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Synthesis and Structure of the Elusive [a^2-$B_{20}H_{19}$]$^{3-}$ Anion

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The apical−apical isomer of the polyhedral borane anion [a^2-$B_{20}H_{18}$]$^{4-}$ reacts with various proton sources in dichloromethane to produce the protonated species [a^2-$B_{20}H_{19}$]$^{3-}$ in high yield. The mixed tetraethylammonium−pyridinium salt of [a^2-$B_{20}H_{19}$]$^{3-}$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.223(3)$ Å, $b = 10.970(3)$ Å, $c = 15.328(4)$ Å, $\beta = 106.06(1)°$, $V = 1819$ Å^3, and $Z = 2$. Data were collected on a Syntex P$\bar{1}$ diffractometer using Cu Kα radiation, to a maximum $2\theta = 115°$, giving 2359 unique reflections, and the structure was solved by direct methods (SHELX86). The final discrepancy indices were $R = 0.062$ and $R_w = 0.086$ for 1967 independent reflections with $I > 3\sigma(I)$. The structure of the [a^2-$B_{20}H_{19}$]$^{3-}$ anion is similar to that of its apical−apical [a^2-$B_{20}H_{18}$]$^{4-}$ precursor with the addition of a hydrogen bridge connecting the two 10-boron atom cages. The boron−hydrogen−boron bond forms an angle of 91(3)° although the component $B_{10}H_9$ cages share a common axis through their B(1)−B(10) vertices.

Aqueous Fe^{3+} oxidation of the [$B_{10}H_{10}$]$^{2-}$ ion produces the [$B_{20}H_{18}$]$^{2-}$ anion,[1] whose reduction with sodium in liquid ammonia[2] yields a kinetically controlled [e^2-$B_{20}H_{18}$]$^{4-}$ product composed of two 10-boron atom cages linked by an equatorial−equatorial (e^2) two-electron two-center boron−boron bond[2] structurally confirmed by X-ray diffraction.[3] Protonation of the [e^2-$B_{20}H_{18}$]$^{4-}$ ion leads to an isomeric mixture of [$B_{20}H_{19}$]$^{3-}$ ions which, upon basification, results in two other isomers of [$B_{20}H_{18}$]$^{4-}$ characterized by two 10-boron atom cages linked by a two-center apical−equatorial (*ae*) or a two-center apical−apical (a^2) boron−boron bond[2,3] depending upon conditions (Figure 1). Consequently, isomeric [$B_{20}H_{19}$]$^{3-}$ ions appear to serve as reaction intermediates[2] and their structures have long been sought.[2] Although protonation of the electron-rich B−B bonds present in the isomeric [$B_{20}H_{18}$]$^{4-}$ ions is attractive on an *a priori* basis, protonation of edges and faces of the square pyramidal regions nearest the B−B interactions would also produce viable species.[4] We here report the solid state structure of the [a^2-$B_{20}H_{19}$]$^{3-}$ ion.

Both experimental and theoretical studies have been performed on a variety of protonated borane anions. *Ab Initio* calculations have been carried out for both the [$B_{10}H_{11}$]$^-$ and the [B_7H_8]$^-$ anions.[4] The structures of the [B_6H_7]$^-$ and [$B_{10}H_{11}$]$^-$ anions have been determined crystallographically.[5,6] However, as noted above, structural data on the protonated [a^2-$B_{20}H_{19}$]$^{3-}$ species have proved elusive, and ^{11}B NMR studies have indicated that at least two isomers of [a^2-$B_{20}H_{19}$]$^{3-}$ exist in solution.[2b]

