Ionic Organoboranes. IV. Preparation and Properties of the $C_7H_6B_{10}H_9^-$ and $C_7H_6B_{12}H_{11}^-$ Hemiousenide Ions[1,2]

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Abstract: Reaction of 2 moles of tropenylium ion with $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ yields tropenyliumyl-*closo*-nonahydrodecaborate(1−) or tropenyliumyl-*closo*-undecahydrododecaborate(1−) ion and cycloheptatriene; these highly colored anions form salts with considerable chemical and thermal stability. Infrared, electronic, and ^1H and ^{11}B nmr spectra, Z-value correlations, and polarographic reduction potentials show that in both ions a cationic carbocyclic ring is attached to the boron cage with a C–B bond, and that significant cage-to-ring electron donation occurs in both ground and excited states.

A number of monoanions and neutral molecules have been prepared by the substitution of one or two cationic groups such as diazonium,[3a] carbonyl,[3a–c] ammonium,[3a,d–h] sulfonium,[3a,h–k] phosphonium,[3h] arsonium,[3h] or phenyliodonium[3l] for hydrogen on the *closo*-decahydrodecaborate(2−) and *closo*-dodecahydrodecaborate(2−) ions. Many of these substances are of considerable synthetic and theoretical interest; however, none of these species offers significant opportunity for catenation. We wish to report on the preparation and properties of the tropenyliumyl-*closo*-nonahydrodecaborate(1−)[4] ion (**1**, Figure 1) and the tropenyliumyl-*closo*-undecahydrodecaborate(1−) ion (**2**, Figure 1), the parent members of a new family of highly stable, fully aromatic ionic organoboranes.

If we consider a type species in which one or two fully aromatic, carbocyclic cationic rings are attached to a *closo*-borane anion or *closo*-carborane polyhedron, it is possible to formulate over 200 new compounds at this time. For the sake of simplicity we suggest the following nomenclature system for compounds of this type: (1) the parent trivial name *ousene* (Greek *ous*, ear) is assigned to a $B_nH_n^{2-}$ anion substituted with two fully aromatic, carbocyclic, cationic rings; (2) the numbers of carbons in the rings and borons in the cage are given in brackets before the name, with the boron number always last; (3) superscript numbers on the boron number are used to designate the positions of the rings, if known; (4) the prefix *hemi*- is used for a cage with one ring; (5) the endings *-ium* and *-ide* are used for cations and anions, respectively; and (6) carborane derivatives are named by incorporating *carba*- or *dicarba*- into the name; the positions of the carbons are indicated by numbers preceding the *carba*- or *dicarba*-. Examples of this nomenclature applied to the known[1,6,7] ousene-type compounds are given in Figure 1.

Results

The formation of the hemiousenide ions is believed to occur by electrophilic attack on the $B_nH_n^{2-}$ anion[8] by tropenylium ion[10] followed by hydride transfer to tropenylium ion[12] from the 7-boranylcycloheptatriene so formed; at least 1 mole of cycloheptatriene per mole of hemiousenide ion can be isolated from the preparative reactions. The lowered reactivity of $B_{12}H_{12}^{2-}$ ion with tropenylium ion (see Experimental Section) relative to that of $B_{10}H_{10}^{2-}$ is in accord with its lower nucleophilicity.[9b] When tropenylium ion reacts with a $B_nH_n^{2-}$ anion, a confusing welter of substitutions and hydride transfers can occur, for example

$$C_7H_7^+ + B_{10}H_{10}^{2-} = \underset{\mathbf{5}}{C_7H_7\text{–}B_{10}H_9^{2-}} + H^+ \tag{1}$$

$$C_7H_7^+ + C_7H_7\text{–}B_{10}H_9^{2-} = C_7H_8 + \underset{\mathbf{1}}{C_7H_6\text{–}B_{10}H_9^-} \tag{2}$$

$$C_7H_6\text{–}B_{10}H_9^- + C_7H_7^+ = \underset{\mathbf{6}}{C_7H_6\text{–}B_{10}H_8\text{–}C_7H_7^-} + H^+ \tag{3}$$

$$C_7H_6\text{–}B_{10}H_8\text{–}C_7H_7^- + C_7H_7^+ = \underset{\mathbf{3}}{C_7H_6\text{–}B_{10}H_8\text{–}C_7H_6} + C_7H_8 \tag{4}$$

$$C_7H_7\text{–}B_{10}H_9^{2-} + C_7H_7^+ = \underset{\mathbf{7}}{C_7H_7\text{–}B_{10}H_8\text{–}C_7H_7^{2-}} + H^+ \tag{5}$$

$$C_7H_7\text{–}B_{10}H_8\text{–}C_7H_7^{2-} + 2C_7H_7^+ = \underset{\mathbf{3'}}{C_7H_6\text{–}B_{10}H_8\text{–}C_7H_6} + 2C_7H_8 \tag{6}$$

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[1] Paper III: K. M. Harmon, A. B. Harmon, and B. C. Thompson, *J. Am. Chem. Soc.*, **89**, 5309 (1967).

[2] Work supported by the National Science Foundation (GP-5444) and the Petroleum Research Fund (443-A).

[3] (a) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964); (b) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *Inorg. Chem.*, 4, 288 (1965); (c) W. H. Knoth, J. C. Sauer, J. H. Balthis, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **89**, 4842 (1967); (d) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963); (e) W. R. Hertler and M. S. Raasch, *ibid.*, **86**, 3661 (1964); (f) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *ibid.*, **86**, 5434 (1964); (g) W. R. Hertler, *Inorg. Chem.*, **3**, 1195 (1964); (h) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **3**, 1456 (1964); (i) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *ibid.*, 4, 280 (1965); (j) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962); (k) W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *ibid.*, **86**, 3973 (1964); (l) H. C. Miller, W. R. Hertler, E. L. Muetterties, W. H. Knoth, and N. E. Miller, *Inorg. Chem.*, 4, 1216 (1965).

[4] The tropenylium–tropenyliumyl nomenclature has been discussed.[1,5]

[5] H. J. Dauben, Jr., and D. F. Rhoades, *J. Am. Chem. Soc.*, **89**, 6764 (1967).

[6] K. M. Harmon, A. B. Harmon, and A. A. MacDonald, *ibid.*, **86**, 5036 (1964).

[7] A. B. Harmon and K. M. Harmon, *ibid.*, **88**, 4093 (1966).

