Table II. Interatomic Distances (Å) and Bond Angles[a] (deg) with Their Estimated Standard Deviations in the Last Figure (in Parentheses)

Hg-O(1)	2.11 (6)	O(1)-O(3)	3.36 (9)
Hg-O(2)	2.06 (6)	O(2)-O(3)	3.57 (9)
Hg-O(3)	2.75 (6)	O(2)-F	3.29 (10)
Hg-F	2.26 (8)	O(2)-F(4)	3.51 (10)
Hg-F(1)	2.60 (8)	O(3)-F(1)	3.75 (10)
Hg-F(4)	2.48 (8)	O(3)-F(4)	3.76 (10)
O(1)-(F)	2.80 (10)	F-F(1)	3.33 (11)
O(1)-F(1)	3.48 (10)	F-F(4)	3.43 (11)
O(1)-F(4) O(2)-F(1)	3.06 (10)	O(2)· · ·F(5) O(5)· · ·F(4)	2.76 (10)
O(1)-Hg-O(2)	175.9 (24)	F-Hg-O(2)	99.0 (26)
F(1)-Hg-F(4)	177.7 (26)	O(3)-Hg-O(1)	86.2 (21)
F-Hg-O(3)	164.4 (23)	Hg-O(1)-Hg(3)	110.8 (28)
F(1)-Hg-O(1)	94.9 (25)	Hg-F(4)-Hg(3)	84.9 (25)
F(4)-Hg-O(1)	81.1 (25)	Hg-O(2)-F(5)	103.6 (28)
F(4)-Hg-O(2)	100.9 (25)	Hg-F(4)-O(5)	110.4 (31)
F(1)-Hg-O(2)	81.1 (25)	Hg(5)-F(5)-O(2)	103.1 (31)
		Hg(6)-O(5)-F(4)	89.5 (24)

[a] The positions without a label are given by x, y, z as in Table I; labels are as follows: (1) $-^1/_2 + x, ^1/_2 - y, 1 - z$; (2) $1 - x, ^1/_2 + y, ^1/_2 - z$; (3) $^1/_2 - x, 1 - y, ^1/_2 + z$; (4) $1 - x, ^1/_2 + y, ^3/_2 - z$; (5) $^1/_2 + x, ^1/_2 - y, 1 - z$; (6) $1 - x, -^1/_2 + y, ^3/_2 - z$.

of these bonds differs only slightly from the sum of the corresponding covalent radii of mercury and oxygen.[2,3,15]

The other mercury-oxygen and mercury-fluorine distances within the coordination octahedron are greater than the sum of covalent radii but smaller than the sum of van der Waals radii as observed so far in the majority of the crystal structures containing mercury.[2,15] Even the shortest mercury-fluorine distance of 2.26 Å is greater than the sum of the covalent radii and also greater than the Hg-F distance of 2.24 Å found in the structure of $RbHgF_3$.[16] The contact of mercury to the nearest oxygen atom (*viz.*, Hg-O(3)) from the next zigzag chain of 2.75 Å is also equal to the usually observed value for the analogous contacts in other mercury structures containing oxygen.[2,3]

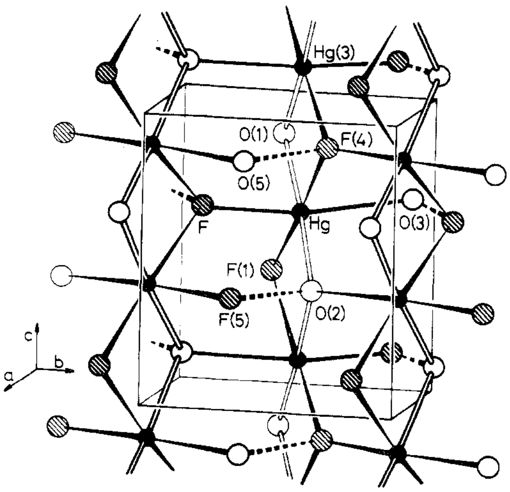

Figure 1. Clinographic projection of the crystal structure of Hg(OH)F.

It would not be possible to determine the hydrogen atom position from the present intensity data. But, from geometrical and chemical considerations, it follows undoubtedly that the oxygen-to-fluorine atom contacts of 2.76 Å belong to hydrogen bonds of the O-H· · ·F type. These contacts, shown in Figure 1 as O(2)· · ·F(5) and O(5)· · ·F(4) related by the screw symmetry operation, are located in channels formed by columns alternating along the [001] direction. The bond angle at the oxygen atom, Hg-O(2)-F(5), as well as that at the fluorine atom, Hg-F(4)-O(5), with values of 103.6 and 110.4°, respectively, is also favorable for the O-H· · ·F bond formation. There is no previous example of the O-H· · ·F bond observed in the crystal structure known to the authors. It is equivalent to an O-H· · ·O bond[17] with the length of 2.83 Å which is the most frequently observed value.

Registry No. Hg(OH)F, 37164-31-1.