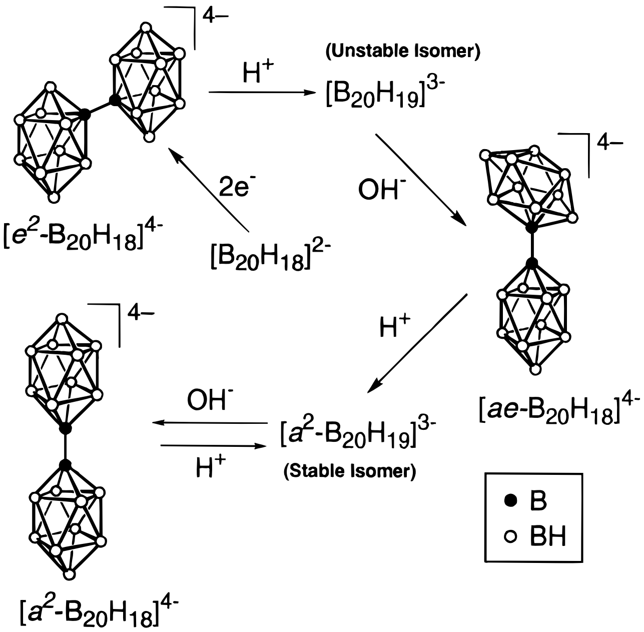

Figure 1. Acid-catalyzed conversion of the equatorial−equatorial [e^2-$B_{20}H_{18}$]$^{4-}$ ion to the apical−apical [a^2-$B_{20}H_{18}$]$^{4-}$ ion.[2b]

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During an attempted carbonylation of the $[a^2\text{-}B_{20}H_{18}]^{4-}$ species with oxalyl chloride,[11] a synthetic route was developed which results in a high yield of one $[a^2\text{-}B_{20}H_{19}]^{3-}$ isomer. Simple acidification of $[a^2\text{-}B_{20}H_{18}]^{4-}$ with HCl in dichloromethane produces this same ion. The structure of this $[a^2\text{-}B_{20}H_{19}]^{3-}$ isomer has now been successfully determined by a single-crystal X-ray diffraction study.

Experimental Section

Materials and General Procedures. The potassium salt of $[a^2\text{-}B_{20}H_{18}\cdot xH_2O]^{4-}$ was prepared by published methods.[3] Oxalyl chloride was obtained from Aldrich as a 2.0 M solution in dichloromethane. Dichloromethane was freshly distilled over calcium hydride. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted. The ^{11}B NMR spectra were recorded on a Bruker ARX 500 NMR spectrometer and referenced to external $BF_3\cdot O(C_2H_5)_2$. Peaks upfield with respect to the reference are designated as negative. Infrared spectra were obtained as Nujol mulls with a Nicolet 205 FT-IR spectrometer. Standard glovebox, Schlenk, and vacuum-line techniques were employed for all manipulations of air- and moisture-sensitive compounds.

Preparation of $([(C_2H_5)_4N]_2[C_5H_5NH])[a^2\text{-}B_{20}H_{19}]$. The tetraethylammonium salt of the $[a^2\text{-}B_{20}H_{18}\cdot xH_2O]^{4-}$ species was prepared from a hot saturated aqueous solution of $K_4[a^2\text{-}B_{20}H_{18}\cdot xH_2O]$ by the addition of saturated aqueous tetraethylammonium bromide. The precipitated $[(C_2H_5)_4N]_4[a^2\text{-}B_{20}H_{18}\cdot xH_2O]$ was filtered off, dried overnight under vacuum, and kept under nitrogen.

A slurry of $[(C_2H_5)_4N]_4[a^2\text{-}B_{20}H_{18}\cdot xH_2O]$ (1.03 g, 1.36 mmol) in dichloromethane (150 mL) was prepared and cooled in an ice bath. Pyridine (2.00 mL, 24.7 mmol) and a 2.0 M solution of oxalyl chloride in dichloromethane (7.00 mL, 14.0 mmol) were added sequentially. Immediately upon the addition of the oxalyl chloride, the suspension turned bright yellow. The mixture was stirred for 1 h at 0 °C. The solvent, excess pyridine, and excess oxalyl chloride were removed under reduced pressure. Dichloromethane (100 mL) was then added, and the insoluble product, $([(C_2H_5)_4N]_2[C_5H_5NH])[a^2\text{-}B_{20}H_{19}]$, was removed by filtration as a yellow solid and washed three times with dichloromethane (3 × 20 mL). A minor byproduct, $[(C_2H_5)_4N]_2B_{20}H_{18}$, was also identified in the dichloromethane filtrate and washings. No carbonyl product was found. $([(C_2H_5)_4N]_2[C_5H_5NH])[a^2\text{-}B_{20}H_{19}]$ was obtained in 92% yield (0.718 g, 1.25 mmol). Single crystals were obtained by recrystallization from dimethyl sulfoxide/ethanol. IR (Nujol): 2498 cm^{-1} (B−H); 1851 cm^{-1} (B−H−B). ^{11}B NMR (dimethyl sulfoxide): 7.94 (d), 6.71 (d), 0.80 (d), −1.73 (d), −4.86 (s), −22.20 (d), −26.25 (d) ppm.