[8] Electrophilic substitution of hydrogen on $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ by a variety of reagents has been demonstrated.[3a,b,e,g,i–k,9]

[9] (a) M. F. Hawthorne and F. P. Olsen, *J. Am. Chem. Soc.*, **86**, 4219 (1964); (b) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

[10] Tropenylium ion has been shown[11] to act as an electrophile toward reactive aromatic compounds.

[11] For example, see R. van Helden, A. P. ter Borg, and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 599 (1962).

[12] Hydride transfer to tropenylium ion by cycloheptatrienes with electron-donating substituents in the 7 position has been demonstrated.[13]

[13] (a) T. Ikemi, T. Nozoe, and H. Sugiyama, *Chem. Ind.* (London), 932 (1960); (b) A. P. ter Borg, R. van Hilden, A. F. Bickel, W. Renold, and A. S. Dreiding, *Helv. Chim. Acta*, 43, 457 (1960); (c) M. E. Vol'pin, Z. N. Parnes, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 959 (1960); (d) K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961).

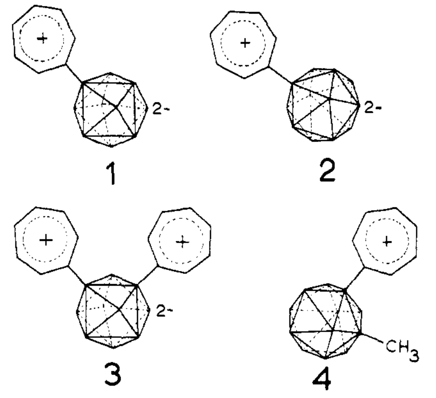

Figure 1. Structures of ousene-type compounds: **1**, [7.10^2]hemiousenide ion (2-tropenyliumyl-*closo*-nonahydrodecaborate(1−)ion); **2**, [7.12]hemiousenide ion (tropenyliumyl-*closo*-undecahydrododecaborate(1−) ion; **3**, [7.7.10^{2,3}]ousene (2,3-bistropenyliumyl-*closo*-octahydrodecaborate(0), representative, actual substitution positions not known); **4**, 1-methyl[7.12^2]-1,2-dicarbahemiousenium ion (1-methyl-2-tropenyliumyl-1,2-dicarba-*closo*-dodecaborane(12) cation).

Preliminary studies indicate that (1) is fast with respect to (2), that (5) is fast with respect to (3) (*i.e.*, the dianion **5** is a better nucleophile than **1**), and that (3) followed by (4) probably gives a material that is a position isomer of the product of (5) followed by (6) (*i.e.*, the position of electrophilic attack on **5** is not the same as it is on **1**). Detailed kinetic analyses of this system are under investigation.

The preparative directions given herein represent a maximization of yield by coordinated adjustment of all reaction parameters. Water is the solvent of choice for the synthesis of the hemiousenide ions, since they are soluble in it and ousene and polymer by-products are completely insoluble. The reactions are favored by high dilution and slow addition of tropenylium ion *to* borane anion. Tropenylium salts of good quality should be used, and work-up is improved if cycloheptatriene is removed by a layer of hydrocarbon solvent during the reaction.

When concentrated solutions of the reactants are rapidly mixed, the major product is an amorphous colored solid containing several species including carbonaceous polymers; some of this water-insoluble material forms in all preparative reactions. Continuous extraction of the solid product from the reaction of tropenylium bromide and $B_{10}H_{10}{}^{2-}$ with acetonitrile leaves a uniform maroon powder; the infrared and electronic spectra of this powder are consonant with formulation as a [7.7.10]ousene. Reacton of [7.10^2]-hemiousenide ion with 2 moles of tropenylium ion yields 1 mole of cycloheptatriene and a maroon crystalline material with spectral properties essentially identical with the powder described above. Characterization of these compounds is in progress.

The cesium and tetraalkylammonium salts of the [7.10^2]- and [7.12]hemiousenide ions are highly crystalline materials which are indefinitely air stable and nonhygroscopic. Neither cesium salt shows any change when heated in air to 360°; the tetrabutylammonium salts melt sharply below this temperature without decomposition. The cesium hemiousenides are sparingly soluble in water and in a variety of polar solvents; the tetrabutylammonium salts are almost completely insoluble in water but more soluble in organic solvents. Only dimethylformamide and nitromethane dissolve sufficient quantities of any of the salts to permit single sweep nmr analyses.[14] The anions are stable in water or in aqueous acid but are irreversibly converted to new species in basic solution.

The nature of these new species is not known. Tropenylium ion can be smoothly and reversibly titrated with dilute base[15] to a covalent alcohol, and certain substituted tropenylium ions react with water or base to yield tropone;[16] however, neither process appears to operate here. The titration of the [7.10^2]hemiousenide ion with base is very sluggish and is incompletely reversible with acid, and if the ion is allowed to stand for several days in dilute hydroxide solution the spectrum of the ion is replaced by new absorptions at 239 nm (ϵ 23,000) and 333 (ϵ 6180) nm, but not by the spectrum of tropone. Addition of acid does not destroy this new absorbing species. The spectrum is suggestive of a substituted tropenylium ion[16] in which either the ring is a poorer electron acceptor or the substituent is a poorer electron donor than is the case with [7.10^2]-hemiousenide ion.

Experimental Section

Methylene chloride, cyclohexane, acetonitrile, and ether were all as previously described;[17,18] *n*-decane was Phillips pure grade untreated. Matheson Coleman and Bell Spectroquality Reagent acetonitrile was used where required. Eastman Kodak White Label 1,2-dichloroethane, tetrabutylammonium bromide, and tetramethylammonium iodide, Alfa Inorganics, Inc., cesium bromide, and Baker and Adamson reagent potassium chloride were used as supplied.

Perkin-Elmer 621 and Cary Model 13 spectrophotometers were used for infrared and electronic spectra; a Varian A-60 nmr spectrophotometer and a modified Varian instrument operating at 12.8 MHz were used for ^1H and ^{11}B nmr spectra, respectively.[19] Melting points were made with a Fisher-Johns block and are corrected. A Sargent XXI polarograph was used for polarograms and as a source of constant potential in the millicoulometric experiment.

