NCH$Me_2$); b) *N,N'*-bis(cyclohexyl)glyoxaldiimine: $^1$H NMR ([D$_8$]THF, 20 °C): $\delta = 7.85$ (s, 2H; N=CH), 3.14 (m, 2H; NC*H*, *cyclo*-$C_6H_{11}$), 1.83 – 1.78 (m, 20H; *cyclo*-$C_6H_{11}$); $^{13}$C NMR ([D$_8$]THF, 25 °C): $\delta = 160.87$ (ddd, $^1J(C,H) = 161.6$, $^2J(C,H) = 11.3$, $^3J(C,H) = 8.7$ Hz; N=CH), 70.13 (d, $^1J(C,H) = 130.1$ Hz; *cyclo*-$C_6H_{11}$), 34.91 (t, $^1J(C,H) = 127.9$ Hz; *cyclo*-$C_6H_{11}$), 26.52, 25.16 (t; *cyclo*-$C_6H_{11}$).

[10] a) H. J. Rieger, Dissertation, Universität Hamburg, **1992**; b) J. Scholz, H. Görls, unpublished results.

[11] a) Crystal structure analysis of **2b**: $C_{22}H_{40}N_2O_2Cl_2Ti$, $M_r = 483.36$, red parallelpipeds, crystal dimensions $0.40 \times 0.38 \times 0.36$ mm$^3$, monoclinic, space group $P2_1/m$ (no. 11), $a = 8.759(2)$, $b = 12.243(2)$, $c = 14.292(3)$ Å, $\beta = 90.49(3)°$, $V = 1532.6(5)$ Å$^3$, $T = 183(1)$ K, $Z = 2$, $\rho_{calcd} = 1.047$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 0.470$ mm$^{-1}$, $F(000) = 516$, Enraf-Nonius-CAD4 diffractometer, $\lambda = 0.71069$ Å, $\omega/2\theta$ scan, 3877 measured reflections, of which 3648 are symmetry-independent reflections in the range $2.72° \le \theta \le 27.41°$, $R_{int} = 0.075$, 3174 reflections with $F_o > 4\sigma(F_o)$, Lorentz and polarization correction, structure solution with direct methods (SHELXS), structure refinement against $F_o^2$ (SHELX-93), hydrogen atoms localized from difference Fourier syntheses and refined isotropically, 263 parameters, $R_{obs} = 0.056$, $wR2_{obs} = 0.145$, GOOF = 1.057, min./max. residual electron density $-0.89/0.79$ e Å$^{-3}$; b) crystal structure analysis of **4a**: $C_{12}H_{24}N_2OCl_3Nb$, $M_r = 411.59$, brown parallelpipeds, crystal dimensions $0.40 \times 0.36 \times 0.32$ mm$^3$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.451(1)$, $b = 14.461(3)$, $c = 11.764(2)$ Å, $\beta = 99.14(1)°$, $V = 1755.3(5)$ Å$^3$, $T = 183(1)$ K, $Z = 4$, $\rho_{calcd} = 1.557$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 1.137$ mm$^{-1}$, $F(000) = 840$, Enraf-Nonius-CAD4 diffractometer, $\lambda = 0.71069$ Å, $\omega/2\theta$ scan, 3740 measured reflections, of which 3545 are symmetry-independent reflections in the range $2.42° \le \theta \le 26.28°$, $R_{int} = 0.015$, 2930 reflections with $F_o > 4\sigma(F_o)$, Lorentz and polarization correction, absorption correction PSI scan, min./max. transmission 0.213/0.271, structure solution with direct methods (SHELXS), structure refinement against $F_o^2$ (SHELX-93), hydrogen atoms localized from difference Fourier syntheses and refined isotropically, 237 parameters, $R_{obs} = 0.029$, $wR2_{obs} = 0.073$, GOOF = 1.036, min./max. residual electron density $-0.55/0.34$ e Å$^{-3}$. c) Further details of the crystal structure investigations may 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-408006 and CSD-408007.

[12] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441 – 451; b) A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, London, **1973**.

[13] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc. Dalton Trans.* **1989**, S1 – S83.

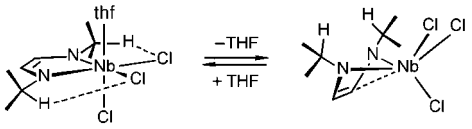
[14] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.