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Crystal Structure of Tetramethylammonium Tetradecahydrodecaborate. Structure of the $B_{10}H_{14}{}^{2-}$ Ion

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The $B_{10}H_{14}{}^{2-}$ ion has two BH_2 groups and two bridging hydrogen atoms, in a 2632 topology of three-center bond theory. The isolated ion has C_{2v} symmetry. Unit cell parameters of tetramethylammonium tetradecahydrodecaborate, $(N(CH_3)_4)_2B_{10}H_{14}$, are $a = 9.60$ (1) Å, $b = 16.29$ (1) Å, $c = 12.27$ (1) Å, $\beta = 91.63$ (1)°, and $z = 4$, and the crystal symmetry is $P2_1/c$. Full-matrix least-squares refinement of the structure yields a value of $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ of 0.085 for 2058 X-ray diffraction maxima measured on a four-circle diffractometer. The relationships of the structure of $B_{10}H_{14}{}^{2-}$ to its bonding and probable reactivity are discussed briefly.

The two-electron reduction of $B_{10}H_{14}$ to $B_{10}H_{14}{}^{2-}$ was predicted from three-center valence theory,[1] and the ion was subsequently synthesized[2] by reduction of $B_{10}H_{14}$ by sodi-

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um in liquid ammonia. A more convenient preparative procedure involves reduction of $B_{10}H_{14}$ by borohydride.[3] Formal addition of two electrons to the boron framework also occurs when $B_{10}H_{12}(NCCH_3)_2$[4] is prepared; its structure and related derivatives[5,6] suggested that the parent $B_{10}H_{14}^{2-}$ ion has 2632 topology[7] rather than a structure with four bridging hydrogens like that of $B_{10}H_{14}$. This suggestion, that $B_{10}H_{14}^{2-}$ has two bridge hydrogens and two BH_2 groups in solution, has been confirmed in a recent nmr study of the ^{11}B spectrum at 80.5 MHz.[8] The crystallographic study described below shows that the $B_{10}H_{14}^{2-}$ ion has this same structure in the ionic solid phase where $N(CH_3)_4^+$ is the positive ion and provides molecular parameters suitable for molecular structure studies and correlation with reactivity. In particular we hope to explore the relationship of electrophilic and nucleophilic reactivity to the molecular wave function calculated both from three-center bond theory and from self-consistent theory. This relationship, particularly good for $B_{10}H_{14}$[9] and for the carboranes, suggests close relationships between the initially formed reactive complex and the dominant transition state for some reactions of boranes and carboranes.

Experimental Section

Preparation. Decaborane was reduced by potassium borohydride in water to yield a solution containing $B_{10}H_{14}^{2-}$. Addition of a saturated solution of tetramethylammonium bromide and cooling to 0° produced crystals. Three recrystallizations were done by cooling a water solution saturated at 35° to 0° and filtering. An infrared spectrum of the resulting crystals was indicative of $B_{10}H_{14}^{2-}$.

X-Ray Data. Crystals for the X-ray diffraction study were grown by placing a saturated aqueous solution at 35° into a cold room at 4°. After several days of evaporation of water from this solution, large single crystals were formed.

The Laue symmetry of C_{2h}-$2/m$ was indicated from precession photographs of $h0l$, $h1l$, $h2l$, $0kl$, and $1kl$ levels. Extinctions of all $h0l$ for l odd and of $0k0$ for k odd indicate the space group $P2_1/c$. Unit cell parameters of $a = 9.60$ (1) Å, $b = 16.29$ (1) Å, and $c = 12.27$ (1) Å, and $\beta = 91.63$ (1)° were determined by a least-squares fit of 14 Bragg reflection angles after accurate centering of the crystal on a Picker automated diffractometer. These parameters and the assumption of four formula weights per unit cell give a calculated density of 0.942 g/cm³, in excellent agreement with our experimental value of 0.94 g/cm³ measured by suspension of the crystals in a mixture of xylene and bromobenzene.

A crystal of rectangular cross section 0.3 mm × 0.15 mm, elongated along the c axis, was cut to a 0.5-mm length and again to a 0.6-mm length. Data from these two crystalline fragments were recorded on a four-circle Picker automated diffractometer, using Cu Kα radiation filtered through Ni foil. A scan rate of 1°/min was employed in the ω-scan technique, over a scan interval of 2.0°. Stationary-background counts were taken before and after each scan. Collimators 1 mm in size were used for both incident and diffracted beams, and the takeoff angle was 3.3°.

Periodic monitoring of two check reflections during the data collection revealed a gradual slight decline in intensities upon X-ray exposure. Diffraction data were therefore taken successively on two crystals, maintained at 4° by use of a stream of cold air. The decline of check reflections was thereby kept to less than 5% of the monitor intensities.

No absorption corrections were made on the crystals in view of the value of 3.23 cm⁻¹ for the linear absorption coefficient. Both crystals were mounted with the crystallographic c axis nearly parallel to the ϕ axis of the diffractometer. Each measurement was assigned a standard deviation as follows: $\sigma(I)/I = (CT + B)^{1/2}/CN + 0.02$ where CT is the total count for the scan, B is the background, and CN is the net count (CT $- B$). The two asymmetric units of data for $2\theta < 118°$ yielded 2058 reflections having $I > \sigma(I)$, of which 1722 reflections have $I > 3\sigma(I)$.