Hydronium [7.10^2]Hemiousenide. A. Preparation. A solution of $[(C_2H_5)_3NH]_2B_{10}H_{10}$[20] (1.08 g, 3.34 mmol) in water (25 ml) was converted to the acid form over Dowex 50W-X8 resin and then brought to a volume of 3.7 l. with water. This solution was covered with cyclohexane (300 ml) and stirred vigorously while a solution of tropenylium bromide[16,17] (2.30 g, 13.5 mmol) in water (1 l.) was added dropwise over 4 hr. Stirring was continued overnight; then the aqueous layer was extracted with fresh cyclohexane (two 100-ml portions), filtered through diatomaceous earth to remove a suspension of purple solids, and collected as a clear, red-orange solution which contained a 38% yield[21] of hydronium [7.10^2]hemiousenide (1.28 mmol). An aliquot of this filtrate was concentrated to a red, gummy oil with an infrared spectrum identical with that of cesium [7.10^2]hemiousenide with additional bands of hydronium ion. The cyclohexane layer was shown by spectral analysis[17] to contain a yield of 46% cycloheptatriene (1.54 mmol).

B. Determination of Cycloheptatriene Yield Ratio. Tropenylium bromide (0.0060 g, 0.035 mmol) in water (1 ml) and $(H_3O)_2$-

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(14) The salts are reasonably soluble in dimethyl sulfoxide but are slowly destroyed, apparently by nucleophilic attack on the cationic ring.

(15) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(16) (a) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957); (b) H. J. Dauben, Jr., and K. M. Harmon, unpublished work in Ph.D. thesis of K. M. H., University of Washington, 1958; *Dissertation Abstr.*, **19**, 1563 (1959).

(17) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Am. Chem. Soc.*, **84**, 3349 (1962).

(18) K. M. Harmon, A. B. Harmon, and F. E. Cummings, *ibid.*, **86**, 5511 (1964).

(19) We wish to thank Robert E. Williams for ^{11}B nmr spectra.

(20) M. F. Hawthorne and R. L. Pilling, *Inorg. Syn.*, **9**, 16 (1967).

(21) The yield was determined by spectral analysis at 439 nm (*vide infra*).

$B_{10}H_{10}$ (0.044 mmol) in water (20 ml) under cyclohexane (25 ml) were allowed to react until the first trace of solid formed; the water layer was immediately separated. Spectral analysis[17,21] showed the water to contain 10.5% [7.10^2]hemiousenide ion (3.7 μmol) and the cyclohexane to contain 10.5% cycloheptatriene (3.7 μmol).

Cesium [7.10^2]Hemiousenide. Hydronium [7.10^2]hemiousenide (1.16 mmol) in water (4.8 l.) was concentrated *in vacuo* at 40° to 200 ml and filtered;[22] then cesium bromide (10 g) in water (15 ml) was added dropwise with swirling to the concentrate. After 12 hr the precipitate was filtered, washed quickly with water, and dried *in vacuo* to yield 94% cesium [7.10^2]hemiousenide (0.371 g, 1.09 mmol) as thin, red-orange plates,[23] no melting point below 360°; electronic spectrum (water): λ_{max} 217 nm (ϵ 39,400), 262 (10,900), and 439 (13,600); recrystallized when necessary by solution in *minimal* acetonitrile, followed by slow addition of methylene chloride.

Anal. Calcd for $C_7H_{15}B_{10}Cs$: C, 24.70; H, 4.44; B, 31.79. Found:[25] C, 24.39; H, 4.54; B, 31.95.

Tetrabutylammonium [7.10]Hemiousenide. Tetrabutylammonium bromide (1.8 g) in water (150 ml) was added all at once to a solution of hydronium [7.10^2]hemiousenide (1.28 mmol) in water (4.5 l.); after 12 hr the precipitate was separated by filtration to afford 95% tetrabutylammonium [7.10^2]hemiousenide (0.549 g, 1.22 mmol), purple needles (red by transmitted light, iridescent green by reflected light) from ethanol; mp 200–201.5°; electronic spectrum (acetonitrile): λ_{max} 264 (ϵ 8300) and 512 (ϵ 14,300) nm.

Anal. Calcd for $C_{23}H_{51}B_{10}N$: C, 61.40; H, 11.43; B, 24.05. Found:[25] C, 60.76; H, 11.53; B, 23.96.

Tetramethylammonium [7.10^2]Hemiousenide. A few milliliters of a saturated aqueous solution of tetramethylammonium iodide was added to a filtered concentrate of hydronium [7.10^2]hemiousenide (0.13 mmol) in water (50 ml); this precipitated an amorphous red-orange powder which was dried *in vacuo* to give 20 mg of crude product. This was recrystallized twice from ethanol to yield brilliant red crystals of tetramethylammonium [7.10^2]hemiousenide; no mp below 300°.

Anal. Calcd for $C_{11}H_{27}B_{10}N$: C, 46.92; H, 9.67; B, 38.43. Found:[25] C, 46.86; H, 10.12; B, 37.56.

Hydronium [7.12]Hemiousenide. $[(C_2H_5)_3NH]_2B_{12}H_{12}$[26] (0.27 g, 0.80 mmol) was converted to its acid form by ion exchange in acetonitrile (50 ml) with Dowex 50W-X8 resin prepared with aqueous hydrochloric acid and then rinsed with acetonitrile; the effluent was mixed with water (50 ml) and evaporated to an entirely aqueous solution of $(H_3O)_2B_{12}H_{12}$ which was then diluted to 1500 ml, covered with *n*-decane (200 ml), and brought to reflux. Tropenylium bromide (0.54 g, 3.18 mmol) in water (500 ml) was added dropwise over 5 hr, and reflux was maintained for 2 hr. The aqueous layer was extracted with *n*-decane (2 × 100 ml), filtered through diatomaceous earth to remove a suspension of brown solids, and collected as a clear, pale yellow solution containing an 86% yield[29] of hydronium [7.12]hemiousenide (0.69 mmol). Spectral analysis[17] of the *n*-decane layer showed 131% yield of cycloheptatriene (1.05 mmol).

Cesium [7.12]Hemiousenide. Hydronium [7.12]hemiousenide (1.14 mmol) in water (2 l.) was concentrated *in vacuo* at 50–55° to 330 ml and filtered from a white solid (not characterized). A clear solution of cesium bromide (12 g) in water (15 ml) was rapidly dripped into the yellow concentrate; after several hours the precipitate was collected by filtration to afford 89% cesium [7.12]hemiousenide (0.367 g, 1.01 mmol) as yellow-orange needles, recrystallized from *minimal* acetonitrile by slow addition of methylene chloride as orange needles; no melting point below 360°; electronic spectra (water): λ_{max} 215 nm (ϵ 33,800), 261.5 (13,000), and 349 (10,300); (acetonitrile): λ_{max} 215.5 nm (ϵ 39,700), 266.5 (10,900), and 384 (11,700).