[15] Based on crystal structure investigations of selected enamines a relationship was determined between nitrogen hybridization, C – N bond lengths, and $p_\pi - p_\pi$ interactions. A measure for the $p_\pi - p_\pi$ interaction is the sum of angles at the N atom. If the sum of angles is 360°, as for **2b** or **4a**, then the nitrogen atom is sp$^2$-hybridized, which indicates a maximal $p_\pi - p_\pi$ interaction. In contrast, if the $p_\pi - p_\pi$ interaction decreases then the sp$^3$ hybridization share of the nitrogen and thus the degree of the pyramidalization increases. a) A. G. Cook, *Enamines*, Marcel Dekker, 2nd ed., New York, **1988**; b) K. L. Brown, L. Damm, J. D. Dunitz, A. Eschenmoser, R. Hobi, C. Kratky, *Helv. Chim. Acta* **1978**, *61*, 3108 – 135.

[16] a) Ti – Cl bond lengths for comparison: $[TiCl_6]^{2-}$: 2.341(9) Å (average), I. A. Guzei, C. H. Winter, *Inorg. Chem.* **1997**, *36*, 4415 – 4420; b) $TiCl_4 \cdot (Me_2NCH_2CH_2NMe_2)$: 2.280(3) – 2.256(3) Å, P. Sobota, J. Utko, S. Szafert, K. Szczegot, *J. Chem. Soc. Dalton Trans.* **1997**, 679 – 683; c) $TiCl_4 \cdot 2THF$: 2.293(2) (*trans*), 2.265(23) (*cis*) Å, T. Lis, J. Ejfler, J. Utko, P. Sobota, *Pol. J. Chem.* **1992**, *66*, 93 – 99; d) G. J. Palenik, *Inorg. Chem.* **1997**, *36*, 3394 – 3397.

[17] It is also possible to describe the arrangement of the three chlorine atoms in **4a** as *facial* and in **7** as *meridional*. J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, 2nd edition Harper & Row, New York, **1978**, p. 448.

[18] In the $^1$H NMR spectra of **4a** and **4b** recorded at room temperature the signals of the methine protons of the isopropyl and the cyclohexyl groups and those of the azomethine protons are not shifted as far to lowfield and to highfield, respectively, as for the titanium halide complexes. This indicates a rapid exchange process in which the THF is reversibly cleaved from the complex. We assume that an increase in the C–H ··· Cl distances is associated with this change in the complex geometry, which leads to the breakage of the hydrogen bonds. At the same time the Nb(N1-C1=C2-N2) ring is also more strongly folded [Eq. (1)]. This molecular dynamic is supported by the low-temperature $^1$H NMR spectra: At $-80$ °C the equilibrium of this exchange process evidently shifts to the side of the THF complex with a six-coordinate niobium and intact C–H ··· Cl bonds, since the signals of the methine protons of the isopropyl or cyclohexyl groups move to lower field and the signals of the azomethine protons move to higher field.




(1)

[19] A great deal of effort has been invested in trying to understand the nature of the hydrogen bonds but a fully satisfactory theory for the explanation of all the properties of the hydrogen bonds still remains to be established. Nevertheless it is indisputable that the C–H ··· X interaction (X = O, N, Cl) is not a van der Waals, but mainly an electrostatic interaction. It decreases far more slowly with distance and is therefore still effective at distances that correspond to the van der Waals limits or are larger than these.[1c–e]

## Formation of a Novel Amidinium-Bridged Polyhedral Borane Ion by Incorporation of an Acetonitrile Solvent Molecule**

Fangbiao Li, Kenneth Shelly, Carolyn B. Knobler, and M. Frederick Hawthorne*

The derivative chemistry of the polyhedral borane ion $[B_{20}H_{18}]^{2-}$[1] has been of considerable interest for a number of years. Recently, we showed that oxidation of the oxygen-substituted derivatives *ae*-$[B_{20}H_{17}OR]^{4-}$ produced polyhedral borane anions $[\mu\text{-}B_{20}H_{18}OR]^{2-}$,[2] which contained both hydrogen and oxygen bridges. This observation, together with the availability of amine-substituted species suitable as candidate target species for boron neutron capture therapy (BNCT) of cancer,[3] prompted us to extend these studies to the oxidation of *ae*-$[B_{20}H_{17}NH_3]^{3-}$ (**1**, Scheme 1).[3, 4] The ion **1** and related amine derivatives exhibit excellent tumor uptake and selectivity when delivered by liposomes in vivo.[3, 4] This has been attributed to the facile intracellular oxidation of the

