provides a *theoretical* link between pericyclic transition states and normal molecules.[1] As yet an *experimental* link has not existed. Von E. Doering's seminal design and first examples of molecules that are fluxional because of a very fast degenerate Cope rearrangement[2] were followed by Zimmerman's discovery of semibullvalene[3] and the demonstration that the ground state and the transition state for its Cope rearrangement differ in energy by just a few kcal mol^{-1}.[4] Hoffmann and Stohrer[5] and Dewar and Lo[6] predicted substitution patterns for semibullvalenes that would lower and eventually abandon this energy gap, and thus result in stable delocalized, bishomoaromatic semibullvalenes.[7] A similar formal mutation of shallow degenerate double-well potentials into single-minimum systems is known from the pyramidal inversion of ammonia and its derivatives.[8]

The discovery that the semibullvalenedicarbonitrile **1a** is thermochromic suggested an equilibrium between the classical, localized structure **1a** and its delocalized, bishomoaromatic isomer **1a***, which was estimated to be higher in energy by about 11 kJ mol^{-1} (Scheme 1).[9] Subsequently, the semibullvalenes **1b**[10] and **3**[11] and the barbaralanes **2b**[12] and **2c**[13] showed that thermochromism is common to degenerate systems with extremely low Cope barriers.[14] We report here the quantitative analysis of this phenomenon. Enthalpy differences of as little as 1 kJ mol^{-1} are found to govern the equilibrium between the two degenerate ground states **A**, **A′** and the species **A*** which absorb at long wavelengths. The latter are interpreted as higher, delocalized states, located just above the flat potential barrier between the two ground states, namely, where vibronic interaction is strong.



1a: R = H; **1b**, **2b**: R = Ph; **2c**: R = CN

Scheme 1.

UV/Vis spectra were recorded at various temperatures for degassed solutions of **1**–**3** in butyronitrile. This solvent was chosen because it is sufficiently transparent in the near-UV region and has a broad temperature range in the liquid state. Careful attention has been given to the reversibility of the temperature-driven changes in the spectra. The absorbance was corrected for the thermal expansion of the solvent with the help of density data[15] and refers to a temperature of 298 K.

For the determination of the enthalpy difference ΔH^0 between the differently absorbing species by means of the temperature-dependent long-wavelength bands, we regard their integrated absorbance A_{int} as a measure of the fraction f^* which exists in the higher state **A***. The integrated absorbance A_{int} is obtained by deconvolution of the UV/Vis spectra with Gauss curves[16] (Figures 1–3). Toward this end, Gauss curves

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