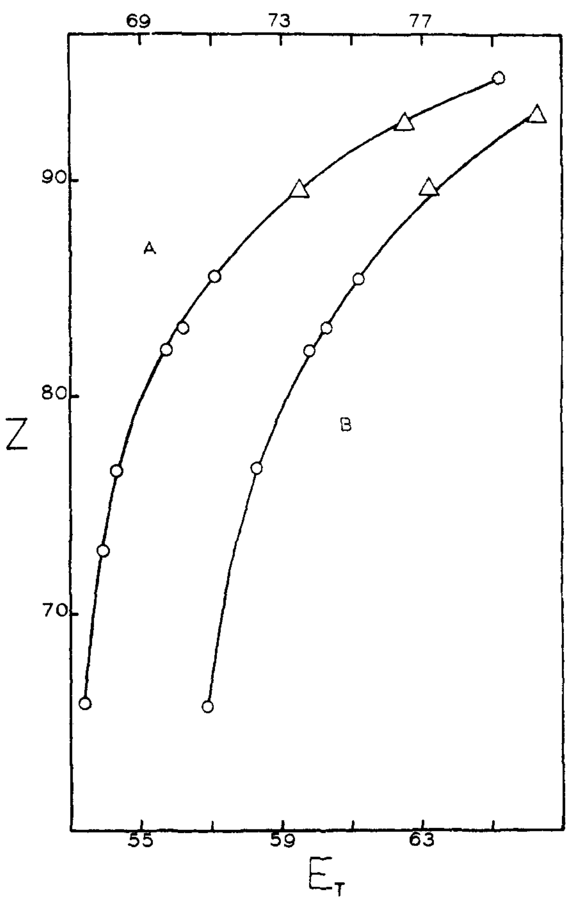

Figure 2. Plots of Kosower Z values against E_t (kcal/mol) for solutions of hemiousenide ions in water-acetone mixtures: (A) [7.10^2]-hemiousenide ion (lower scale); (B) [7.12]hemiousenide ion (upper scale). For Δ points Z calculated from Y values.[30]

Anal. Calcd for $C_7H_{17}B_{12}Cs$: C, 23.10; H, 4.71; B, 35.68. Found:[25] C, 23.23; H, 4.66; B, 35.66.

Tetrabutylammonium [7.12]Hemiousenide. Tetrabutylammonium bromide (10 g) in concentrated aqueous solution was added all at once with swirling to a solution of hydronium [7.12]hemiousenide (0.70 mmol) in water (2 l.); after 12 hr the precipitate was separated by filtration to afford 70% tetrabutylammonium [7.12]hemiousenide (0.232 g, 0.49 mmol) as a light yellow powder, gold plates from 1,2-dichloroethane by slow addition of ether; mp 188.5–189.5°.

Anal. Calcd for $C_{23}H_{53}B_{12}N$: C, 58.33; H, 11.29; B, 27.42. Found:[25] C, 58.57; H, 11.49; B, 27.39.

Z-Value Determinations.[30] Cesium [7.10^2]hemiousenide and cesium [7.12]hemiousenide stock solutions were prepared in water; binary solutions were made with acetone (Baker and Adamson reagent grade dried over Linde 4A molecular sieves) and absolute ethanol. Transfers were by gas-tight syringe. Spectra were recorded at 25° in stoppered silica cells; results are shown in Figure 2.

Polarographic Studies. A. Reductions. Solutions in 1 *M* KCl of cesium [7.10^2]- and [7.12]hemiousenide were reduced irreversibly at the dme (Table I) in a standard H-cell with sce reference.

B. Millicoulometric Determination of *n* for [7.10^2]Hemiousenide Ion. The method was that of DeVries and Kroon[31] with cells modified so that mercury entered the reservoir from a standpipe of such a height and small diameter that the solutions being reduced remained undisturbed; excess mercury drained from the reservoir through an outlet lower than the standpipe. Anodes were prepared of silver–silver chloride;[32] dropping mercury electrodes were

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(22) During the concentration an uncharacterized white solid is formed (no melting point below 300°; does not burn or char; infrared absorption only at 1240 cm^{-1} (vw); ultraviolet absorption undistinguishing (cyclohexane); soluble in benzene, insoluble in polar organic or in inorganic solvents). However, spectral analysis before and after concentration showed no change in the amount of [7.10^2]hemiousenide.

(23) Sometimes as light red needles. Needles and plates appear to to have an identical unit cell[24] and have identical infrared and electronic spectra.

(24) W. G. Sly and D. M. Barnhart, private communication.

(25) Analysis by Schwarzkopf Microanalytical Laboratory.

(26) Prepared in one sequence from diborane[27] and sodium borohydride through the triborohydride intermediate by the method of Schaeffer.[28]

(27) H. C. Brown and P. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).

(28) I. A. Ellis, D. F. Gaines, and R. Schaeffer, *ibid.*, **85**, 3885 (1963).

(29) Yield was determined by spectral analysis at 349 nm (*vide infra*).

(30) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(31) T. DeVries and J. L. Kroon, *ibid.*, **75**, 2484 (1953).

(32) A. S. Brown, *ibid.*, **56**, 646 (1934).

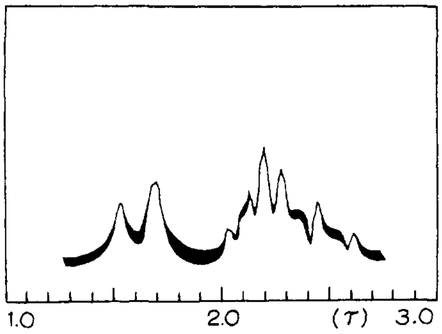

Figure 3. Nmr spectrum of ring protons of [7.10²]hemiousenide ion in nitromethane (shaded line width measures noise level).