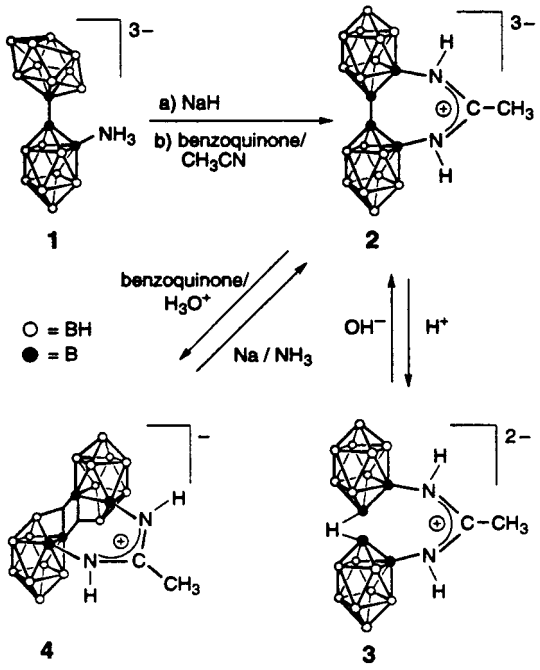
[*] Prof. M. F. Hawthorne, F. Li, Dr. K. Shelly, Dr. C. B. Knobler
Department of Chemistry and Biochemistry
University of California at Los Angeles
Los Angeles, CA 90095 – 1569 (USA)
Fax: (+1) 310-825-5490
E-mail: mfh@chem.ucla.edu

[**] This work was supported by the U.S. Department of Energy (DE-FG02-95ER61975). The following prefixes are used as isomer designations: *ae* = apical – equatorial isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[1\text{-}(2\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$); $a^2$ = apical – apical isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[1\text{-}(1\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$); $e^2$ = equatorial – equatorial isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[2\text{-}(2\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$).

$[B_{20}H_{17}NH_2R]^{3-}$ ion to a $[B_{20}H_{17}NH_2R]^-$ species thought to be responsible for bonding with intracellular protein. The isolation and reactivity of an oxidized product of *ae*-$[B_{20}H_{17}NH_3]^{3-}$ would support the proposed mechanism of tumor retention.

During the investigation of the oxidation of **1**, a method was sought for this procedure in nonaqueous media. Benzoquinone and tetrachlorobenzoquinone in acetonitrile are effective reagents for the oxidation of $[B_{10}H_{10}]^{2-}$ or $[B_{20}H_{18}]^{4-}$ to the $[B_{20}H_{18}]^{2-}$ ion.[5] However, when the oxidation of **1** was attempted with benzoquinone in acetonitrile, an unusual product was observed due to the unexpected participation of the solvent. The novel $a^2$-$[\{\mu\text{-}CH_3C(NH)_2\}B_{20}H_{16}]^{3-}$ ion (**2**, Scheme 1), with an amidinium-bridged structure, was formed. Further oxidation with additional benzoquinone under acidic aqueous conditions produced the $[\{\mu\text{-}CH_3C(NH)_2\}B_{20}H_{16}]^-$ ion (**4**, Scheme 1). Both **2** and **4** contain an amidinium group that bridges the two $B_{10}$ cage fragments. In the formation of **2**, the bridging amidinium group results from the incorporation of an acetonitrile molecule in the presence of the oxidant benzoquinone. We report here the synthesis, structural analysis, and reactions of **4**.

Following the treatment of $[(Me_3NH)_3][\mathbf{1}]$ with NaH in dry acetonitrile (no reaction was observed unless the ammonio ligand was deprotonated), addition of benzoquinone resulted in the formation of the ion **2** (Scheme 1). Acidification of




Scheme 1. Oxidation of **1**.

an aqueous solution of **2** produced the $[(\mu\text{-}H)\{\mu\text{-}CH_3C(NH)_2\}B_{20}H_{16}]^{2-}$ ion (**3**, Scheme 1), which was isolated in 12% yield as the tetramethylammonium salt. Both **2** and **3** were characterized by $^{11}B$ NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The structure of $[(Me_4N)_2][\mathbf{3}]$ has been confirmed by X-ray crystallographic analysis.[6]

