

The Preparation and Rearrangement of the Three Isomeric $B_{20}H_{18}^{-4}$ Ions

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The ceric ion oxidation of $B_{10}H_{10}^{-2}$ produced $B_{20}H_{18}^{-2}$ and a $B_{20}H_{19}^{-3}$ ion. Sodium in liquid ammonia reduced $B_{20}H_{18}^{-2}$ to a $B_{20}H_{18}^{-4}$ ion having an equatorial-equatorial two-center linkage between polyhedra. Subsequent acid-catalyzed rearrangement of this $B_{20}H_{18}^{-4}$ isomer produced two other isomers of $B_{20}H_{18}^{-4}$ which were characterized by apical-equatorial and apical-apical two-center linkages, respectively. A mechanism for these rearrangement reactions is proposed which involves $B_{20}H_{19}^{-3}$ intermediates. Two $B_{20}H_{19}^{-3}$ ions were isolated.

Introduction

The aqueous ferric ion oxidation of the polyhedral $B_{10}H_{10}^{-2}$ ion was previously reported² to produce the $B_{20}H_{18}^{-2}$ ion, and Lipscomb suggested³ a doubly H-bridged structure for this ion. The now established^{4,5} structure of $B_{20}H_{18}^{-2}$ is presented in Figure 1.

The aqueous ceric ion oxidation of $B_{10}H_{10}^{-2}$ at 0° produced a crystalline material (A) which differed from the then known $B_{20}H_{18}^{-2}$. A was incorrectly assumed⁶ to be an isomer of $B_{20}H_{18}^{-2}$ on the basis of its elemental analysis, its ultraviolet absorption spectrum, and its conversion to authentic $B_{20}H_{18}^{-2}$ in aqueous acid solution. In the wake of these reports, work was commenced upon the chemistry of A. This paper is concerned with subsequent developments and was presented, in part, as a preliminary communication.⁷ Unknown to us at the time, workers at the du Pont Co. were pursuing a closely related problem. Their results have recently been reported.⁸

Results and Discussion

Ceric Ion Oxidation of $B_{10}H_{10}^{-2}$. The addition of an aqueous solution of $B_{10}H_{10}^{-2}(Et_3N^+H)_2$ to ceric ion in dilute sulfuric acid at 0° led to the immediate precipitation of A. Elemental analyses of A were not in agreement with those previously reported⁶ and the conversion of A to authentic $B_{20}H_{18}^{-2}(Et_3N^+H)_2$ was erratic (*vide infra*). Treatment of A with tetramethylammonium ion in an acetonitrile-ethanol-water mixture precipitated a tetramethylammonium salt (B) which exhibited no absorption in the 290-m μ

region characteristic of both A and $B_{20}H_{18}^{-2}$. Addition of water to the filtrate precipitated authentic $B_{20}H_{18}^{-2}$ as the tetramethylammonium salt. Elemental analysis of B and the cesium and triethylammonium salts derived from it by ion exchange suggested that the anion present in B was a $B_{20}H_{19}^{-3}$ ion. Crystallization of an equimolar solution of $B_{20}H_{19}^{-3}(Et_3N^+H)_3$, which was prepared from B, and $B_{20}H_{18}^{-2}(Et_3N^+H)_2$ produced A in 72% yield and identified A as a double salt, $B_{20}H_{18}^{-2} \cdot B_{20}H_{19}^{-3}(Et_3N^+H)_3$. The $B_{20}H_{19}^{-3}$ ion present in B displayed an apparent H-bridge stretching band at 1850 cm.⁻¹ in the infrared. These results are in agreement with those of Chamberland and Muettterties,⁸ who report salts of $B_{20}H_{18}^{-2}$ and $B_{20}H_{19}^{-3}$ as the products of ceric ion oxidation of $B_{10}H_{10}^{-2}$.

Reactions of the $B_{20}H_{19}^{-3}$ Present in B. The reaction of the $B_{20}H_{19}^{-3}$ present in B with 1 equiv. of hydroxide ion was quantitative and the product of this reaction was a $B_{20}H_{18}^{-4}$ ion (a²) which could be reconverted to the original $B_{20}H_{19}^{-3}$ upon acidification. Equivalent weights, formula weights, and elemental analyses for a² were in agreement with this formulation. The pK_A of $B_{20}H_{19}^{-3}$ was found to be 6.0, a value lower than that previously reported.^{7,8} The higher values previously reported may have been due to the presence of $B_{20}H_{18}^{-4}$ isomers (*vide infra*) in earlier samples.

Oxidation of $B_{20}H_{19}^{-3}$ with hydrogen peroxide or ferric ion in aqueous acid solution produced $B_{20}H_{18}^{-2}$ in moderate yields. Air oxidation of acidified solutions of $B_{20}H_{19}^{-3}$ also produced $B_{20}H_{18}^{-2}$. These observations are in agreement with those of Chamberland and Muettterties.⁸ The latter observation accounts for the previously reported⁶ conversion of A to $B_{20}H_{18}^{-2}$ since no precautions were taken to exclude air from the reaction mixture in the earlier experiments. It is quite possible that the observed air oxidation was catalyzed by traces of residual ferric ion present in the purified $B_{20}H_{18}^{-4}$ and $B_{20}H_{19}^{-3}$ salts.