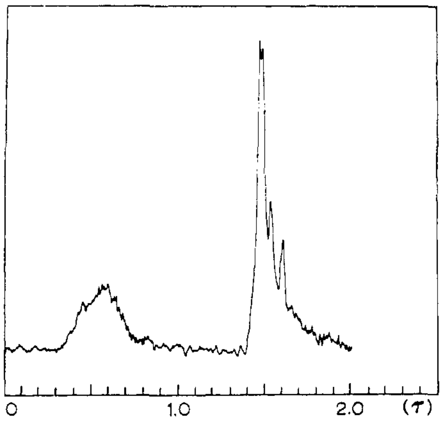

Figure 4. Nmr spectrum of ring protons of [7.12]hemiousenide ion in nitromethane.

drawn from capillary tubing (0.02 mm i.d.). Solutions were protected from oxygen with a slow flow of nitrogen, and from evaporation by passing the nitrogen through 1 *M* KCl and by covering the cells with glass wool. Aliquots (5 ml) of 1 *M* KCl solutions of cadmium chloride (1.11×10^{-3} *M*)[33] and of cesium [7.10²]hemiousenide (1.57 m*M*), each containing gelatin suppressor (1 drop of 1%), were deoxygenated by nitrogen passed through 1 *M* KCl; 0.2 ml of each was transferred by a gas-tight syringe to its millicoulometric cell.

Table I. Polarographic Reductions of Cesium Hemiousenides at 25° in 1 *N* KCl

Quantity	$C_7H_6B_{10}H_9^-$	$C_7H_6B_{12}H_{11}^-$
$E_{1/2}$, V	−0.792	−0.715
i_d, μA	7.44	8.88
n, electron	0.980[a]	0.975[b]
D, 10^6 cm²/sec	20.1[c]	19.0[c]
C, m*M*	1.57	1.93
m, mg/sec	1.54	1.54
t, sec	4.83	4.92

[a] From millicoulometric determination. [b] Calculated using *D* = 20.1. [c] Calculated using *n* = 1.00.

Initial values of i_d and of *t* for each solution were determined in these cells by individual polarograms using silver–silver chloride anodes, then the cells were connected in series, and a constant potential (−1.5 V) was applied for 140 min. Individual polarograms were then repeated for final values of i_d and *t* (Table II).

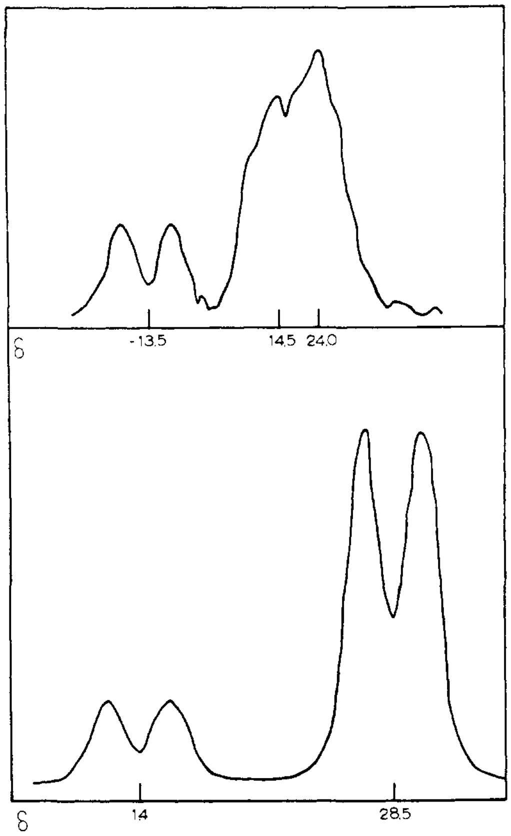

Figure 5. ¹¹B nmr spectra of [7,10²]hemiousenide ion (top) and $B_{10}H_{10}^{2-}$ (bottom).

Nuclear Magnetic Resonance Spectra. Hemiousenide salts are difficultly soluble in acetonitrile; ring proton signals can be observed in this solvent, but our previously reported values[7] require revision.[35] Satisfactory spectra were obtained of the tetrabutylammonium hemiousenide salts in nitromethane (Figures 3 and 4). The spectra were integrated against the eight α-methylene protons of the tetrabutylammonium cation, which are well separated from the remaining alkyl protons. Since the upfield ¹³C satellite of nitromethane falls within the α-methylene signal, the downfield satellite was integrated and this amount subtracted from the whole integration of the α-methylene region.

Table II. Millicoulometric Reduction of Cesium [7.10²]Hemiousenide

Solution	i_d,μA	*t*, sec
$CdCl_2$ (initial)	4.92	4.00
$CdCl_2$ (final)	4.27	3.96
$CsC_7H_6B_{10}H_9$ (initial)	4.28	5.02
$CsC_7H_6B_{10}H_9$ (final)	3.44	3.90

The ¹H nmr spectrum of [7,10²]hemiousenide ion (τ, CH_3NO_2) showed the following: doublet 1.53, 1.69 (2 H); heptet 2.03, 2.13, 2.19, 2.28, 2.35, 2.45, 2.61 (4 H). The ¹H nmr spectrum of [7.12]-hemiousenide ion (τ, CH_3NO_2) showed: broad singlet 0.59 (2 H); quartet 1.47, 1.48, 1.55, 1.62 (4 H).

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[33] The cadmium ion concentration in 1 *M* KCl solution made with $CdCl_2(H_2O)_{2.5}$ (Baker and Adamson reagent grade) was determined polarographically (dme *vs.* sce) on an aliquot diluted to 0.1 *M* in KCl.[34]

[34] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd ed, Interscience Publishers, New York, N. Y., 1952, p 504.

[35] The solubility of tetrabutylammonium [7.12]hemiousenide in acetonitrile is too low to allow observation of the low-field broad singlet which is observed in nitromethane; the upfield multiplet which was observed is very similar to the resonance of chlorotropenylium and appeared on graphical integration to give a similar 4:2 pattern. The ring proton spectrum of tetrabutylammonium [7.10²]hemiousenide is resolved in acetonitrile but the reported values are in error; the correct values are (τ, CH_3CN): doublet 1.51, 1.66 (2 H); multiplet 2.07–2.78 (4 H). The conclusions drawn from the reported spectra[7] are not affected by these corrections.