Further oxidation of **2** at room temperature by benzoquinone in acidic aqueous solution produced the ion **4**, which was isolated in 25% yield as the corresponding tetramethylammonium salt (Scheme 1). The product was characterized by ESI-MS and $^1H$, $^{13}C$, and $^{11}B$ NMR spectroscopy. The structure of $[Me_4N][\mathbf{4}]$ was determined by single-crystal X-ray diffraction studies.[7]

An ORTEP drawing of the structure of **4** is presented in Figure 1. [7] The polyhedral borane anion **4** consists of two

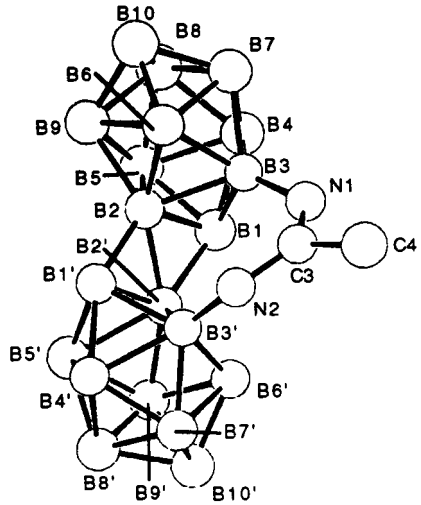


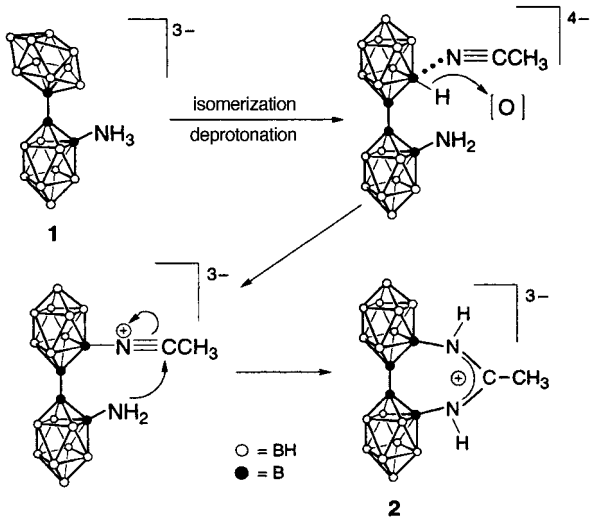

Figure 1. ORTEP representation of the structure of the anion **4**, and the numbering scheme. For clarity, the terminal B–H hydrogen atoms have been omitted. Selected interatomic distances [Å] and angles [°] (estimated standard deviations in parentheses): B3–N1 1.502(9), B3′–N2 1.521(9), N1–H1(N1) 0.95(8), N2–H2(N2) 1.03(8), N1–C3 1.319(8), N2–C3 1.335(8) C3–C4 1.533(10); B3-N1-C3 128.8(6), B3-N1-H1(N1) 124(5), C3-N1-H1(N1) 106(5), N1-C3-N2 125.8(6), N1-C3-C4 117.9(6), C4-C3-N2 116.4(6), C3-N2-H2(N2) 116(4), C3-N2-B3′ 126.4(5), B3′-N2-H2(N2) 115(4).

intact decaborate cages joined together by a bridging amidinium group and two three-center, two-electron (3c–2e) bonds. The bonding distances within the two decaborate cages are normal and similar to those found in other structures derived from $[B_{10}H_{10}]^{2-}$. Similar 3c–2e bonds were first structurally characterized in the polyhedral borane anion $[B_{20}H_{18}]^{2-}$.[8]

To our knowledge, **4** is the first amidinium derivative of a polyhedral borane to be crystallographically characterized. The delocalization of the positive charge of the amidinium group is clearly indicated by the geometrical parameters of the structure. The three covalent bonds around C3 (C3–N2, C3–N1, and C3–C4) are coplanar, and the sum of the bond angles about C3 is 360.1(6)°. The C3–C4 bond length is 1.533(10) Å, which is in the normal range for a C–C single bond. However, the C–N bonds are much shorter than expected for a normal C–N single bond, indicating considerable double-bond character. The C3–N1 and C3–N2 bond lengths are 1.319(8) and 1.335(8) Å, respectively. As a result of the $sp^2$ character of the nitrogen atoms, the three bonds around these centers are also coplanar. The sum of the three bond angles surrounding N1 and N2 are 357.4(6)° and 358.8(5)°, respectively.