Isomeric $B_{20}H_{18}^{-4}$ Ions. The oxidation of $B_{20}H_{19}^{-3}$ to $B_{20}H_{18}^{-2}$ suggested that an oxidation-reduction equilibrium might exist between $B_{20}H_{18}^{-2}$ and $B_{20}H_{18}^{-4}$. Accordingly, a successful attempt was made to reduce $B_{20}H_{18}^{-2}$ to $B_{20}H_{18}^{-4}$ with sodium in liquid ammonia. The $B_{20}H_{18}^{-4}$ obtained from this reaction, although compositionally identical in all respects, was not the $B_{20}H_{18}^{-4}$ ion prepared by neutralization of $B_{20}H_{19}^{-3}$ with base. Thus, evidence for the existence of a second isomer in the $B_{20}H_{18}^{-4}$ series was brought to light. This second isomer will be denoted as e² hereafter. Potentiometric titration of e² with aqueous acid proved that one proton was taken up per e² ion to produce a $B_{20}H_{19}^{-3}$ species. The apparent pK_B of e² was observed to be 8.8. However, these pK_B determinations were not reproducible owing to a

- (1) Alfred P. Sloan Research Fellow.
- (2) A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).
- (3) W. N. Lipscomb, *ibid.*, **47**, 1791 (1961).
- (4) R. L. Pilling, M. F. Hawthorne, and E. A. Pier, *J. Am. Chem. Soc.*, **86**, 3568 (1964).
- (5) E. L. Muettterties and K. Babcock, private communication.
- (6) A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3026 (1962).
- (7) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *ibid.*, **85**, 3704 (1963).
- (8) B. L. Chamberland and E. L. Muettterties, *Inorg. Chem.*, **3**, 1450 (1964).

slow upward drift of the pH during titration. Acidification of e^2 at 70° followed by neutralization with hydroxide ion after several minutes had elapsed produced the $B_{20}H_{18}^{-4}$ isomer, a^2 . Isolation of the $B_{20}H_{19}^{-3}$ ion (tetramethylammonium salt) which resulted after e^2 had been in aqueous acid solution for several minutes proved it to be identical with that produced by the ceric ion oxidation of $B_{10}H_{10}^{-2}$ or by acidification of a^2 . Thus, the rearrangement of e^2 to a^2 appeared to be an acid-catalyzed process.

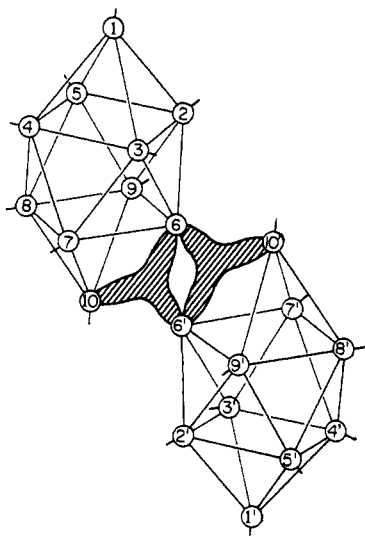


Figure 1. Structure of $B_{20}H_{18}^{-2}$ ion. Boron atoms are indicated by circles and all except the 6-6' atoms have terminal hydrogens. The shaded areas represent three-center bonds linking the two polyhedra.

On the basis of ^{11}B n.m.r. spectra to be discussed below, a^2 and e^2 appeared to be isomeric $B_{20}H_{18}^{-4}$ ions which contained apical-apical and equatorial-equatorial two-center B-B bonds, respectively, which joined a pair of polyhedral $B_{10}H_9^{-2}$ fragments. Furthermore, it appeared that the acid-catalyzed conversion of e^2 to the more thermodynamically stable a^2 probably passed through a third isomer which contained an apical-equatorial two-center linkage (isomer ae). The ae isomer of $B_{20}H_{18}^{-4}$ was successfully prepared along with a similar quantity of the a^2 isomer by extremely rapid acidification and neutralization of e^2 at 0° . Yields of ae prepared in this fashion varied between 30 and 60%. The e^2 isomer could never be recovered from these reactions. The ae and a^2 isomers were separated by fractional crystallization of their potassium salts from water at low temperatures. The analytical and ^{11}B n.m.r. data obtained for ae were in agreement with its assigned structure.

Since e^2 was very rapidly converted to ae by treatment with aqueous acid, a search was made for the $B_{20}H_{19}^{-3}$ intermediate assumed to be involved in this isomerization reaction. The addition of aqueous acid to a cold aqueous solution of the tetramethylammonium salt of e^2 resulted in the instantaneous precipitation of a tetramethylammonium salt of a previously unobserved anion. Attempts to purify this salt by recrystallization at low temperatures resulted in its immediate and virtually quantitative conversion to the corresponding

salt of the previously isolated $B_{20}H_{19}^{-3}$. The infrared spectrum of this protonated anion contained four distinct absorption bands in the H-bridge region (2050, 1890, 1750, and 1630 cm^{-1}). The more stable $B_{20}H_{19}^{-3}$ exhibited only a single sharp band at 1850 cm^{-1} in this same region. Attempts to obtain an ^{11}B n.m.r. spectrum of the unstable anion were unsuccessful owing to its rapid conversion to the stable $B_{20}H_{19}^{-3}$. It is presently assumed that the new anion is a $B_{20}H_{19}^{-3}$ ion although conclusive analytical data could not be obtained.

The ^{11}B n.m.r. Spectra of $B_{20}H_{18}^{-4}$ Isomers. The charge and empirical formula of the $B_{20}H_{18}^{-4}$ ions suggest that their structures may be formally described as two $B_{10}H_9^{-2}$ fragments joined by a two-center B-B bond. There are three obvious ways in which the two $B_{10}H_9^{-2}$ fragments may be linked: by apical-apical, apical-equatorial, or equatorial-equatorial bonds (Figure 2). The $B_{10}H_9^{-2}$ fragments will be

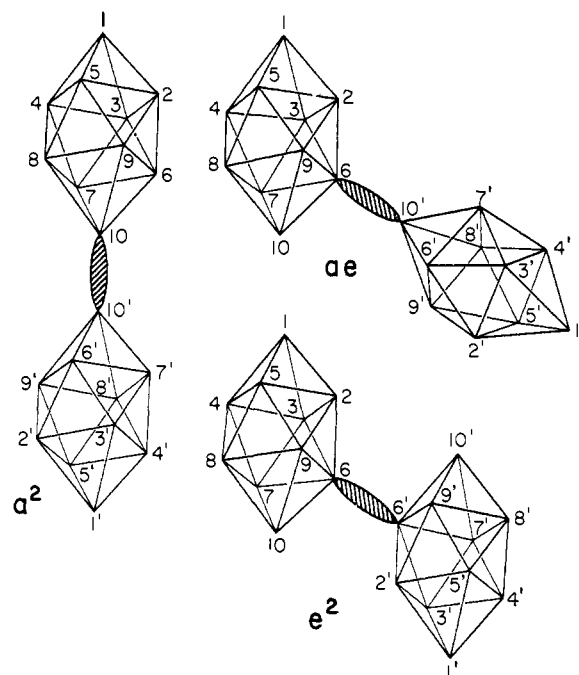


Figure 2. Structures of the three possible $B_{20}H_{18}^{-4}$ isomers in which two $B_{10}H_9^{-2}$ fragments are joined by a two-center B-B bond.