Table III. Electronic Spectra of Hemiousenide Ions in Several Solvents

Ion	Solvent	Spectrum, λ_{max}, nm (ϵ)		
[7.10]	96% H_2SO_4	215 (39,400)	261 (10,700)	373 (6500)[a]
[7.10]	12 *N* HCl	217 (. . .[b])	262	427
[7.10]	H_2O	217 (39,400)	262 (10,900)	439 (13,600)
[7.10]	50% CH_3CN	221 (. . .[b])	263	485
[7.10]	CH_3CN	220 (16,500)	264 (8,300)	512 (14,300)
[7.10]	$(CH_3)_2CO$	. . .[c]	. . .[c]	536 (15,500)
[7.12]	96% H_2SO_4	213 (38,700)	258 (14,100)	332 (10,100)[a]
[7.12]	H_2O	215 (33,800)	261 (13,000)	349 (10,300)
[7.12]	CH_3CN	215 (39,700)	266 (10,900)	384 (11,700)

[a] Taken after 5 min; spectra change slowly with time. [b] Qualitative. [c] Solvent interferes.

Satisfactory ^{11}B nmr spectra were obtained in acetonitrile:[19] ^{11}B nmr spectrum (Figure 5) of [7.10^2]hemiousenide ion (δ, CH_3CN),[36] doublet -13.5 (2 B; J = 130 Hz), structured doublet 14.5, 24.0 (8 B); ^{11}B nmr spectrum of [7.12]hemiousenide ion (δ, CH_3CN),[36] doublet 13.7 (J = 184 Hz).

Discussion

The formulation of a hemiousenide ion as a cationic ring attached by a carbon–boron bond to an anionic borane cage is supported by a variety of physical measurements; these also serve to rule out other possible structures such as a simple salt colored by charge transfer[17] or a ferrocene-like molecular complex.[37]

Tropenylium ions with a single alkyl or $-I$ substituent show electronic spectra[1,16] which can be ascribed to slight perturbation of the two-band spectrum[39] of tropenylium ion itself, while those with $+T$ substituents[16,40] show quite different and characteristic spectra which consist of two bands in the ultraviolet and one in the visible region; the visible band has been ascribed[40b] to intramolecular charge transfer. The hemiousenide ions have electronic spectra (Figure 6) strikingly similar to those of $+T$ substituted tropenylium ions[41] and differ from each other mainly in the position of the long-wavelength band. Both the position and intensity of this band in the hemiousenide ions are extremely sensitive to changes in solvent (Table III); for example, the [7.10^2]hemiousenide ion is yellow in sulfuric acid, orange in water, and deep purple in acetone. Similarly, changes in cation affect the color of the anion in the solid state; cesium [7.10^2]hemiousenide is orange, the tetramethylammonium salt is red, and the tetrabutylammonium salt is purple.

The two transitions shown by substituted tropenylium ions in the region of 220 and 260 nm are relatively unaffected by changes in substituents or solvent, and undoubtedly represent transitions within the tropenylium ring itself. The strong hypsochromic shift of the long-wavelength bands of the hemiousenide ions with increasing solvent polarity or decreasing cation radius suggests that these transitions occur with an internal decrease in dipole moment and are hindered by solvation of the ground state in polar media. Plots of the energies of these transitions against Kosower **Z** values[30] give positive slopes[44] (Figure 2) as expected for anion-to-cation charge transfer, the intensities are directly proportional to concentration of ion over the measurable range, and the absorptions persist in strongly dissociating solvents. These facts are in agreement with an assignment of the long-wavelength bands in the electronic spectra of the hemiousenide ions to intramolecular charge transfer between the negative boron cage and a cationic substituent ring. The greater sensitivity to solvent polarity of the charge-transfer band of the [7.10^2]hemiousenide ion indicates that the $-B_{10}H_9{}^{2-}$ group is a better donor than the $-B_{12}H_{11}{}^{2-}$ group in accord with previous observations.[41]

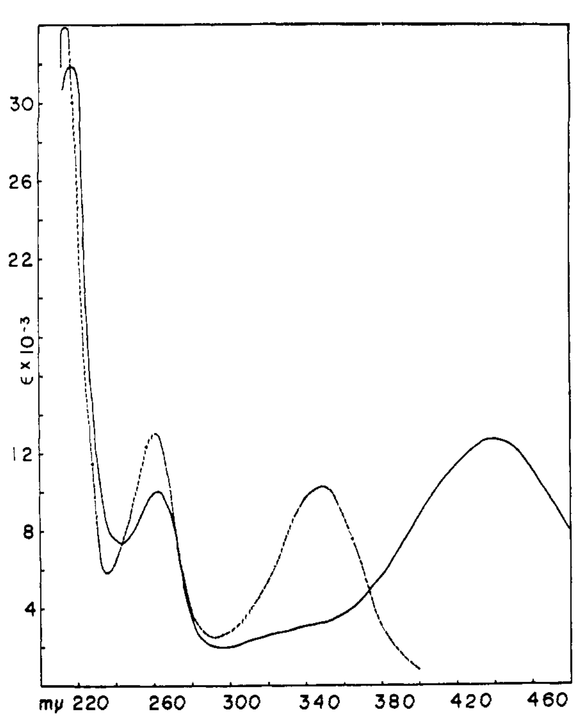

Figure 6. Electronic spectra of [7.10^2]hemiousenide ion (solid) and [7.12]hemiousenide ion (dashed) in water.

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(36) ^{11}B nmr values are ppm (δ) relative to boron trifluoride etherate = 0.

(37) A simple salt would show the spectrum of tropenylium ion in dissociating solvents, since the $B_nH_n{}^{2-}$ ions have no electronic absorptions above 200 nm and would show equivalent ring protons; a ferrocene-like tropenylium ion complex would also show equivalent ring protons[38] and would not fit reasonably with other physical and analytical data.

(38) H. J. Dauben, Jr., and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).

(39) J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Phys.*, **23**, 2347 (1955).

(40) (a) J. W. Wilt and D. Piskiewicz, *Chem. Ind.* (London), 1761 (1963); (b) G. Hohlneicher, R. Kiessling, H. C. Jutz, and P. A. Straub, *Ber. Bunsenges. Physik. Chem.*, 70, 60 (1966); (c) H. C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29, 1337, 1349, 1590 (1964).

(41) The $+T$ interaction of anionic borane cages with organic π systems has been demonstrated by a variety of means.[3e,k,9a,42,43]

(42) M. F. Hawthorne and F. P. Olsen, *J. Am. Chem. Soc.*, **87**, 2366 (1965).

(43) W. H. Knoth, *ibid.*, **88**, 935 (1966).

(44) The plots are not straight lines as the slope of a **Z** *vs.* E_t plot is a function of the specific solvent;[30] at one end of the plots the bulk solvent is water and at the other end, acetone.