Solution and Refinement. X-Ray data were scaled with the use of a Wilson plot and normalized structure factors E were calculated from the results. In a direct-methods procedure,[10] the 126 reflections having $E > 2.0$ yielded eight sets of signs for 107 reflections using symbolic addition. One particular set, which showed far fewer conflicts among symbolic interactions, was then extended with the use of the tangent formula to yield signs for 494 of the 505 reflections having $E > 1.30$. From these normalized structure factors and signs a three-dimensional map showed all nonhydrogen atoms. The value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ from these coordinates refined easily from 0.39 to 0.16, as anisotropic thermal parameters were assigned in the least-squares procedure. A difference electron density map indicated all hydrogen atom positions, including those of the methyl groups, and their introduction reduced R to 0.12. In subsequent refinements we varied all coordinates, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms. Finally, a full-matrix refinement of all parameters for the tetramethylammonium ions was followed by a full-matrix refinement of all parameters for the $B_{10}H_{14}^{2-}$ ion. For the 2058 reflections for which $I > \sigma(I)$, the value of R is 0.085, while $R_w = [\Sigma w(k^2|F_o|^2 - |F_c|^2)/\Sigma w(k|F_o|)^4]^{1/2}$ is 0.126. For those 1722 reflections for which $I > 3\sigma(I)$, the value of R is 0.070. In these refinements we minimized $\Sigma w(k^2|F_o|^2 - |F_c|^2)^2$, where k is the scale factor and $\sqrt{w} = 1/F_o$ for $F_o \geqslant 9.24$ and $\sqrt{w} = 1/\sqrt{F \times 9.24}$ for $F_o < 9.24$. A final difference electron density map from which all atoms were subtracted showed no peaks higher than 0.23 e/Å³. In a final Fourier map the hydrogen atoms of the $B_{10}H_{14}^{2-}$ ion ranged from 0.61 to 1.02 e/Å³. The B, C, and N atomic scattering factors are from the "International Tables for X-Ray Crystallography." The H atomic scattering factor was especially prepared for covalent hydrogen for use in the CRYM computing system,[11] which was used for all refinement and electron density maps.

Results

Final coordinates are listed in Table I, along with thermal parameters for B, C, and N atoms. Hydrogen atom parameters are given in Table II, bond distances in Table III, and bond angles only for the $B_{10}H_{14}^{2-}$ ion in Table IV. Observed and calculated structure factors have been deposited elsewhere.[12]

The crystal structure projected along the a axis is shown in Figure 1. Most of the intermolecular contacts occur between hydrogen atoms of the $B_{10}H_{14}^{2-}$ ion and hydrogen atoms of the $N(CH_3)_4^+$ ions, and many of these are near the 3.2-Å distance, the sum of van der Waals distances between a methyl group and hydrogen. Hydrogen atoms of different $B_{10}H_{14}^{2-}$ show one approach of 2.9 Å and only two others less than 4 Å. One methyl carbon is 3.58 Å away from the methyl carbon of another $N(CH_3)_4^+$ ion, but all other such contacts are greater than 4 Å.

The $B_{10}H_{14}^{2-}$ ion (Figure 2) has a structure, in this $N(CH_3)_4^+$ salt, with two bridge hydrogens (H5-10 and H7-8) and two BH_2 groups (at B6 and B9). Within experimental error the symmetry of the $B_{10}H_{14}^{2-}$ ion, if isolated from the crystalline environment, is C_{2v}. In Table V we show B–B distances averaged over this C_{2v} symmetry for $B_{10}H_{14}^{2-}$, for comparison with results for $B_{10}H_{12}(NCCH_3)_2$, $B_{10}H_{12}$-

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(12) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-546.

Table I. Coordinates and Anisotropic Thermal Parameters[a-c]