similar in character to $B_{10}H_{10}^{-2}$ ions in which a B-H bond has been substituted by a B-B bond. The ^{11}B n.m.r. spectra of the $B_{20}H_{18}^{-4}$ ions might thus be expected to be low symmetry versions of the spectrum of $B_{10}H_{10}^{-2}$ in which the resonances of the apical boron atoms occur at low field and those of the equatorial boron atoms occur at higher field.⁹ This expectation is confirmed by the fact that the ^{11}B n.m.r. spectra of the three isomeric ions can be split into two regions, a low-field region between -12 and $+6$ p.p.m. ($BF_3 \cdot OEt_2 = 0$) with a total integrated area of approximately 4, and a high-field region centered near 28 p.p.m. with an area of approximately 16. These two regions are assigned, respectively, to the apical boron

(9) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5833 (1959).

atoms and the equatorial boron atoms of the B_{10} polyhedral units.¹⁰

The 60-Mc./sec. ^{11}B n.m.r. spectrum of the e^2 isomer is shown in Figure 3. This spectrum is compatible with an equatorial-equatorial B-B linkage between the polyhedra as illustrated in Figure 2. The proposed

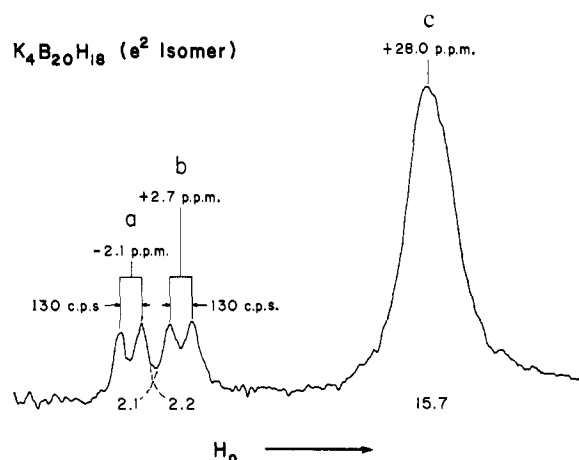


Figure 3. The ^{11}B n.m.r. spectrum of $\text{K}_4\text{B}_{20}\text{H}_{18}$ (e^2 isomer) in H_2O at 60 Mc./sec. Chemical shifts were measured at 32.1 Mc./sec. relative to $\text{BF}_3\cdot\text{OEt}_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

structure is centrosymmetric and contains two types of apical B-H groups, 1-1' and 10-10', a B-B bond between 6 and 6', and four types of equatorial B-H groups, 7-9-7'-9', 8-8', 2-3-2'-3', and 4-5-4'-5'. Thus, this structure would be expected to exhibit two doublets of area 2 in the low-field (apical) region, a singlet area 2, a doublet area 2, and three doublets area 4 in the high-field (equatorial) region. The ^{11}B n.m.r. spectrum actually shows two low-field doublets a and b of area 2.1 and 2.2 and an unresolved high-field singlet c of total area 15.7. The nature of the low-field group is confirmed by a similar spectrum of $\text{B}_{20}\text{D}_{18}^{-4}$ (e^2 isomer) in which both doublets have been collapsed to singlets of equal area. On deuteration, the high-field peak appears to narrow from 290 to 177 c.p.s. at half-peak height, when measured at 19.3 Mc./sec. The two low-field doublets are thus assigned to boron atoms 1-1' and 10-10', each of which must carry a terminal hydrogen atom, which leaves only equatorial boron atoms for joining the polyhedra.

The most symmetrical of the proposed $\text{B}_{20}\text{H}_{18}^{-4}$ structures contains an apical-apical B-B bond, which may be correlated with the 32.1-Mc./sec. ^{11}B n.m.r. spectrum of the a^2 isomer shown in Figure 4. This spectrum contains a low-field singlet (a) of area 1.8, a low-field doublet (b) of area 2.0, and a symmetrical high-field doublet (c) of area 16.2. The corresponding perdeuterated anion exhibits collapse of the doublets b and c; the resulting high-field singlet is approximately 25% wider at half-peak height than the collapsed low-field peak. These results suggest that only two apical boron atoms carry terminal hydrogen atoms

(10) The assignment by analogy with $\text{B}_{10}\text{H}_{10}^{-2}$ appears to be satisfactory in the case of $\text{B}_{20}\text{H}_{18}^{-4}$ ions, but it is unreliable when applied to B_{10} polyhedra linked by three-center bonds; see ref. 4.