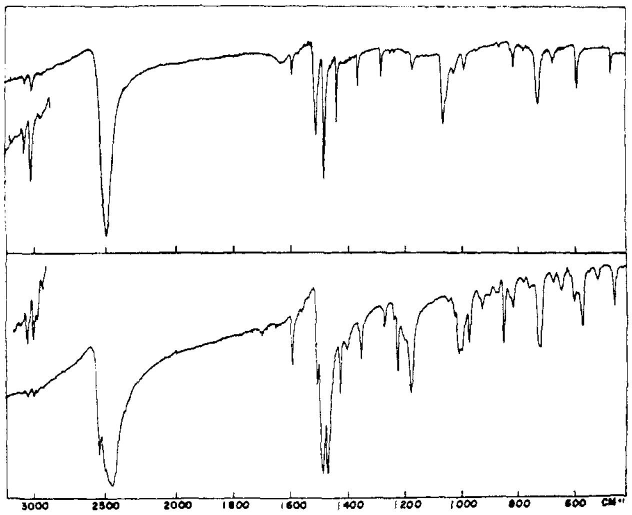

Figure 7. Infrared spectra (KBr disks) of cesium [7.12]hemiousenide (top) and cesium [7.10²]hemiousenide (bottom).

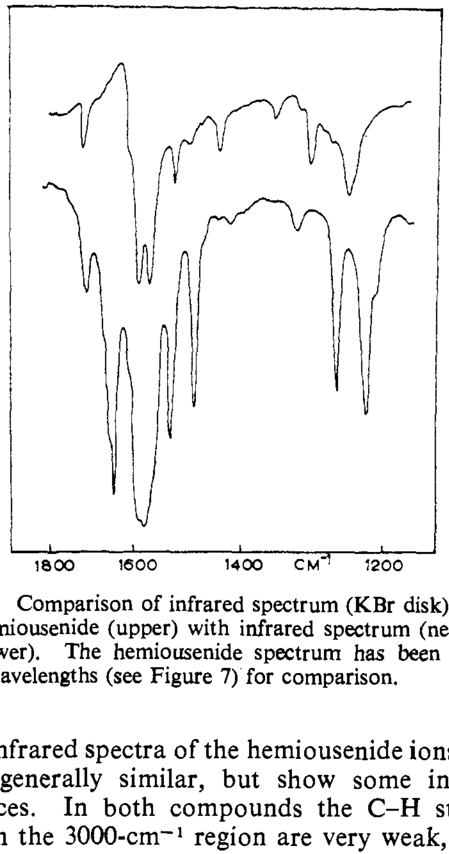

Figure 8. Comparison of infrared spectrum (KBr disk) of cesium [7.10²]hemiousenide (upper) with infrared spectrum (neat) of tropone (lower). The hemiousenide spectrum has been shifted to shorter wavelengths (see Figure 7) for comparison.

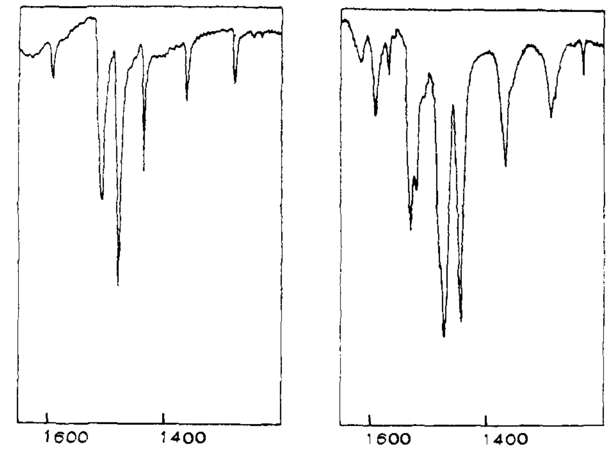

Figure 9. Comparison of infrared spectra (KBr disks) of cesium [7.12]hemiousenide (left) with chlorotropenylium fluoroborate (right).

The infrared spectra of the hemiousenide ions (Figure 7) are generally similar, but show some interesting differences. In both compounds the C–H stretching bands in the 3000-cm^{-1} region are very weak, which is typical of cycloheptatrienylium species. The B–H stretching band of the [7.10²]hemiousenide ion at 2450 cm^{-1} shows a shoulder spike at 2540 cm^{-1} due to apical hydrogens,[45,46] while that of the [7.12]hemiousenide ion is a singlet at 2490 cm^{-1}. The bands at 1010 and 1062 cm^{-1} in the [7.10²]- and [7.12]hemiousenide ions, respectively, are assigned to cage absorptions, since they correspond closely with the main cage absorption frequencies of the parent borane anions.[45] In the 1600–1100-cm^{-1} region, the spectrum of the [7.10²]-hemiousenide ion closely resembles that of tropone (Figure 8); in particular, the peaks at 1228 and 1180 cm^{-1} ascribed to C–H in-plane deformations[47] closely resemble the same bands in tropone.[48] These bands are prominent in substituted tropenylium ions with considerable substituent to ring electron donation such as tropone[49] or iodotropenylium ion,[16] but are weak or absent in tropenylium ions with weakly interacting substituents and are forbidden in tropenylium ion itself.[51] There are no prominent bands assignable to in-plane C–H deformations in the spectrum of the [7.12]hemiousenide ion, and in the 1600–1100-cm^{-1} region (Figure 9) the spectrum of this ion resembles that of a substance such as chlorotropenylium ion. Comparison of the C–C single and double bond stretching regions of the spectra of the two hemiousenide ions shows a quartet of peaks in common at 1598, 1510, 1430, and 1355 cm^{-1} in the [7.10²] ion and at 1594, 1510, 1438, and 1363 cm^{-1} in the [7.12] ion; however, the single spike at 1482 cm^{-1} in the spectrum of the [7.12] ion is strongly enhanced and split in the case of the [7.10²]hemiousenide ion. Such exaltation of the C=C stretching frequencies is typical of enhanced conjugation between a substituent and an aromatic ring.[52]

The ^{11}B nmr spectrum of the [7.10²]hemiousenide ion (Figure 5) establishes the equatorial position of attachment of the cationic ring. Comparison of the spectrum of this ion with that of $B_{10}H_{10}^{2-}$ shows that the shape of the low-field doublet of the apical borons is undisturbed, while the high-field doublet of the equatorial borons is significantly altered by the downfield

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(45) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(46) Comparison of the spectrum of the [7.10²]hemiousenide ion with that of $B_{10}H_{10}^{2-}$ shows the apical B–H spike to be equally prominent in both. Our previous report[6] that the B–H band in the [7.10²]hemiousenide ion was not split was a result of the low resolving power of the Perkin-Elmer Model 21 spectrophotometer compared to our present Perkin-Elmer Model 621 instrument.