  1433-7851/98/3713-1866 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **1998**, *37*, No. 13/14

A possible mechanism for the formation of **2** is shown in Scheme 2. Initially, the anion undergoes a facile rearrangement to the $a^2$ isomer,[3] and the ammonio group is deprotonated by NaH. The oxidant (benzoquinone) could subsequently remove a hydride ion from the borane cage to produce a transient, positively charged boron vertex with an empty orbital. This reactive boron vertex could then react with an acetonitrile molecule from the solvent. The nitrogen atom of the amino group would attack the activated nitrile carbon atom of the acetonitrile ligand. The formation of **2** represents a new route for the preparation of disubstituted polyhedral boranes derived from the $[B_{20}H_{18}]^{2-}$ and $[B_{20}H_{18}]^{4-}$ skeletal structures.

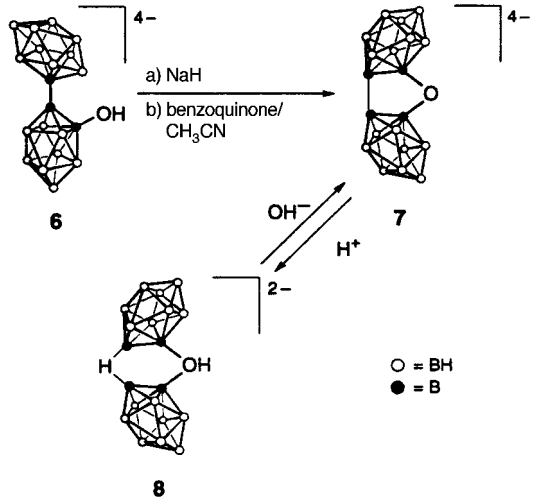



Scheme 2. Proposed mechanism for the formation of **2**. [O] = oxidant (benzoquinone)

The bridging hydrogen atom in **3** is acidic and can be titrated by an aqueous base (Scheme 1). Deprotonation results in the formation of **2**, which can be easily distinguished from **3** in the $^{11}B$ NMR spectrum. The estimated $pK_a$ of the bridging hydrogen atom of the dianion **3** is 3.5,[9] which is, as expected, more acidic than for $a^2$-$[B_{20}H_{19}]^{3-}$ ($pK_a = 7.3$), a hydrogen-bridged species that does not contain the bridging amidinium group of **3**.

The ion **4** is relatively unstable in aqueous solution. The hydrolysis of $[Me_4N][\mathbf{4}]$ in boiling water produces the known $[2\text{-}B_{10}H_9NH_3]^-$ ion (**5**),[10] which was identified by its $^{11}B$ NMR and ESI mass spectra. The anion **4** could be reduced by sodium metal in liquid ammonia to regenerate **2**, identified by $^{11}B$ NMR spectroscopy and ESI mass spectrometry (Scheme 1). When a solution of **2** produced in this manner was acidified, $[(Me_4N)_2][\mathbf{3}]$ was generated and isolated in 29% yield.

In addition, it was found that *ae*-$[B_{20}H_{17}OH]^{4-}$ (**6**) could be oxidized by benzoquinone in acetonitrile to produce the oxygen-bridged polyhedral borane anion $[\mu\text{-}B_{20}H_{16}O]^{4-}$ (**7**, Scheme 3). Acidification of an aqueous solution of **7** produced the $[\mu\text{-}B_{20}H_{17}OH]^{2-}$ anion (**8**), which isolated as the tetramethylammonium salt in approximately 72% yield. The anion **8** was previously reported to arise from the hydrolysis of $[\mu\text{-}B_{20}H_{17}OR]^{2-}$.[2]




Scheme 3. Oxidation of **6**.

Oxidation of other polyhedral borane anions by benzoquinone in nonaqueous media could also lead to a variety of new species with potential utility in BNCT.

*Experimental Section*

Reactions were performed under an atmosphere of dry nitrogen using Schlenk techniques. Acetonitrile was dried over $CaH_2$ and distilled prior to use. Silica gel (230–400 mesh) was used for chromatography. 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 $BF_3 \cdot Et_2O$ in $C_6D_6$; peaks upfield of the reference are designated as negative. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM-400 spectrometer and referenced to tetramethylsilane as the external reference. ESI mass spectra were recorded by injecting samples dissolved in $CH_3CN$/water (50/50) into an ionspray source. The mass spectrometer was operated in the negative-ion mode, with signals of the multiply charged ion series from a separate introduction of polypropylene glycol.