	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
B1	0.7362 (5)	−0.0047 (3)	0.2698 (4)	15.26 (60)	2.70 (18)	6.34 (34)	1.92 (60)	−0.81 (78)	−0.56 (45)
B2	0.6330 (5)	0.0546 (3)	0.1769 (4)	11.49 (53)	3.52 (20)	7.30 (35)	−1.19 (60)	−3.12 (74)	0.63 (47)
B3	0.8175 (5)	0.0664 (3)	0.1781 (4)	11.73 (52)	3.89 (21)	6.87 (34)	1.46 (60)	2.87 (76)	−0.12 (48)
B4	0.8723 (4)	0.0620 (3)	0.3180 (4)	9.75 (48)	4.40 (21)	6.85 (35)	2.88 (62)	0.01 (72)	−0.14 (53)
B5	0.5744 (5)	0.0382 (3)	0.3101 (4)	11.02 (54)	3.25 (18)	7.38 (37)	−3.38 (54)	−1.61 (77)	−0.28 (47)
B6	0.5397 (4)	0.1362 (3)	0.2336 (4)	8.06 (47)	4.07 (23)	8.38 (39)	−0.22 (55)	−1.50 (74)	1.58 (49)
B7	0.7052 (5)	0.1529 (3)	0.1593 (4)	11.43 (54)	3.33 (18)	5.82 (31)	−0.10 (57)	−0.43 (71)	1.19 (44)
B8	0.8658 (4)	0.1566 (3)	0.2524 (4)	8.35 (48)	3.93 (21)	7.92 (37)	−1.08 (56)	1.39 (73)	0.22 (50)
B9	0.8276 (5)	0.1440 (3)	0.4007 (4)	9.55 (48)	3.53 (21)	7.14 (36)	−1.89 (56)	−0.06 (72)	−0.46 (48)
B10	0.7348 (4)	0.0413 (3)	0.4018 (4)	10.71 (51)	2.99 (18)	6.10 (33)	0.24 (56)	−0.72 (69)	−0.07 (44)
N11	0.2905 (3)	0.2235 (2)	0.4933 (3)	7.92 (36)	3.51 (15)	6.96 (27)	0.22 (41)	0.70 (50)	0.44 (36)
C12	0.2280 (4)	0.1664 (3)	0.4108 (4)	11.11 (54)	6.23 (25)	9.00 (36)	−0.13 (61)	−1.34 (81)	−2.57 (55)
C16	0.4178 (4)	0.1839 (3)	0.5460 (4)	10.83 (49)	4.75 (21)	9.32 (35)	2.04 (57)	−3.73 (74)	−0.54 (50)
C20	0.1876 (4)	0.2377 (3)	0.5818 (4)	11.43 (55)	7.41 (27)	8.43 (35)	−0.40 (65)	3.56 (75)	−1.58 (54)
C24	0.3312 (5)	0.3025 (3)	0.4448 (4)	16.28 (61)	4.23 (20)	12.21 (47)	1.26 (67)	2.16 (93)	2.85 (59)
N28	0.7910 (3)	0.0880 (2)	0.8108 (2)	8.73 (37)	2.80 (12)	5.65 (22)	0.21 (36)	0.05 (45)	−1.04 (32)
C29	0.7876 (4)	−0.0004 (3)	0.8360 (4)	11.58 (48)	2.99 (18)	10.48 (40)	−0.10 (52)	0.17 (71)	−0.42 (51)
C33	0.8051 (5)	0.1027 (3)	0.6908 (3)	15.05 (56)	5.13 (22)	6.83 (35)	1.65 (61)	2.96 (70)	−0.62 (53)
C37	0.6581 (4)	0.1280 (3)	0.8460 (3)	10.03 (44)	4.46 (21)	9.03 (36)	1.29 (53)	2.61 (70)	−3.76 (42)
C41	0.9109 (5)	0.1280 (3)	0.8709 (4)	11.03 (50)	4.65 (22)	10.12 (36)	−1.99 (54)	−2.61 (73)	−0.93 (48)

[a] Anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. [b] Standard deviations in parentheses are from full-matrix least squares. [c] Atoms 11–27 belong to one tetramethylammonium group; atoms 28–44, to the other.

Table II. Hydrogen Coordinates and Thermal Parameters[a]

	x	y	z	B, Å^2
H1	0.7540 (29)	−0.0773 (18)	0.2622 (24)	3.35 (0.71)
H2	0.5712 (34)	0.0205 (20)	0.0940 (26)	4.74 (0.80)
H3	0.8904 (31)	0.0357 (21)	0.1011 (25)	4.04 (0.75)
H4	0.9814 (34)	0.0322 (22)	0.3470 (26)	5.04 (0.82)
H5	0.4933 (32)	−0.0102 (20)	0.3354 (25)	4.33 (0.77)
H6	0.4384 (35)	0.1442 (25)	0.1866 (27)	5.44 (0.86)
H′6	0.5557 (30)	0.1880 (19)	0.2992 (25)	3.83 (0.74)
H7	0.7108 (32)	0.1944 (22)	0.0868 (25)	4.36 (0.78)
H8	0.9532 (36)	0.2022 (24)	0.2189 (27)	5.11 (0.84)
H9	0.9138 (34)	0.1554 (21)	0.4647 (27)	5.02 (0.81)
H′9	0.7423 (35)	0.1965 (21)	0.4018 (29)	5.32 (0.85)
H10	0.7364 (31)	−0.0061 (21)	0.4763 (25)	3.94 (0.74)
H5–10	0.6173 (42)	0.0775 (26)	0.3930 (30)	6.75 (0.92)
H7–8	0.7586 (39)	0.2133 (25)	0.2335 (31)	6.90 (0.95)
H13	0.2968 (41)	0.1477 (26)	0.3522 (30)	6.2 (1.1)
H14	0.1607 (44)	0.1954 (26)	0.3745 (31)	7.2 (1.1)
H15	0.2007 (38)	0.1080 (24)	0.4521 (30)	6.4 (1.0)
H17	0.3935 (40)	0.1166 (26)	0.5689 (33)	7.4 (1.1)
H18	0.4745 (42)	0.1741 (24)	0.4873 (33)	6.7 (1.1)
H19	0.4580 (44)	0.2235 (26)	0.6049 (31)	7.3 (1.2)
H21	0.1681 (43)	0.1678 (28)	0.6178 (32)	8.2 (1.2)
H22	0.1125 (40)	0.2668 (27)	0.5573 (37)	7.6 (1.1)
H23	0.2271 (41)	0.2907 (27)	0.6306 (33)	7.2 (1.1)
H25	0.3589 (48)	0.3599 (31)	0.5016 (38)	10.8 (1.5)
H26	0.2576 (46)	0.3328 (25)	0.4184 (34)	7.6 (1.3)
H27	0.3849 (46)	0.2860 (32)	0.3807 (33)	8.2 (1.3)
H30	0.7734 (40)	−0.0084 (24)	0.9181 (31)	6.1 (1.0)
H31	0.7229 (43)	−0.0263 (22)	0.8045 (29)	5.3 (0.9)
H32	0.8609 (38)	−0.0330 (23)	0.8223 (30)	6.6 (1.0)
H34	0.7397 (43)	0.0772 (27)	0.6537 (31)	7.2 (1.1)
H35	0.8866 (46)	0.07536 (26)	0.6668 (32)	7.3 (1.2)
H36	0.8125 (38)	0.1769 (24)	0.6807 (30)	5.7 (1.0)
H38	0.5829 (39)	0.1067 (24)	0.7989 (31)	6.9 (1.1)
H39	0.6415 (40)	0.1138 (26)	0.9271 (31)	7.3 (1.1)
H40	0.6607 (36)	0.2008 (23)	0.8263 (31)	5.1 (1.0)
H42	0.9786 (39)	0.1060 (25)	0.8461 (29)	6.4 (1.0)
H43	0.9047 (49)	0.1145 (26)	0.9483 (34)	6.9 (1.2)
H44	0.9046 (36)	0.1991 (22)	0.8495 (27)	4.5 (0.9)