(47) Assignment by analogy to tropone, the spectrum of which has been analyzed in detail.

(48) Y. Ikegami, *Bull. Chem. Soc. Japan*, **35**, 967 (1962).

(49) The C–O bond in tropone has been calculated to possess 84% double bond character.[50]

(50) H. Hosoya, J. Tanaka, and S. Nagakura, *Tetrahedron*, **18**, 859 (1962).

(51) W. G. Fateley, B. Curnutte, and E. R. Lippincott, *J. Chem. Phys.*, **26**, 1471 (1957).

(52) (a) D. W. A. Sharp and N. A. Sheppard, *J. Chem. Soc.*, 674 (1957); (b) H. Gotz, E. Heilbronner, A. R. Katritzky, and R. A. Jones, *Helv. Chim. Acta*, **44**, 387 (1961); (c) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 71 ff.

shift of one or more borons. The area ratio of the two absorptions remains unchanged. The spectrum of the [7.10^2]hemiousenide ion is essentially identical with that of the 2-$B_{10}H_9NH_3^-$ ion[3e] in which the substituent has been assigned to an equatorial position. Comparison of the spectra of 2-$B_{10}H_9N(CH_3)_3^-$ ion,[3e] 2-$B_{10}H_9NH_3^-$ ion,[3e] and the [7.10^2]hemiousenide ion shows that the $-I$ effect of the substituents as reflected by the downfield chemical shift of the equatorial boron is in the order $(CH_3)_3N\text{-}^+ > H_3N\text{-}^+ > C_7H_6\text{-}^+$. In addition to the perturbation of the equatorial boron resonance, the entire spectrum of the [7.10^2]hemiousenide ion shows a strong downfield chemical shift of all boron resonances, which indicates extensive ground-state deshielding of the cage by electron donation to the ring. The $B_{12}H_{12}^{2-}$ ion shows a symmetrical doublet at 16.9 ppm[36,45] while the [7.12]hemiousenide ion shows an unsymmetrical doublet at 13.7 ppm. Deshielding of the cage by electron donation to the ring is thus significantly less in the [7.12]- than in the [7.10^2]-hemiousenide ion.

The complex ring proton nmr spectra of the hemiousenide ions rule out any formulation requiring a symmetrical C_7 species. The pattern of the spectrum of the [7.10^2]hemiousenide ion (Figure 3) is quite similar to that of other tropenylium ions with $-I$, $+T$ substituents, such as bromotropenylium ion;[53] however, the ring protons are strongly shielded relative to tropenylium ion (nmr spectrum (τ, CH_3NO_2), 0.64). The spectrum of the [7.12]hemiousenide shows a similar split into two downfield protons and four upfield protons; however, the downfield peak is not split, but appears as a broad singlet (Figure 4). The ring protons of the [7.12]hemiousenide ion are much less shielded than those of the [7.10^2]hemiousenide ion, and the downfield protons are actually deshielded relative to tropenylium ion. It seems reasonable that the downfield pair of protons in the spectra of compounds of this type are those adjacent to the site of attachment to the electronegative substituent and are deshielded relative to the other ring protons by the action of the $-I$ effect of the substituent through the σ system of the molecule. The ring protons taken as a whole, however, show increased shielding through $+T$ donation of electrons from substituent to ring in the order $\text{-}B_{10}H_9^{2-} > \text{-}B_{12}H_{11}^{2-} > \text{-Br}$.

Both the [7.10^2]- and [7.12]hemiousenide ions reduce smoothly at the dme; data for representative examples of such reductions are given in Table I. The half-wave potential is affected by concentration; for example, a fourfold increase in the concentration of [7.10^2]hemiousenide ion increases $E_{1/2}$ by about 0.5 V. A millicoulometric determination of n for the [7.10^2]-hemiousenide ion (see Experimental Section) yielded a value of 0.980, which indicates a one-electron process. Using $n = 1.00$, a value of 20.1×10^6 cm^2/sec was calculated from the Ilkovic equation for the diffusion constant of the [7.10^2]-hemiousenide ion and, on the assumption that the two hemiousenide ions should have similar diffusion constants, this value of D was used in the Ilkovic equation to calculate n for the reduction of the [7.12]hemiousenide ion. The calculated value of $n = 0.975$ again shows a one-electron process; using $n = 1.00$, the value of $D = 19.0 \times 10^6$ cm^2/sec was found for the [7.12]hemiousenide ion. Plots of E against log $[i/(i_d - i)]$ for the reductions of the two ions gave straight lines with slopes -0.0343 and -0.0340 for the [7.10^2]- and [7.12]hemiousenide ions, respectively. The significant departure from the theoretical value of -0.059 demonstrates that the reactions are irreversible and that a slow step occurs in the electrode process.[55]

In comparison, tropenylium ion is reduced at the dme in 1 N KCl in a one-electron, concentration-dependent, irreversible process with $E_{1/2}$ of about -0.3 V (sce reference),[56] and both $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are inert to polarographic reduction.[45] It is likely that we are observing one-electron reduction of the cationic ring followed by radical coupling;[56] however, regardless of where the electron enters the hemiousenide ion it is clear that either the cationic ring is more difficult to reduce than the unsubstituted tropenylium ion, or else the cage is easier to reduce than the free borane anion. Either interpretation is in accord with significant electron donation from cage to ring, with this effect greatest in the [7.10^2]hemiousenide ion.

Acknowledgment. We wish to thank M. Frederick Hawthorne, Richard L. Pilling, and Robert E. Williams for helpful discussions, and Susan M. Cummins for technical assistance.

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(53) Bromotropenylium ion[16] shows an nmr spectrum (τ, CH_3CN): doublet 0.64, 0.74 (2 H); multiplet 0.90–1.15 (4 H).[54]

(54) H. J. Dauben, Jr., and K. M. Harmon, unpublished work.

(55) For example, see L. Meites and H. C. Thomas, "Advanced Analytical Chemistry," McGraw-Hill Book Co., New York, N. Y., 1958, p 159 ff.

(56) P. Zuman, J. Chodkowski, and F. Santavy, *Collection Czech. Chem. Commun.*, **26**, 380 (1961).