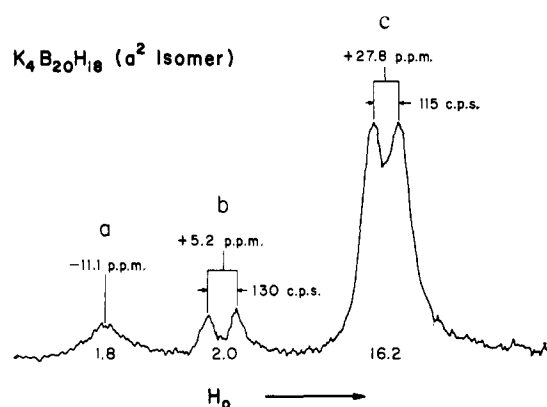


Figure 4. The ^{11}B n.m.r. spectrum of $\text{K}_4\text{B}_{20}\text{H}_{18}$ (a^2 isomer) in H_2O at 32.1 Mc./sec. Chemical shifts are relative to $\text{BF}_3\cdot\text{OEt}_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

and that the remaining apical boron atoms are used to join the two B_{10} polyhedra.^{7,11} The ^{11}B n.m.r. spectrum expected for this structure would contain a singlet of area 2 (boron atoms 10-10'), a doublet of area 2 (boron atoms 1-1') at low field, and two doublets of area 8 at high field due to boron atoms 2-3-4-5-2'-3'-4'-5' and 6-7-8-9-6'-7'-8'-9'. The low resolution of the high-field doublet observed in this spectrum when compared with that of $\text{B}_{10}\text{H}_{10}^{-2}$ could be accounted for by either a broadening of the peaks in the $\text{B}_{20}\text{H}_{18}^{-4}$ ion or by the presence of two doublets which have slightly different δ -values. The previously published⁸ spectrum of $\text{B}_{20}\text{H}_{18}^{-4}$ at 19.25 Mc./sec. shows similar groupings of peaks and chemical shifts but integrated as 1:2-2.5:5-12. This result could be due to the presence of more than one $\text{B}_{20}\text{H}_{18}^{-4}$ isomer.

The 32.1-Mc./sec. ^{11}B n.m.r. spectrum of the ae isomer is presented in Figure 5. The low-field region is more complex than that of the a^2 or e^2 isomers and suggests a structure of lower symmetry. At lowest

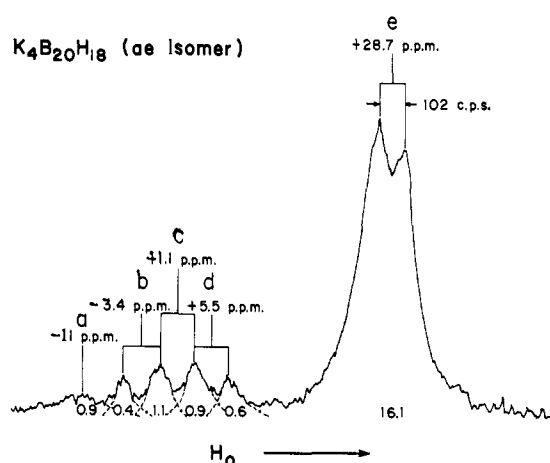


Figure 5. The ^{11}B n.m.r. spectrum of $\text{K}_4\text{B}_{20}\text{H}_{18}$ (ae isomer) in H_2O at 32.1 Mc./sec. Chemical shifts are relative to $\text{BF}_3\cdot\text{OEt}_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

(11) This skeleton has been previously suggested as a possible $\text{B}_{20}\text{H}_{18}^{-4}$ structure: W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 149; see also ref. 3.

field there is a broad singlet (a) of area 0.9 associated with a quartet with area 0.4:1.1:0.9:0.6. Interpretation of the quartet as three doublets, b, c, and d, of area 1 is in good agreement with the spectrum obtained at 19.3 Mc./sec. The width of the high-field doublet is between that of the corresponding group in a^2 and e^2 , and it is also asymmetric. The predicted pattern for the ae structure shown in Figure 2 is: low field—a singlet of area 1 (boron 10'), three doublets of area 1 (boron atoms 1, 10, and 1'); high field—a singlet of area 1 (boron 6), a doublet of area 1 (boron 8), three doublets of area 2 (boron atoms 7-9, 2-4, and 3-5), and two doublets of area 4 (boron atoms 2'-3'-4'-5' and 6'-7'-8'-9'). The observed low-field group is in good agreement with this pattern and the apical-equatorial structure is therefore assigned to the ae isomer.

The ^{11}B N.m.r. Spectrum of $\text{B}_{20}\text{H}_{19}^{-3}$. Of the two isomeric $\text{B}_{20}\text{H}_{19}^{-3}$ ions isolated, it was possible to obtain only ^{11}B n.m.r. spectra of the more stable one owing to the rapid rearrangement of the unstable isomer in solution. The 32.1-Mc./sec. ^{11}B n.m.r. spectra of $\text{B}_{20}\text{H}_{19}^{-3}$ and $\text{B}_{20}\text{D}_{19}^{-3}$ are shown in Figures 6 and 7, respectively. These are in agreement with

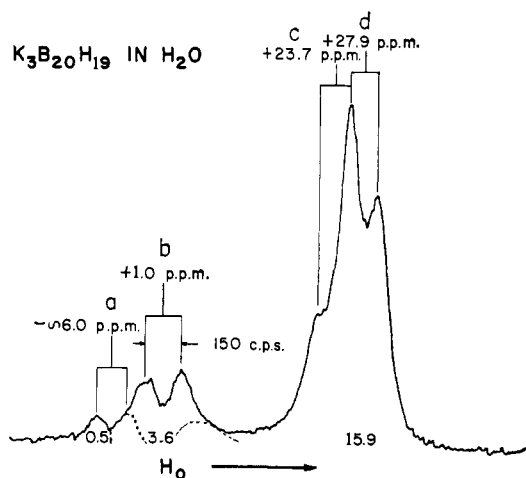


Figure 6. The ^{11}B n.m.r. spectrum of $\text{K}_3\text{B}_{20}\text{H}_{19}$ in H_2O at 32.1 Mc./sec. Chemical shifts are relative to $\text{BF}_3 \cdot \text{OEt}_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

the previously published spectrum obtained at 19.25 Mc./sec.⁸ As in the case of the $\text{B}_{20}\text{H}_{18}^{-4}$ isomers, the ^{11}B n.m.r. spectrum may be separated into a low-field region of area 4 and a high-field region of area 16. Again, the low-field region is assigned to the apical boron atoms. Comparison of the two spectra indicates that the apparent low-field singlet of area 0.5 in the spectrum of $\text{B}_{20}\text{H}_{19}^{-3}$ is actually one-half of a doublet of area 1. After subtraction of this doublet there remains a doublet of area 2 superimposed upon either a doublet or singlet of area 1. Subtraction of a doublet of area 2 from the low-field array suggests that the remaining area probably represents a singlet. The high-field group consists of two doublets c and d of relative area 5:11. Since this $\text{B}_{20}\text{H}_{19}^{-3}$ isomer may be formed from both ae and a^2 , it is quite likely that the boron skeleton will resemble