[a] Standard deviations in parentheses are from full-matrix least squares.

Table III. Bond Distances (Å) with Standard Deviations in Parentheses

	$B_{10}H_{14}^{2-}$		
B1–B2	1.774 (0.010)	B5–B6	1.876 (0.007)
B3	1.807 (0.009)	B10	1.882 (0.012)
B4	1.786 (0.008)	H5	1.16 (0.03)
B5	1.787 (0.008)	H5–10	1.26 (0.04)
B10	1.784 (0.007)	B6–B7	1.874 (0.011)
H1	1.20 (0.03)	H6	1.12 (0.03)
B2–B3	1.781 (0.007)	H′6	1.17 (0.03)
B5	1.763 (0.009)	B7–B8	1.892 (0.012)
B6	1.757 (0.008)	H7	1.12 (0.03)
B7	1.760 (0.007)	H7–8	1.43 (0.04)
H2	1.29 (0.03)	B8–B9	1.877 (0.008)
B3–B4	1.782 (0.009)	H8	1.21 (0.04)
B7	1.784 (0.007)	H7–8	1.40 (0.04)
B8	1.783 (0.007)	B9–B10	1.896 (0.007)
H3	1.29 (0.03)	H9	1.14 (0.03)
B4–B8	1.739 (0.007)	H′9	1.18 (0.04)
B9	1.740 (0.007)	B10–H10	1.20 (0.03)
B10	1.729 (0.011)	H5–10	1.27 (0.04)
H4	1.20 (0.03)		
	Tetramethylammonium Ion		
N11–C12	1.488 (7)	N28–C29	1.474 (6)
C16	1.511 (8)	C33	1.501 (5)
C20	1.507 (9)	C37	1.507 (6)
C24	1.474 (6)	C41	1.498 (8)
C12–H13	1.04 (4)	C29–H30	1.03 (4)
H14	0.91 (4)	H31	0.84 (4)
H15	1.11 (4)	H32	0.90 (4)
C16–H17	1.16 (4)	C33–H34	0.87 (4)
H18	0.93 (4)	H35	0.95 (4)
H19	1.04 (4)	H36	1.22 (4)
C20–H21	1.24 (5)	C37–H38	0.98 (4)
H22	0.91 (4)	H39	1.04 (4)
H23	1.11 (4)	H40	1.21 (4)
C24–H25	1.19 (5)	C41–H42	0.81 (4)
H26	0.91 (4)	H43	0.98 (4)
H27	0.99 (4)	H44	1.19 (4)

$[S(CH_3)_2]_2$, and $B_{10}H_{14}$. The B–H terminal bonds in $B_{10}H_{14}^{2-}$, including both hydrogens of each BH_2 group, range from 1.12 to 1.29 Å and show an average value of 1.19 Å. It is surprising, in view of the expected[13] displacement of electrons into the B–H bonds, that the average is so close to that found by neutron diffraction[14] for the internuclear B–H distances in $B_{10}H_{14}$. However, these B–H values in $B_{10}H_{14}^{2-}$ show such large standard deviations that they cannot be regarded as reliable.