**2**: Dry $[(Me_3NH)_3][\mathbf{1}]$[3, 4] (2.00 g, 4.6 mmol) was added to a stirred suspension of NaH (0.50 g, 20.8 mmol) in $CH_3CN$ (100 mL); hydrogen gas was evolved. The mixture was stirred for 1 h and filtered, and then $CH_3CN$ and $Me_3N$ were removed from the filtrate in vacuo. The residue was dissolved in dry $CH_3CN$ (100 mL). Benzoquinone (1.50 g, 14.1 mmol) was added, and the solution was stirred for 3 h and filtered. The crude product $Na_3[\mathbf{2}]$ was obtained by removal of the solvent in vacuo. $^{11}B\{^1H\}$ NMR ($H_2O$): $\delta = 6.7$ (2B, B–B); $-5.4$ (2B, apical B–H); $-13.7$ (2B, B–N); $-22.1$, $-24.3$, $-27.3$, and $-29.7$ (total of 14B, equatorial B–H); ESI-MS: *m/z*: 291.1 $[\{(H)_2CH_3C(NH)_2B_{20}H_{16}\}^-]$, 313.1 $[\{(Na)(H)CH_3C(NH)_2B_{20}H_{16}\}^-]$.

**3**: The crude product $Na_3[\mathbf{2}]$ obtained above was dissolved in aqueous $Me_4NCl$ (50 mL, 1N solution). The addition of excess HCl (1N) solution resulted in a brown precipitate of crude $[(Me_4N)_2][\mathbf{3}]$. The precipitate was isolated by filtration and dissolved in $CH_3CN/CHCl_3$ (50 mL, 1/1), and the resulting solution was passed through a silica gel column (3 × 45 cm, elution with the same solvent mixture). The yellow eluent was collected, and the solvent was removed in vacuo. The residue was dissolved in $H_2O$ (20 mL), and aqueous $Me_4NCl$ (5 mL, 1N) was added to precipitate $[(Me_4N)_2][\mathbf{3}]$. The product was collected by filtration and purified by recrystallization from $CH_3CN$/isopropanol. It was dried in vacuo to yield $(Me_4N)_2[\mathbf{3}]$ (0.25 g, 12%) as a white powder. $^{11}B\{^1H\}$ NMR ($H_2O$): $\delta = 9.3$ (2B, apical B–H); $-11.8$ (2B, B–B); $-14.0$ (2B, B–N); $-18.1$, $-22.9$, and $-25.2$ (total of 14B, equatorial B–H); ESI-MS: *m/z*: 291.3 $[\{(H)(CH_3C(NH)_2B_{20}H_{17}\}^-]$, 365.3 $[\{(Me_4N)(CH_3C(NH)_2B_{20}H_{17}\}^-]$; $^1H$ NMR ($CD_3CN$): $\delta = 5.7$ (s, NH); 1.7(s, $CH_3$); $^{13}C$ NMR ($CD_3CN$): $\delta = 163.5$ ($CCH_3$), 26.1 ($CH_3$).

  1433-7851/98/3713-1867 $ 17.50+.50/0 

**4**: Crude $Na_3$[**2**] was prepared from $(Me_3NH)_3$[**1**] (2.00 g, 4.64 mmol) as described above. The crude $Na_3$[**2**] was dissolved in water (50 mL), and the solution was acidified to pH 2 with HCl (2 N). The mixture was stirred for 5 min and filtered. Aqueous $Me_4NCl$ (5 N) was added until precipitation was complete. The brown precipitate was collected by filtration, the solid dissolved in acetone/chloroform (40 mL, 1/1), and the resulting solution passed through silica gel column (3 × 45 cm, elution with the same solvent mixture). The yellow solution was collected, and the solvent was removed in vacuo. The residue was dissolved in $H_2O$ (20 mL), and aqueous $Me_4NCl$ (5 mL, 1 N) was added to precipitate crude $(Me_4N)_2$[**4**]. The product was purified by recrystallization from acetone/ether and dried in vacuo to yield $(Me_4N)$[**4**] (0.42 g, 25 %) as bright yellow crystals. $^{11}B\{^1H\}$ NMR ($H_2O$): $\delta =$ 31.3 (2 B, apical B–H); 15.6 (2 B, B–B); −0.5 (2 B, B–N); −4.4, −12.5, −16.7, −19.0 (total of 12 B, equatorial B–H); −29.1 (2 B, apical B–H); ESI-MS: *m/z*: 289.3 [$\{(CH_3C(NH)_2B_{20}H_{16}\}^-$]; $^1H$ NMR ($CD_3CN$): $\delta = 5.9$ (s, NH); 1.7 (s, $CH_3$); $^{13}C$ NMR ($CD_3CN$): $\delta = 169.1$ ($CCH_3$), 24.2 ($CH_3$).