After the successful synthesis and characterization of the $[a^2\text{-}B_{20}H_{19}]^{3-}$ species using the above procedure, additional synthetic routes were explored. The simplest synthetic route for the preparation of the $[a^2\text{-}B_{20}H_{19}]^{3-}$ ion is the reaction of $[(C_2H_5)_4N]_4[a^2\text{-}B_{20}H_{18}\cdot xH_2O]$ in dichloromethane with dry HCl(g). A slurry of $[(C_2H_5)_4N]_4[a^2\text{-}B_{20}H_{18}\cdot xH_2O]$ (1.37 g, 1.82 mmol) in dichloromethane was prepared and cooled in an ice bath. Dry HCl(g) was bubbled through the slurry for 15 min. The insoluble product, $[(C_2H_5)_4N]_3[a^2\text{-}B_{20}H_{19}]$, was removed by filtration and washed with additional dichloromethane (3 × 20 mL). The salt $[(C_2H_5)_4N]_3[a^2\text{-}B_{20}H_{19}]$ (1.13 g, 1.80 mmol) was isolated in 99% yield. In addition, the reaction of $[(C_2H_5)_4N]_4[a^2\text{-}B_{20}H_{18}\cdot xH_2O]$ in dichloromethane with freshly distilled acetyl chloride also produced the $[a^2\text{-}B_{20}H_{19}]^{3-}$ species in high yield. From both alternate synthetic routes, the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion was identified using ^{11}B NMR. Additional single crystals containing the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion were obtained from dimethyl sulfoxide/ethanol solutions. The presence of pyridine in any of the synthesis routes described above leads to the formation of the minor byproduct $[(C_2H_5)_4N]_2B_{20}H_{18}$. In the absence of pyridine, these reactions yield the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion exclusively.

Collection and Reduction of X-ray Data for $([(C_2H_5)_4N]_2[C_5H_5NH])[a^2\text{-}B_{20}H_{19}]$.[7] A colorless crystal, obtained from a dimethyl sulfoxide/ethanol solution, was mounted on a fiber and placed on a Syntex $P\bar{1}$ diffractometer (Cu Kα radiation). Data were collected for $+h,+k,\pm l$ reflections. Unit cell parameters were determined from a least-squares fit of 18 accurately centered reflections ($17.4 < 2\theta < 40.5°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table 1. Three intense reflections (3,2,−4; 2,−1,0; 2,1,1) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (25.1 h). Of the 2359 unique reflection measured, 1967 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis.

Table 1. Crystallographic Data Collection for $([(C_2H_5)_4N]_2[C_5H_5NH])[a^2\text{-}B_{20}H_{19}]$

temp/K	85
cryst size/mm	0.32 × 0.2 × 0.4
normal to faces	101, 011, 011
appearance	colorless parallelepiped
radiation (graphite monochromator)	Cu Kα
wavelength/Å	1.5418
space group	$P2_1/n$
a/Å	11.223(3)
b/Å	10.970(3)
c/Å	15.328(4)
β/deg	106.06(1)
V/Å^3	1813
Z	2
ρ(calcd)/g cm^{-3}	1.05
μ/cm^{-1}	3.39
scan width below Kα_1/deg	1.3
scan width above Kα_2/deg	1.6
scan rate/deg min^{-1}	6
no. of unique reflns	2359
no. of observed ($I > 3\sigma(I)$) reflns	1967
2θ max/deg	115
data collected	$+h,+k,\pm l$
no. of parameters refined	251
R, R_w, GOF[a]	0.062, 0.086, 2.91

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$. $GOF = [\sum w(|F_o - F_c|)^2/(N_o - N_v)]^{1/2}$.