that present in one of these ions. Furthermore, the infrared spectrum of the more stable $\text{B}_{20}\text{H}_{19}^{-3}$ ion contains a moderately strong band at 1850 cm^{-1} which suggests the presence of a B-H-B bridge. Consideration of the most likely structural possibilities based upon the ae and a^2 configurations and the ^{11}B n.m.r. spectra leads to the conclusion that the more stable $\text{B}_{20}\text{H}_{19}^{-3}$ ion contains a B-H-B bridge between two B_{10}H_9 polyhedral fragments³ which assume an ae relationship. This model has been previously proposed for the more stable $\text{B}_{20}\text{H}_{19}^{-3}$ by Chamberland and Muettterties.⁸ The H-bridge bonded ae model requires three doublets of relative area 1 and a singlet of area 1 in the apical boron atom region of its ^{11}B n.m.r. spectrum. The observed spectrum (*vide ultra*) is in agreement with this assumption if two of the low-field doublets of area 1 are accidentally superimposed. As a working hypothesis we have accepted this formulation of the more stable $\text{B}_{20}\text{H}_{19}^{-3}$ ion.

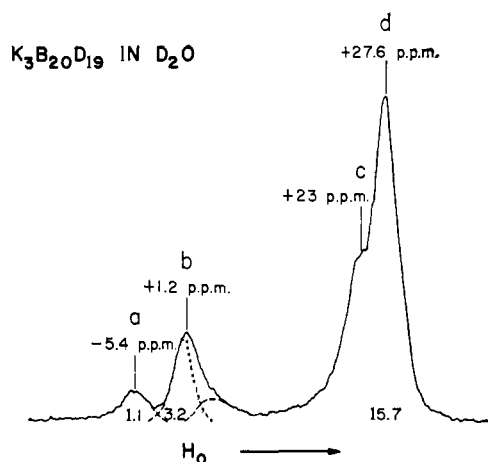
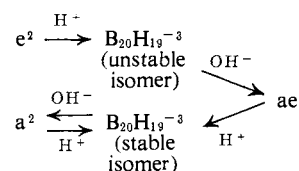


Figure 7. The ^{11}B n.m.r. spectrum of $\text{K}_3\text{B}_{20}\text{D}_{19}$ in D_2O at 32.1 Mc./sec. Chemical shifts are relative to $\text{BF}_3 \cdot \text{OEt}_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

Mechanism of $\text{B}_{20}\text{H}_{18}^{-4}$ Isomerization Reactions. The facile conversion of the e^2 $\text{B}_{20}\text{H}_{18}^{-4}$ isomer to the ae and a^2 isomers poses an interesting mechanistic problem. Although the slow rearrangement of e^2 to a^2 occurs at $75\text{--}100^\circ$ in aqueous media at a pH as high as 9, the conversion of e^2 to a mixture of ae and a^2 and the conversion of ae to a^2 is very rapid in acidic aqueous solution and apparently proceeds *via* intermediate $\text{B}_{20}\text{H}_{19}^{-3}$ ions. This view is further strengthened by the very rapid rearrangement of the least stable $\text{B}_{20}\text{H}_{19}^{-3}$ isomer to the more stable $\text{B}_{20}\text{H}_{19}^{-3}$ isomer



without isolation of ae . These rearrangements do not appear to be polyhedral rearrangements² since well-documented polyhedral rearrangements have required

elevated temperatures¹² and no unique role of acid catalysis has been associated with these processes. If the $B_{20}H_{19}^{-3}$ ions are true intermediates in the rearrangement reactions, an acceptable mechanism might involve an intramolecular electrophilic attack of a terminal boron orbital in the B-H-B bridge upon an edge of the neighboring polyhedron. The resulting edge-bonded structure might represent either a transition state or an unstable intermediate. The fact that only a^2 is obtained by neutralization of the more stable $B_{20}H_{19}^{-3}$ requires the hydrogen-bridged structures with a^2 and ae skeletons to be in very rapid equilibrium with the protonated ae species predominant. While no detailed evidence exists for the support of this proposed mechanism, it accounts for the role of acid catalysis in $B_{20}H_{18}^{-4}$ rearrangements and makes use of the well-established propensity of $B_{10}H_{10}^{-2}$ polyhedra toward electrophilic attack.¹³ In addition, the proposed edge-bonded transition state (or unstable intermediate) contains a B-B-B three-center bond similar to those known^{4,5} to be present in $B_{20}H_{18}^{-2}$. Oxidation of a similar intermediate derived from protonated e^2 could lead to $B_{20}H_{18}^{-2}$.

Experimental

Materials. Decaborane was sublimed before use. Reagent grade triethylamine was distilled with a spinning-band column. All other chemicals were reagent grade.

¹¹B N.m.r. Spectra. The ¹¹B n.m.r. spectra reported at 60 Mc./sec. were obtained using an experimental n.m.r. spectrometer which employed a cryogenic magnet.^{14,15} A Varian Associates HR-100 spectrometer was used at 32.1 Mc./sec., and at 19.3 Mc./sec. a Varian Associates HR-60 n.m.r. spectrometer was employed. The n.m.r. spectra were obtained in water, deuterium oxide, or acetonitrile solutions. In all cases chemical shifts were obtained with BF_3OEt_2 as standard.

Infrared Spectra. Infrared spectra were obtained as Nujol mulls with a Beckman IR-5 spectrophotometer.

Ultraviolet Spectra. The ultraviolet spectra of the compounds were obtained in acetonitrile solution using a Beckman Model DB or a Carey Model 14 spectrophotometer.