Discussion

In spite of the difference in hydrogen arrangements in

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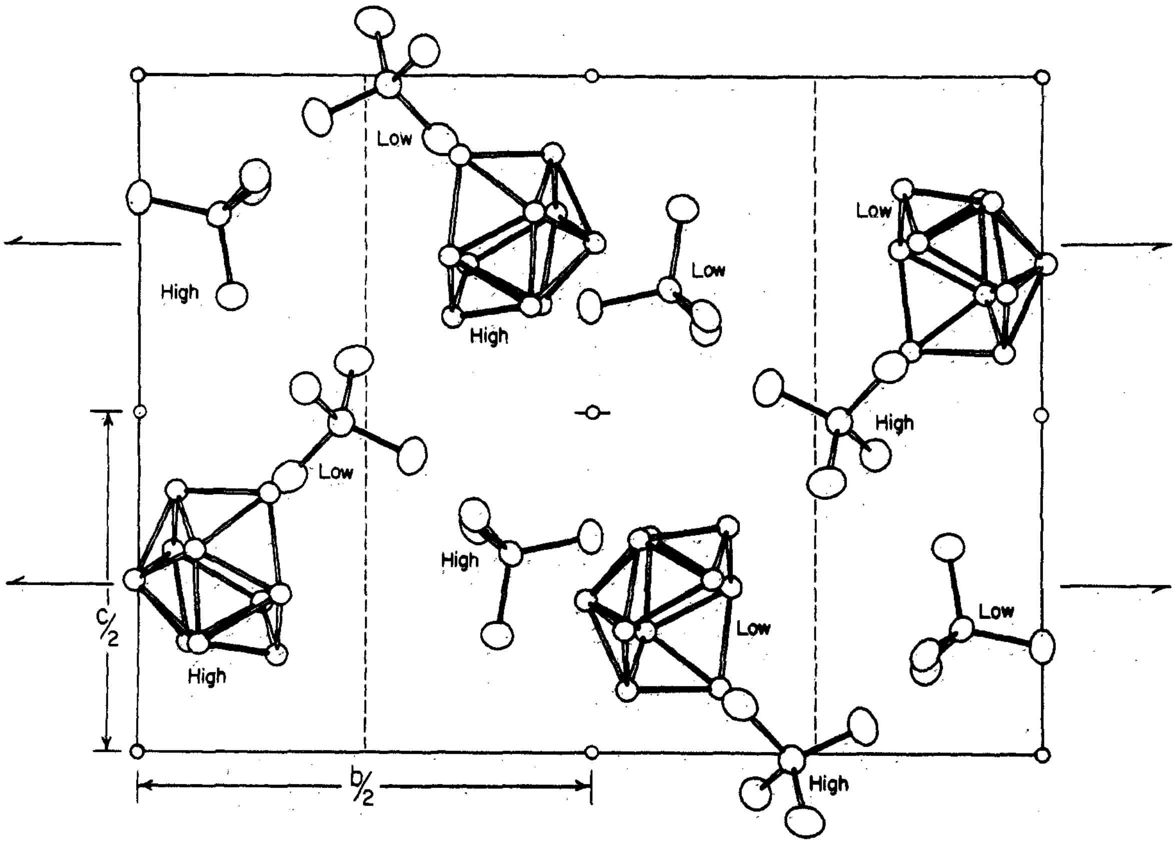

Figure 1. The crystal structure of $[N(CH_3)_4]_2B_{10}H_{14}$ in projection along the *a* axis. Ions marked high and low are toward and away from the reader, respectively.

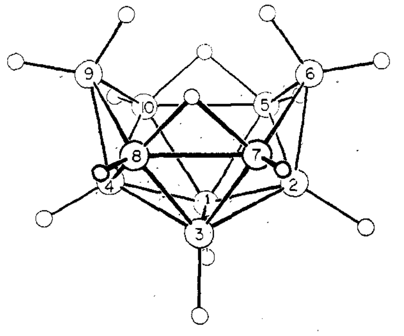

Figure 2. The structure of the $B_{10}H_{14}{}^{2-}$ ion, showing the numbering system.

$B_{10}H_{14}$ and $B_{10}H_{14}{}^{2-}$, the boron frameworks have almost the same geometry. Although the B6· · ·B9 distance is longer (3.57 Å) in $B_{10}H_{14}$ than that (3.39 Å) in $B_{10}H_{14}{}^{2-}$, the latter is *slightly* more expanded having an average B-B distance of 1.803 Å as compared with the average of 1.790 Å for $B_{10}H_{14}$. These changes are associated with shortening of B5-B10 and lengthening of B5-B6 (and equivalent distances). The species having the shorter bond has the distance spanned with bridge hydrogens, and there are two bridges in $B_{10}H_{14}{}^{2-}$ and four in $B_{10}H_{14}$. We note first that the B6· · ·B9 distances are 3.21 Å in $B_{10}H_{12}[S(CH_3)_2]_2$, 3.32 Å in $B_{10}H_{12}(NCCH_3)_2$, and 3.39 Å in $B_{10}H_{14}{}^{2-}$, perhaps correlating with an increase in ligand bond strength which may leave the boron framework slightly depleted of electrons. Second we observe that the very small differences in geometries of $B_{10}H_{14}$ and $B_{10}H_{14}{}^{2-}$ do not fit the usual nido and arachno properties of other members of the boranes and carboranes; but the existence of B_4Cl_4, the failure of $B_5H_5{}^{2-}$ to be found (so far), the valence structures of $B_{11}H_{11}{}^{2-}$, and a host of relative stability problems limit the usefulness of the formal B_nH_{n+2}, B_nH_{n+4}, and B_nH_{n+6} concepts or their complete equivalents as electron-counting rules.

Turning from overall shape and size we now ask, "Why does $B_{10}H_{14}$ prefer four bridge hydrogens, while $B_{10}H_{14}{}^{2-}$ favors two bridge hydrogens and two BH_2 groups?" Geometrical constraints appear not to be a major problem (the H′6 to H′9 distance in $B_{10}H_{14}{}^{2-}$ is 2.15 Å). Three-center bond theory appears to give a very clear answer based upon the stability conferred by resonance structures.[15,16] For the four-bridge-hydrogen geometry the 4620 topology of $B_{10}H_{14}$ yields 24 central three-center bond resonance structures, while the 4450 topology of $B_{10}H_{14}{}^{2-}$ has only one valence structure. For the two-bridge, $2BH_2$ type of geometry the 2802 topology of $B_{10}H_{14}$ has only one valence structure, while the 2632 topology of $B_{10}H_{14}{}^{2-}$ has 24 central three-center bond resonance structures (Figure 3).