Solution and Refinement of the Structure of $([(C_2H_5)_4N]_2[C_5H_5NH])[a^2\text{-}B_{20}H_{19}]$. A pyridinium cation is located at a center of symmetry. One position (and its equivalent position) is occupied half of the time by carbon and half of the time by nitrogen. The hydrogen atom attached to this carbon atom has been included at half-occupancy. All non-hydrogen atoms were refined with anisotropic thermal parameters. All methyl and methylene hydrogens were included in calculated positions, C−H = 1.0 Å. Positional parameters for hydrogen atoms of the anion and the pyridinium cation were allowed to vary. Hydrogen atoms were assigned isotropic displacement values based approximately on the value for the attached atom.[8] Crystallographic data and selected bond distances and angles are reported in Tables 1 and 2.

Results and Discussion

As previously reported,[1b,2b] the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion is formed by the acidification of the $[a^2\text{-}B_{20}H_{18}]^{4-}$ species. Oxalyl chloride and acetyl chloride can both serve as proton sources upon exposure to trace amounts of water present in the starting material, since HCl is a byproduct of the hydrolysis of either acid chloride. Dry HCl(g) was also demonstrated to be a useful proton source in the absence of pyridine. Protonation of the $[a^2\text{-}B_{20}H_{18}]^{4-}$ ion is thereby readily achieved. The presence of pyridine (pK_a of the pyridinium ion 5.23)[12] does not impair the formation of the $[a^2\text{-}B_{20}H_{19}]^{3-}$ ion, a weak acid with a pK_a of approximately 7.3,[2c] but it does facilitate the formation of the $[B_{20}H_{18}]^{2-}$ anion as a byproduct. The latter reaction is presumed to result from the ability of the pyridinium ion to act as a mild oxidizing agent,[9] although this point was not investigated further.

All of the above synthetic routes result in products which exhibit identical ^{11}B NMR spectra in solution. The ^{11}B NMR

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Table 2. Selected Interatomic Distances (Å) and Angles (deg)

B1−B3	1.674(5)	B1−B1	1.936(6)
B2−B6	1.799(5)	B3−B6	1.801(5)
B4−B7	1.802(5)	B5−B9	1.796(5)
B6−B10	1.697(5)	B8−B9	1.821(5)
H1br−B1	1.35(5)	B1−B4	1.664(6)
B2−B3	1.825(6)	B2−B9	1.794(6)
B3−B7	1.798(5)	B4−B8	1.794(5)
B6−B7	1.819(5)	B7−B8	1.838(5)
B8−B10	1.687(5)	B10−B10	9.195(0)
B1−B2	1.675(6)	B1−B5	1.671(7)
B3−B4	1.860(5)	B4−B5	1.828(6)
B5−B8	1.787(5)	B6−B9	1.821(5)
B7−B10	1.683(6)	B9−B10	1.687(6)
B1−H1br	1.36(5)		
B2−B1−B3	66.0(2)	B2−B1−B4	102.3(3)
B3−B1−B5	102.5(3)	B4−B1−B5	66.5(2)
B1−B2−B3	57.0(2)	B1−B2−B6	112.3(3)
B1−B2−B9	110.3(3)	B3−B2−B5	90.4(3)
B3−B2−B9	102.2(3)	B5−B2−B6	101.9(2)
B5−B2−B9	59.0(2)	B6−B2−B9	60.9(2)
B1−B3−B6	111.1(3)	B6−B3−B7	60.7(2)
B8−B5−B9	61.1(2)	B2−B6−B7	102.2(2)
B2−B6−B10	112.2(3)	B3−B6−B9	102.1(2)
B7−B6−B9	89.9(2)	B9−B6−B10	57.3(2)
B3−B7−B6	59.7(2)	B3−B7−B10	112.6(3)
B6−B7−B8	90.2(2)	B8−B7−B10	57.1(2)
B4−B8−B5	61.4(2)	B4−B8−B9	102.2(2)
B9−B8−B10	57.3(2)	B8−B10−B9	65.3(2)
B3−B1−B1	129.1(3)	B1−H1br−B1	91(3)