**5**: Dry $(Me_4N)$[**4**] (1.00 g, 2.75 mmol) was refluxed in water (30 mL) for 2 h. An aqueous solution of $[Ph_3PMe]Br$ was added until precipitation was complete. The white powder was filtered and purified by recrystallization from $CH_3CN$/ether. The resulting solid was dried in vacuo to yield $[Ph_3PMe]$[**5**] (0.37 g, 33 %) as a white powder. The product was identified by its $^{11}B\{^1H\}$ NMR[10] and ESI mass spectra (*m/z*: 136.4 [$(B_{10}H_9NH_3)^-$]).

**7**: Dry $[(Me_3NH)_4]$[**6**][11] (2.00 g, 4.08 mmol) was added to a stirred suspension of NaH (0.50 g, 20.8 mmol) in dry $CH_3CN$; hydrogen gas was evolved. The mixture was stirred at room temperature for 1 h and filtered, and then the $CH_3CN$ was removed in vacuo. The residue was dissolved in dry $CH_3CN$ (100 mL). Benzoquinone (1.50 g, 14.1 mmol) was added, and the solution was stirred for 3 h. The solution was filtered, and $CH_3CN$ was removed in vacuo. The residue was dissolved in water (50 mL), and the solution was filtered again. The ion **7** in the solution was identified from its $^{11}B\{^1H\}$ NMR spectrum.[2]

**8**: The solution of ion **7** obtained above was acidified with HCl (1 N ) to pH 3, stirred for 5 min, and filtered. Aqueous $Me_4NCl$ (1 N) was added until precipitation was complete. The resulting white solid was collected by filtration and purified by recrystalization from $CH_3CN$/EtOH. It was dried in vacuo to yield $[Me_4N]_2$[**8**] (1.17 g, 72 %). The product was identified by its $^{11}B\{^1H\}$ NMR and ESI mass spectra.[2]

Received: January 26, 1998 [Z 11407 IE]
German version: *Angew. Chem.* **1998**, *110*, 1966 – 1969

**Keywords:** boron · clusters · oxidations

[1] B. L. Chamberland, E. L. Muetterties, *Inorg. Chem.* **1964**, *3*, 1450 – 1456; M. F. Hawthorne, R. L. Pilling, P. F. Stokely, *J. Am. Chem. Soc.* **1965**, *87*, 1893 – 1899.

[2] F. Li, K. Shelly, R. R. Kane, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.* **1996**, *118*, 6506 – 6507.

[3] D. A. Feakes, K. Shelly, C. B. Knobler, M. F. Hawthorne, *Proc. Natl. Acad. Sci. USA* **1994**, *91*, 3029 – 3033.

[4] E. M. Georgiev, K. Shelly, D. A. Feakes, J. Kuniyoshi, S. Romano, M. F. Hawthorne, *Inorg. Chem.* **1996**, *35*, 5412 – 5416; M. F. Hawthorne, K. Shelly, *J. Neuro-Oncol.* **1997**, *33*, 53 – 58.

[5] R. A. Watson-Clark, M. F. Hawthorne, *Inorg. Chem.* **1997**, *36*, 5419 – 5420.

[6] F. Li, K. Shelly, C. B. Knobler, M. F. Hawthorne, unpublished results.