Molecular Weights. Molecular weights were determined in aqueous solution at 25° using a Mechrolab vapor pressure osmometer Model 301A. The osmometer was calibrated using $K_4Fe(CN)_6$ as a standard up to concentrations of 0.30 g.-ion/l. The samples were examined at concentrations between 0.10 and 0.30 g.-ion/l.

Potentiometric Titrations to Determine Equivalent Weights and pK_a Values. (a) Weighed samples (ca. 300 mg.) of the $K_4B_{20}H_{18}$ isomers were dissolved in 25

ml. of distilled water and titrated with a standardized hydrochloric acid solution. The titration was monitored with a Leeds and Northrup pH meter assembly which had been calibrated against standard buffer solutions to within ± 0.02 pH unit over a pH range from 4.00 to 9.18. In all cases the titration curves showed a single end point from which the equivalent weights of the $B_{20}H_{18}^{-4}$ isomers were calculated. In the case of the a^2 isomer, the titration curve showed a pH at half-neutralization of $6.00 \pm 0.05 = pK_a$; complete neutralization corresponded to an equivalent weight of 432. For the ae and e^2 isomers the pH drifted during titration. However, there was a clearly defined end point which corresponded to equivalent weights of 421 for the ae isomer and 420 for the e^2 isomer. Theory requires 427.

(b) Weighed samples (ca. 150 mg.) of the $K_4B_{20}H_{18}$ isomers were dissolved in a minimum quantity of distilled water and passed through a column of Dowex-50 ion-exchange resin in the acid form. The resulting acidic solution was washed out of the column with a further 25 ml. of distilled water, and the whole eluent was titrated against a standard sodium hydroxide solution. The titration was monitored potentiometrically, and in all cases two distinct end points were obtained. On the basis of the equivalent weights calculated in (a) the two end points corresponded to the consumption of 3.0 and 4.0 equiv. of base.

Analyses for Et_3N^+H . Analyses for Et_3N^+H were carried out using a modified Kjeldahl procedure. In a typical experiment 0.122 g. (0.225 mmole) of $(Et_3N^+H)_3B_{20}H_{19}^{-3}$ was added to 20.0 ml. of 0.0546 *N* sodium hydroxide in a conical flask. The solution was boiled down to about two-thirds of its original volume and the triethylamine released was collected in 15 ml. of 0.0544 *N* hydrochloric acid (0.816 mequiv.). Titration of the excess hydrochloric acid against standard base showed that 0.142 mequiv. remained. The estimated Et_3N^+H content of the salt was 0.0688 g. (56.0% Et_3N^+H). Theory for Et_3N^+H in $(Et_3N^+H)_3B_{20}H_{19}^{-3}$ is 56.55%.

Preparation of $(Et_3NH)_2B_{10}H_{10}$. To a solution of 30 g. (0.246 mole) of sublimed decaborane in 300 ml. of xylene under nitrogen was added 90 ml. (0.644 mole) of triethylamine in small portions and with stirring. The temperature was raised to 100° and the reaction mixture stirred under nitrogen for 3 hr., during which time hydrogen gas was evolved. The temperature was then raised to the reflux temperature and the solution stirred and heated for a further 5 hr. The solution was cooled to 0° and filtered. The resulting pale yellow solid was washed five times with 50-ml. portions of 2-propanol which removed most of the yellow impurity. After washing with diethyl ether and drying *in vacuo* for 12 hr., 73.8 g. (0.229 mole) of product was obtained (93% yield). Recrystallization from hot 10% water-ethanol gave a first crop of 62.4 g. of dry white product, m.p. 230–231° dec. Addition of diethyl ether to the mother liquor gave a second crop of 6.85 g. of product, m.p. 231–232° dec. The over-all yield of $(Et_3NH)_2B_{10}H_{10}$ was 87%.

The infrared spectrum showed N-H stretching at 3040 (s) and B-H stretching at 2450 (vs) cm^{-1} . Additional bands appeared at 2747 (w), 2640 (w), 1400 (s), 1270 (w), 1160 (s), 1073 (m), 1057 (m), 1033 (s), 1018

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(s), 917 (vw), 891 (w), 870 (vw), 842 (m), 792 (m), 744 (vw), 722 (vw), and 664 (w) cm^{-1} .

Preparation of $(\text{Et}_3\text{NH})_5\text{B}_{20}\text{H}_{18}\cdot\text{B}_{20}\text{H}_{19}$ (A). To a stirred solution of 32 g. (0.10 mole) of $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{H}_{10}$ in 250 ml. of water cooled to 0° was added dropwise a solution of 105.6 g. (0.20 mole) of $\text{Ce}(\text{HSO}_4)_4$ in 215 ml. of 1 *N* sulfuric acid and 250 ml. of water. Throughout the reaction the solution foamed and the product separated as fine white solid. Foaming could be reduced by carrying out the reaction under reduced pressure. The solid was filtered off, washed with water, and extracted with acetonitrile. The acetonitrile suspension was filtered and ethanol added at room temperature until precipitation started. On cooling, white product separated. After a second recrystallization from acetonitrile-ethanol between room temperature and 0° , 14.6 g. (15 mmoles) of white $(\text{Et}_3\text{NH})_5\text{B}_{20}\text{H}_{18}\cdot\text{B}_{20}\text{H}_{19}$ (yield, 60%) was obtained, m.p. $200\text{--}201^\circ$ dec.

Anal. Calcd. for $(\text{Et}_3\text{NH})_5\text{B}_{20}\text{H}_{18}\cdot\text{B}_{20}\text{H}_{19}$: B, 44.12; C, 36.73; H, 12.01; N, 7.14. Found: B, 45.27; C, 37.17; H, 12.02; N, 6.41.

The infrared spectrum showed N-H stretching at 3086 (s), B-H stretching at 2470 (vs), and possibly B-H-B at 1860 cm^{-1} . Other bands appear at 1400 (m), 1310 (w), 1290 (w), 1176 (m), 1157 (m), 1085 (w), 1059 (w), 1030 (m), 1013 (m), 1000 (m), 968 (w), 909 (vw), 887 (m), 873 (m), 835 (m), 822 (w), 812 (w), 794 (m), 778 (w), 750 (m), 734 (m), 694 (m), and 671 (m) cm^{-1} .