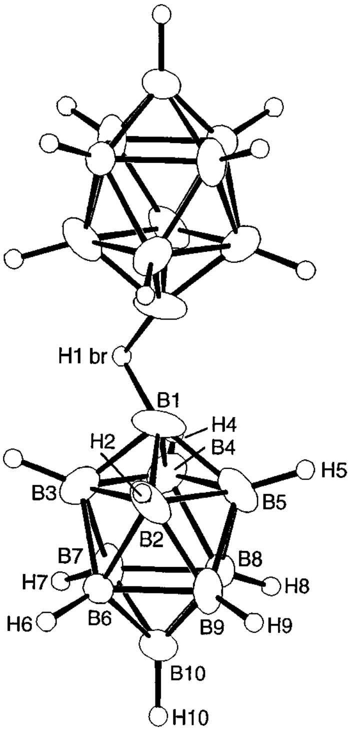

Figure 2. Structure of the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion showing atomic labeling. The anion has C_{2v} symmetry, with a mirror plane passing through B1 and H1br, and is centrosymmetric.

spectra obtained are extremely solvent sensitive and are not indicative of the solid state structure. In dimethyl sulfoxide, two major resonances occur at −22.20 (d) and −26.2 (d) ppm. Five minor resonances appear in the spectra at 7.94 (d), 6.71 (d), 0.80 (d), −1.73 (d), and -4.86 (s) ppm, a region generally associated with apical boron vertices. In water, the spectrum is more complicated. Four major resonances occur at −23.2 (d), −24.26 (d), −27.61 (d), and −29.36 (s) ppm, and six minor resonances at 6.72 (d), 5.83 (d), −0.55 (d), −0.35 (d), −1.46 (d), and −4.14 (s) ppm appear in that region of the spectrum assigned to apical boron vertices. In addition, a second singlet occurs at −20.03 ppm. The simplicity of the solid state structure should be associated with a correspondingly simple ^{11}B NMR spectrum similar to that of the parent $[a^2\text{-}B_{20}H_{18}]^{4-}$ ion. The observed complexity of the solution ^{11}B NMR spectra supports the suggestion that the $[a^2\text{-}B_{20}H_{19}]^{3-}$ species exists in solution as a tautomeric mixture of ions of unknown structure.

As has been found for the $[a^2\text{-}B_{20}H_{18}]^{4-}$ anion, the inner equatorial belts of B−H vertices of the boron cages in the $[a^2\text{-}B_{20}H_{19}]^{3-}$ ion are eclipsed and parallel. The bridging hydrogen atom occupies a position centered between the two boron cages, but to the side of an axis connecting all apical boron atoms. Consequently, the two apical boron atoms closest to the bridging hydrogen atom and the bridging hydrogen atom form an isosceles triangle and the ion has approximate C_{2v} symmetry. The plane containing this triangle bisects the two equatorial boron−boron bonds of each cage perpendicular to the plane and closest to the bridging hydrogen atom. An approximate C_2 axis perpendicular to the axis connecting the apical borons bisects the bridging hydrogen, H1br. A vertical mirror plane is also defined by the bridging hydrogen, H1br, and the apical borons, B1 (Figure 2). The space group of the crystal was centrosymmetric, leaving the placement of the bridging hydrogen at half-occupancy in two positions related by the center of symmetry. This hydrogen is located on either side of the apical boron atoms connecting the two cages.