[7] Crystal structure analysis of $[Me_4N]$[**4**]. Yellow crystals obtained by recrystallization from acetone/ether: $B_{20}C_6H_{33}N_3$, $M_r = 363.6$, crystal dimensions $0.15 \times 0.4 \times 0.4$ mm$^3$, Syntex $P\bar{1}$ diffractometer, $Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, 298 K; $\theta$-$2\theta$ scan mode to $2\theta_{max} = 115^\circ$. The unit-cell parameters were determined from 51 accurately centered reflections ($17.4^\circ < 2\theta < 40.3^\circ$): orthorhomic, space group $P2_12_12_1$, $a =$ 15.404(8), $b = 9.544(5)$, $c = 19.647(10)$ Å, $V = 2889$ Å$^3$, $Z = 4$, $\rho_{calcd} =$ 1.01 g cm$^{-3}$, $\mu = 3.36$ cm$^{-1}$. Of the 2131 unique reflections measured ($+h$, $+k$, $\pm l$), 1620 were considered observed ($I > 3\sigma(I)$), and the structure was solved by direct methods; 212 refined parameters, maximum residual electron density 0.1 e Å$^{-3}$, least-square refinement against $|F^2|$, $R = 0.075$ for the observed reflections, $R_w = 0.092$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101 300. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] R. L. Pilling, M. F. Hawthorne, E. A. Pier, *J. Am. Chem. Soc.* **1964**, *86*, 3568; C. H. Schwalbe, W. N. Lipscomb, *Inorg. Chem.*, **1971**, *10*, 151 – 1971.

[9] The p$K_a$ of the bridging hydrogen atom was estimated from the pH at half neutralization of an aqueous titration of $Na_2$[**3**].

[10] W. R. Hertler, M. S. Raasch, *J. Am. Chem. Soc.* **1964**, *86*, 3661.

[11] M. F. Hawthorne, R. L. Pilling, P. F. Stokely, *J. Am. Chem. Soc.* **1965**, *87*, 4740 – 4746.

# A New Isomer of the $[B_{20}H_{18}]^{2-}$ Ion: Synthesis, Structure, and Reactivity of *cis*-$[B_{20}H_{18}]^{2-}$ and *cis*-$[B_{20}H_{17}NH_3]^-$**

Fangbiao Li, Kenneth Shelly, Carolyn B. Knobler, and M. Frederick Hawthorne*

*Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday*

The well-known polyhedral borane anion $[B_{20}H_{18}]^{2-}$ (**1**),[1] hereafter referred to as *trans*-$[B_{20}H_{18}]^{2-}$, and its photoisomer *iso*-$[B_{20}H_{18}]^{2-}$ (**2**)[2] were first synthesized in the 1960s, soon after the genesis of polyhedral borane chemistry. The electrophilic polyhedral boranes **1** and **2** (Scheme 1 A) have great potential as precursors in reductive substitution reactions which lead to new derivatives for possible employment in boron neutron capture therapy (BNCT).[3] The two $[B_{10}H_9]^-$ cage fragments in **1** are connected by a pair of three-center two-electron (3c – 2e) bonds, while the two $[B_{10}H_9]^-$ cages in **2** are linked by a pair of B-H-B bridges. These bonds are electron deficient and are therefore susceptible to reactions with nucleophiles. In the facile reaction of **1** with hydroxide ion, the initially formed product is *ae*-$[B_{20}H_{17}OH]^{4-}$ (**3**), which is stable under basic conditions. In neutral aqueous media, **3** slowly isomerizes to $a^2$-$[B_{20}H_{17}OH]^{4-}$ (**4**, Scheme 1 B).[4] Although other isomers of $[B_{20}H_{18}]^{2-}$ have been proposed,[5] none have been detected other than the photoisomer **2**.[2]

The reduction of **1** with sodium in liquid ammonia produced a kinetically controlled product, the $e^2$-$[B_{20}H_{18}]^{4-}$ ion (**5**), which could be isomerized to the *ae*-$[B_{20}H_{18}]^{4-}$ ion (**6,** Scheme 1 C).[1] Oxidation of **5** with iron(III) ions under aqueous, acidic conditions at high temperature regenerates **1**.[1] However, recent studies of the low-temperature oxidation

[*] Prof. M. F. Hawthorne, F. Li, Dr. K. Shelly, Dr. C. B. Knobler
Department of Chemistry and Biochemistry
University of California at Los Angeles
Los Angeles, CA 90095 – 1569 (USA)
Fax: (+1) 310-825-5490
E-mail: mfh@chem.ucla.edu

[**] This work was supported by the U.S. Department of Energy (DE-FG02-95ER61975). The following prefixes are used as isomer designations: *ae* = apical – equatorial isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[1\text{-}(2\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$), $a^2$ = apical – apical isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[1\text{-}(1\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$), $e^2$ = equatorial – equatorial isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[2\text{-}(2\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$).

  1433-7851/98/3713-1868 $ 17.50+.50/0 