The ultraviolet spectrum showed maxima at 292 and 223 $\text{m}\mu$ with ϵ 5.5×10^3 and 1.7×10^4 , respectively.

Formation of A from $(\text{Et}_3\text{NH})_2\text{B}_{20}\text{H}_{18}$ and $(\text{Et}_3\text{NH})_3\text{B}_{20}\text{H}_{19}$. By recrystallizing 0.279 g. (0.52 mmole) of $(\text{Et}_3\text{NH})_3\text{B}_{20}\text{H}_{19}$ and 0.220 g. (0.50 mmole) of $(\text{Et}_3\text{NH})_2\text{B}_{20}\text{H}_{18}$ from acetonitrile-ethanol, 0.35 g. (0.36 mmole) of A was obtained (yield, 72%), m.p. $199\text{--}200^\circ$. The infrared spectrum of the product was identical in all respects with that of authentic A.

Preparation of Salts of $\text{B}_{20}\text{H}_{18}^{-2}$ and $\text{B}_{20}\text{H}_{19}^{-3}$. Salts of $\text{B}_{20}\text{H}_{18}^{-2}$ and $\text{B}_{20}\text{H}_{19}^{-3}$ were prepared from $\text{B}_{10}\text{H}_{10}^{-2}$ by methods analogous to those described by Chamberland and Muetterties.⁸

Oxidation of $\text{B}_{20}\text{H}_{19}^{-3}$ to $\text{B}_{20}\text{H}_{18}^{-2}$. The oxidation of $\text{B}_{20}\text{H}_{19}^{-3}$ to $\text{B}_{20}\text{H}_{18}^{-2}$ was carried out using methods similar to those of Chamberland and Muetterties⁸ and with similar results.

Preparation of $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ e^2 Isomer. To a solution of 0.53 g. (23.0 g.-atoms) of metallic sodium in 100 ml. of liquid ammonia at -40° was added 2.50 g. (5.7 mmoles) of $(\text{Et}_3\text{NH})_2\text{B}_{20}\text{H}_{18}$ which was just sufficient to discharge the blue color of the sodium. After all the solvent had been evaporated from the reaction vessel there was obtained 2.1 g. of crude product. The crude $\text{Na}_4\text{B}_{20}\text{H}_{18}$ was dissolved in about 50 ml. of ethanol and a saturated ethanolic solution of potassium acetate was added until no further precipitation occurred. The crude $\text{K}_4\text{B}_{20}\text{H}_{18}$ was recrystallized from a warm ethanol-water mixture. There was obtained 2.3 g. (5.4 mmole) of white needles of $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ e^2 isomer (94% yield).

The infrared spectrum indicated H_2O at 3509 (m) and 1645 (m), and B-H at 2440 (vs) cm^{-1} . Additional bands appeared at 1605 (m), 1070 (m), 1036 (s),

975 (vw), 919 (vw), 722 (w), 690 (w), and 672 (m) cm^{-1} .

The three strongest lines in the X-ray powder pattern using Cu $K\alpha$ radiation with a Ni filter had d values of 3.82, 8.12, and 4.06 \AA .

Anal. Calcd. for $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$: K, 36.63; B, 50.68; H (undried), 5.19; H (dried), 4.25; H_2O , 8.44; equiv. wt., 427; mol. wt., 427. Found: K, 36.61; B, 50.09; H (undried), 5.35; H (dried), 4.43; H_2O , 8.1; equiv. wt., 420; mol. wt., 419.

Preparation of $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ ae Isomer. To a saturated solution of 4.0 g. (9.4 mmoles) of $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ e^2 isomer in water at 0° was added 21.6 ml. of ice-cold 1.0 *N* trifluoroacetic acid (21.6 mmoles). The solution was allowed to react for 20 sec. at 0° and then quenched by the addition of 44 ml. of 1 *N* aqueous potassium hydroxide. Ethanol was added until the solution was turbid at room temperature. On cooling 1.55 g. (3.6 mmoles) of $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ a^2 isomer was precipitated and removed by filtration. Addition of more ethanol and diethyl ether brought about the crystallization of $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ ae isomer. There was isolated 2.38 g. of product at this stage. After further recrystallization from a water-ethanol mixture between 25 and 0° , 2.16 g. (5.1 mmoles) of pure product was obtained (over-all yield, 54.0%).

Anal. Calcd. for $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$: K, 36.63; B, 50.68; H (undried), 5.19; H (dried), 4.25; H_2O , 8.44; equiv. wt., 427; mol. wt., 427. Found: K, 36.16; B, 49.67; H (undried), 5.16; H (dried), 4.46; H_2O , 7.60; equiv. wt., 421 (acid titration); mol. wt., 412.

The infrared spectrum showed bands characteristic of water of crystallization at 3540 (m) and 1610 (s), and B-H stretching at 2415 (vs) cm^{-1} ; further bands occurred at 1050 (sh) 1030 (s), 950 (w), 778 (w), 744 (m), 725 (m), and 687 (m) cm^{-1} . The three strongest lines in the X-ray powder pattern using Cu $K\alpha$ radiation with a Ni filter had d values of 3.82, 10.65, and 5.37 \AA .

Preparation of $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ a^2 Isomer. (a) To a solution of 2.0 g. (36 mmoles) of potassium hydroxide in 12 ml. of water was added 2.0 g. (2.0 mmoles) of $(\text{Et}_3\text{NH})_5\text{B}_{20}\text{H}_{18}\cdot\text{B}_{20}\text{H}_{19}$ (A). Liberated triethylamine was evaporated from the solution with a stream of nitrogen. During the reaction $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ a^2 isomer precipitated. The precipitate was collected and recrystallized from a water-ethanol mixture to give 0.80 g. (1.87 mmoles) of white $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$ a^2 isomer (yield, 92%). The $\text{K}_4\text{B}_{20}\text{H}_{17}\text{OH}$ in the filtrate could be recovered in almost quantitative yield by the further addition of ethanol.