The gross structure of the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion is similar to that of the $[a^2\text{-}B_{20}H_{18}]^{4-}$ anion, except for the addition of a hydrogen bridge between the two boron atoms connecting the cages. In the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion, these B1 atoms are bridged by a hydrogen atom with a boron−hydrogen distance of 1.36(5) or 1.35(5) Å. The B−H−B bridging angle is 91(3)°. Other differences between the $[a^2\text{-}B_{20}H_{19}]^{3-}$ ion and the $[a^2\text{-}B_{20}H_{18}]^{4-}$ ion stem from differing boron−boron bond lengths. In the title anion, the B(1)−B(1) distance is 1.936(6) Å while the comparable distances in the $K_4[a^2\text{-}B_{20}H_{18}\cdot xH_2O]$ structure are 1.699(4) Å in the tetrahydrate and 1.666(12) Å in the dihydrate.[3] In the $[a^2\text{-}B_{20}H_{19}]^{3-}$ species, the apical−equatorial (*a*−*e*) boron−boron bond lengths beginning at the apical boron furthest removed from the apical−apical (*a*−*a*) boron−boron bond, B(10), are slightly longer than the *a*−*e* boron−boron bond lengths beginning at the apical borons involved in the *a*−*a* boron−boron bond (B1), with average lengths of 1.686 and 1.671 Å, respectively. This is opposite the effect found in the $[a^2\text{-}B_{20}H_{18}]^{4-}$ species. In the $[a^2\text{-}B_{20}H_{18}]^{4-}$ anion, the *a*−*e* boron−boron bond lengths closest to the *a*−*a* boron−boron bond average 1.72 Å while the *a*−*e* boron−boron bond lengths furthest removed from the *a*−*a* bond average 1.70 Å. All *a*−*e* bond distances are shorter in the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion than in the $[a^2\text{-}B_{20}H_{18}]^{4-}$ ion. In both anions, the equatorial−equatorial (*e*−*e*) distances are approximately 1.82 Å.[3]

Although the bridging proton seems to be strongly bonded to the two apical boron atoms connecting the two cages, the proton is located to the side of the original boron−boron σ bond present in the $[a^2\text{-}B_{20}H_{18}]^{4-}$ ion rather than being inserted into it. A potentially similar bonding arrangement exists in the $[B_2H_7]^-$ anion, the only other structurally characterized example of an unsupported B−H−B bridge. The angle formed by the B−H−B bridge in the $[B_2H_7]^-$ anion is 136°, significantly larger than that seen in the present structure. In addition, the distance between the bridging boron atoms is quite different. In the $[B_2H_7]^-$ anion, there is no apparent bonding character between the boron atoms, and the distance is 2.107 Å.[10] However, in the $[a^2\text{-}B_{20}H_{19}]^{3-}$ species, the distance is only 1.936(6) Å.

The boron hydrides often display a bent hydrogen bridge derived from the strongly directional pair of sp^3, or similar hybrid, boron orbitals shared with the 1s orbital of the hydrogen bridge. In the [a^2-$B_{20}H_{19}$]$^{3-}$ anion case, the participating apical sp orbitals would be parallel to the axis containing the apical borons of the 10-boron atom cages. Loosely confining the overlap of the apical sp boron orbitals and the hydrogen orbital to the usual pattern would result in a bent structure which forces the two 10-boron atom cages together. This bent structure would be stereoelectronically unfavorable due to the mutual repulsion of the 2− charge associated with each of the cages. The Coulombic repulsion between the two cages would be minimized by increasing the B−H−B bridging angle to 180°. The unusual structure of the [a^2-$B_{20}H_{19}$]$^{3-}$ anion probably results from a compromise between the delocalization available from three-center two-electron bonding in the boron−hydrogen−boron bridge, the Coulombic repulsion between those same cages, and the retention of considerable B−B σ bond character between the apical boron atoms.

In conclusion, the long-sought structure of the [a^2-$B_{20}H_{19}$]$^{3-}$ anion has now been crystallographically determined. Synthesis of the anion is readily accomplished through the protonation of the [a^2-$B_{20}H_{18}$]$^{4-}$ anion using a variety of proton sources. The anion is similar in structure to the [a^2-$B_{20}H_{18}$]$^{4-}$ species with the addition of a proton to the edge of the B−B bond connecting the two 10-boron atom cages at their apices.

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Supporting Information Available: For the ([$(C_2H_5)_4N$]$_2$[C_5H_5NH])[a^2-$B_{20}H_{19}$], listings of final positional and thermal parameters and bond distances and angles (4 pages.) Ordering information is given on any current masthead page.

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