Molecular orbital theory may soon give an illuminating equivalent of this argument about relative stabilities, and it may also shed light on the most preferred localized structures as it already has done in the smaller boranes and carboranes.[16] If the rules can be extrapolated from smaller boranes to $B_{10}H_{14}{}^{2-}$ and $B_{10}H_{14}$, we can expect to see a revision of the open three-center BBB bond and single BB bond to two equivalent fractional three-center bonds (Figure 4). This same feature has already been proposed[9] for the preferred valence structure of $B_{10}H_{14}$, on the basis of a similar feature in B_5H_{11}[17] and in $C_2B_4H_8$.[18]

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(16) W. N. Lipscomb, *Pure Appl. Chem.*, 29, 493 (1972).

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Table IV. $B_{10}H_{14}^{2-}$ Bond Angles (deg) with Standard Deviations in Parentheses

B2-B1-B3	59.6 (4)	B2-B3-B4	105.6 (10)
B2-B1-B4	105.8 (10)	B2-B3-B7	59.2 (3)
B2-B1-B5	59.3 (4)	B2-B3-B8	109.7 (7)
B2-B1-B10	109.6 (9)	B2-B3-H3	120.8 (33)
B2-B1-H1	124.4 (37)	B4-B3-B7	108.5 (9)
B3-B1-B4	59.5 (4)	B4-B3-B8	58.4 (3)
B3-B1-B5	108.4 (10)	B4-B3-H3	122.4 (34)
B3-B1-B10	108.1 (8)	B7-B3-B8	64.1 (5)
B3-B1-H1	121.3 (35)	B7-B3-H3	123.3 (36)
B4-B1-B5	107.7 (6)	B8-B3-H3	123.6 (36)
B4-B1-H1	121.4 (35)	B1-B4-B3	60.9 (4)
B5-B1-B10	63.6 (5)	B1-B4-B8	111.7 (7)
B5-B1-H1	122.2 (35)	B1-B4-B9	118.0 (8)
B10-B1-H1	119.3 (33)	B1-B4-B10	61.0 (4)
B1-B2-B3	61.1 (4)	B1-B4-H4	118.5 (35)
B1-B2-B5	60.7 (4)	B3-B4-B8	60.8 (4)
B1-B2-B6	116.1 (8)	B3-B4-B9	117.4 (8)
B1-B2-B7	111.0 (7)	B3-B4-B10	111.8 (9)
B1-B2-H2	120.5 (35)	B3-B4-H4	122.3 (38)
B3-B2-B5	110.7 (11)	B8-B4-B9	65.3 (4)
B3-B2-B6	115.7 (8)	B8-B4-B10	115.4 (10)
B3-B2-B7	60.5 (3)	B8-B4-H4	121.0 (37)
B3-B2-H2	119.2 (33)	B9-B4-B10	66.3 (4)
B5-B2-B6	64.4 (4)	B9-B4-H4	111.4 (32)
B5-B2-B7	112.9 (9)	B10-B4-H4	114.8 (33)
B5-B2-H2	120.9 (34)	B1-B5-B2	60.0 (4)
B6-B2-B7	64.4 (5)	B1-B5-B6	109.7 (6)
B6-B2-H2	114.2 (30)	B1-B5-B10	58.1 (4)
B7-B2-H2	118.0 (32)	B1-B5-H5	113.9 (31)
B1-B3-B2	59.3 (4)	B1-B5-H5-10	98.9 (29)
B1-B3-B4	59.7 (4)	B2-B5-B6	57.6 (3)
B1-B3-B7	108.5 (6)	B2-B5-B10	105.8 (9)
B1-B3-B8	108.7 (6)	B2-B5-H5	126.0 (40)
B1-B3-H3	117.3 (32)	B2-B5-H5-10	124.4 (42)
B6-B5-B10	114.0 (11)	B4-B8-B9	57.3 (3)
B6-B6-H5	127.1 (39)	B4-B8-H8	133.3 (51)
B6-B5-H5-10	91.2 (25)	B4-B8-B7-8	132.8 (50)
B10-B5-H5	113.8 (31)	B7-B8-B9	113.8 (10)
B10-B5-H5-10	42.3 (19)	B7-B8-H8	112.5 (33)
H5-B5-H5-10	109.6 (55)	B7-B8-H7-8	48.6 (17)
B2-B6-B5	57.9 (4)	B9-B8-H8	123.7 (40)
B2-B6-B7	57.9 (4)	B9-B8-H7-8	94.0 (25)
B2-B6-H6	109.2 (33)	H8-B8-H7-8	93.3 (42)
B2-B6-H'6	139.2 (52)	B4-B9-B8	57.3 (3)
B5-B6-B7	103.0 (7)	B4-B9-B10	56.6 (4)
B5-B6-H6	119.6 (38)	B4-B9-H9	110.0 (31)
B5-B6-H'6	104.5 (26)	B4-B9-H'9	138.0 (56)
B7-B6-H6	117.8 (35)	B8-B9-B10	102.0 (7)
B7-B6-H'6	97.6 (24)	B8-B9-H9	119.5 (35)
H6-B6-H'6	111.3 (53)	B8-B9-H'9	94.9 (26)
B2-B7-B3	60.3 (3)	B10-B9-H9	118.1 (34)
B2-B7-B6	57.7 (4)	B10-B9-H'9	108.2 (30)
B2-B7-B8	105.8 (8)	H9-B9-H'9	111.3 (55)
B2-B7-H7-8	133.3 (50)	B1-B10-B4	61.1 (4)
B3-B7-B6	109.9 (8)	B1-B10-B5	58.3 (4)
B3-B7-B8	57.9 (4)	B1-B10-B9	110.4 (6)
B3-B7-H7	122.4 (39)	B1-B10-H10	115.0 (30)
B3-B7-H7-8	104.9 (30)	B1-B10-H5-10	98.5 (29)
B6-B7-B8	113.5 (8)	B4-B10-B5	106.0 (8)
B6-B7-H7	122.3 (38)	B4-B10-B9	57.1 (3)
B6-B7-H7-8	94.8 (25)	B4-B10-H10	125.9 (40)
B8-B7-H7	113.8 (32)	B4-B10-H5-10	123.3 (45)
B8-B7-H7-8	47.3 (16)	B5-B10-B9	113.4 (9)
H7-B7-H7-8	93.8 (41)	B5-B10-H10	115.6 (32)
B3-B8-B4	60.8 (4)	B5-B10-H5-10	41.8 (18)
B3-B8-B7	58.0 (4)	B9-B10-H10	125.4 (38)
B3-B8-B9	110.5 (6)	B9-B10-H5-10	90.4 (26)
B3-B8-H8	120.5 (39)	H10-B10-H5-10	110.8 (55)
B3-B8-H7-8	106.3 (31)	B5-H5-10-B10	95.9 (29)
B4-B8-B7	105.6 (9)	B7-H7-8-B8	84.2 (22)