The infrared spectrum of the a^2 isomer showed B-H stretching at 2460 (vs), O-H stretching at 3560 (s) and 3500 (s), and OH bending at 1610 (s) cm^{-1} ; other bands occur at 1026 (s), 1002 (m), 839 (vw), 797 (w), 752 (w), 722 (w), 701 (vw), and 687 (vw) cm^{-1} .

The three strongest lines in the X-ray powder pattern obtained using Cu $K\alpha$ radiation with a Ni filter had d values of 5.25, 4.27, and 6.71 \AA .

Anal. Calcd. for $\text{K}_4\text{B}_{20}\text{H}_{18}\cdot 2\text{H}_2\text{O}$: K, 36.63; B, 50.68; H_2O , 8.44; equiv. wt., 427; mol. wt., 427. Found: K, 32.73; B, 50.50; H_2O , 8.30; equiv. wt., 432; mol. wt., 435.

(b) A solution of 1.00 g. (2.34 mmoles) of $K_4B_{20}H_{18} \cdot 2H_2O$ (e^2 or ae isomer) in 20 ml. of water was refluxed for 22 hr. Addition of ethanol and cooling to 0° precipitated 0.94 g. (2.20 mmoles) of $K_4B_{20}H_{18} \cdot 2H_2O$ a^2 isomer (94% yield).

(c) A more rapid conversion of $K_4B_{20}H_{18} \cdot 2H_2O$ (ae or e^2 isomer) to a^2 isomer was obtained as follows. A solution of 500 mg. (1.17 mmoles) of the $K_4B_{20}H_{18} \cdot 2H_2O$ (ae or e^2) isomer in 2.5 ml. of 1 *N* hydrochloric acid was warmed to 70° for 5 min.; on adjusting the solution to pH 10 by addition of solid potassium hydroxide and cooling to 0° , 410 mg. (0.96 mmole) of $K_4B_{20}H_{18} \cdot 2H_2O$ a^2 isomer (82% yield) was obtained. Addition of a little ethanol to the filtrate precipitated an additional 50 mg. of the a^2 isomer giving a total yield of 92%.

(d) $K_4B_{20}H_{18} \cdot 2H_2O$ a^2 isomer was also obtained from the $B_{20}H_{19}^{-3}$ ion. In a typical experiment 500 mg. (0.92 mmole) of $(Et_3NH)_3B_{20}H_{19}$ was treated with a solution of 500 mg. (8.9 mmoles) of potassium hydroxide in 2 ml. of H_2O at room temperature. On adding ethanol and cooling to 0° there was obtained 370 mg. (0.87 mmole) of $K_4B_{20}H_{18} \cdot 2H_2O$ a^2 isomer (95% yield).

Preparation of the Stable $(Me_4N)_3B_{20}H_{19}$ (B). To a solution of 100 mg. (0.234 mmole) of $K_4B_{20}H_{18} \cdot 2H_2O$ (e^2 , ae , or a^2 isomer) in 5 ml. of 1 *N* hydrochloric acid at room temperature was added a 25% solution of tetramethylammonium chloride in water until no further precipitation occurred. The product was separated by filtration and recrystallized from hot water. There was obtained 96 mg. (0.210 mmole) of $(Me_4N)_3B_{20}H_{19}$ (B) (89% yield) whose properties were identical in every way with those of the material obtained by addition of tetramethylammonium chloride to A.

Preparation of the Less Stable $(Me_4N)_3B_{20}H_{19}$. To a saturated solution of 100 mg. (1.9 mmoles) of $(Me_4N)_4B_{20}H_{18}$ e^2 isomer, in water at 0° , was added an ice-cold 1 *N* solution of hydrochloric acid until there was no further precipitation. The resulting white solid was separated by filtration and washed with absolute ethanol, followed by diethyl ether. After drying *in vacuo* there was obtained 80 mg. (1.7 mmoles, 90% yield) of white $(Me_4N)_3B_{20}H_{19}$.

The infrared spectrum showed B-H stretching at 2440 cm.^{-1} (vs) and bands characteristic of OH at 3570 (s) and 1620 cm.^{-1} . Other bands appeared at 2060 (m), 1900 (m), 1750 (m), 1640 (m), 1410 (w), 1280 (s), 1150 (w), 1070 (m), 1000 (vs), 950 (vs), 806 (m), 774 (m), 745 (m), 722 (w), 705 (m), and 660 cm.^{-1} .

Attempted recrystallization of 30 mg. (0.64 mmole) of this salt from a water-ethanol solution gave 22 mg. (0.47 mmole) of $(Me_4N)_3B_{20}H_{19}$ (B) (75% yield) which was identical with the product obtained by the addition of tetramethylammonium chloride to A.

Preparation of Perdeuterated Ions. $(Et_3ND)_2B_{10}D_{10}$ was prepared from $(Et_3NH)_2B_{10}H_{10}$ by repeated exchange in acidic deuterium oxide solution using the method of Muetterties, *et al.*¹⁶

$(Et_3ND)_2B_{20}D_{18}$ was prepared from $(Et_3ND)_2B_{10}D_{10}$ using the method reported above for $(Et_3NH)_2B_{20}H_{18}$ except that deuterium oxide was used as solvent and anhydrous ferric chloride was employed as the oxidizing agent.

$K_4B_{20}D_{18}$ e^2 isomer was prepared by reduction of $(Et_3ND)_2B_{20}D_{18}$ using sodium in liquid ammonia as described above. The product was recrystallized from deuterium oxide using absolute ethanol.

$K_3B_{20}D_{19}$ was prepared in solution by adding deuterium chloride to a solution of $K_4B_{20}D_{18}$ e^2 isomer.

$K_4B_{20}D_{18}$ a^2 isomer was prepared from a^2 $K_4B_{20}H_{18}$ by repeated exchange in acidic deuterium oxide. The rate of exchange appeared to be faster for $B_{20}H_{18}^{-4}$ than for $B_{10}H_{10}^{-2}$.

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