Table V. Bond Distances (Å) Assuming C_{2v} Symmetry

	$B_{10}H_{14}^{2-}$	$B_{10}H_{12}$-$(CH_3CN)_2$[4]	$B_{10}H_{12}$-$[S(CH_3)_2]_2$[5]	$B_{10}H_{14}$[9]
B1-B2	1.781	1.757	1.76	1.778
B1-B3	1.807	1.837	1.84	1.772
B1-B5	1.785	1.778	1.80	1.756
B2-B5	1.748	1.744	1.78	1.786
B2-B6	1.749	1.746	1.75	1.715
B5-B6	1.881	1.855	1.88	1.775
B5-B10	1.887	1.881	1.91	1.973

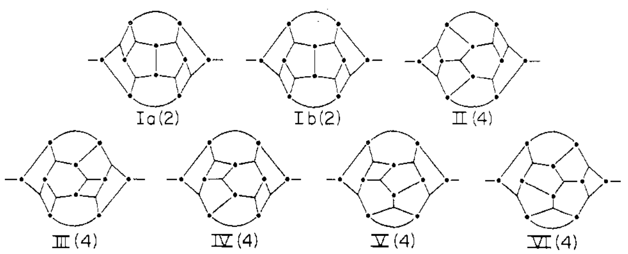

Figure 3. The 24 valence structures for $B_{10}H_{14}^{2-}$ based upon central three-center bond theory. The number of bond permutations required to achieve C_{2v} symmetry is indicated in parentheses. Charge distributions place e/2, e, and e/2 on BHB of bridge hydrogen, e and e on each atom of a single B-B or B-H bond, and 2e/3 on each B atom of a central three-center bond.

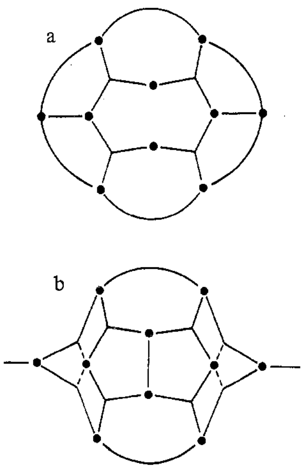

Figure 4. (a) The most symmetrical valence structure of $B_{10}H_{14}^{2-}$ involving some open three-center BBB bonds. (b) A revised equivalent structure in which the open three-center bond and a single B-B bond are replaced by two fractional three-center bonds.[17]

Charge distribution and reactivity of filled and unfilled shells near the valence level require molecular orbital study, for which it is convenient to have the coordinates of Table VI. Here, for a crude start we consider the full complement of valence structures. The charge distribution obtained from averaging the 24 nonorthogonal structures of Figure 3 is summarized in Table VII. The predictions of preferred electrophilic substitution are in the order B6, B1, B2, and B5, while nucleophilic substitution would be guessed in the reverse order. The readiness with which $B_{10}H_{14}^{2-}$ is willing to give up two electrons to become $B_{10}H_{14}$ may tend to dominate much of the chemistry of $B_{10}H_{14}^{2-}$. However, the success[9] of these predictions for $B_{10}H_{14}$ makes it impossible for us to resist these guesses for substitution chemistry in $B_{10}H_{14}^{2-}$.

Attempts to iodinate $B_{10}H_{14}^{2-}$ have yielded[19] $B_{10}H_{14}$ and I^-. Also anhydrous hydrogen chloride converts[20] $B_{10}H_{14}^{2-}$

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(20) R. H. Toeniskoetter, Ph.D. Thesis, St. Louis University, St. Louis, Mo.

Table VI. Coordinates of Unique Atoms in $B_{10}H_{14}^{2-}$ [a]

Atom	x	y	z
H1	0.0	2.8095	−3.0681
H2	4.5626	0.0	−1.1789
H5	2.6852	4.7973	1.4574
H6	5.4043	0.0	3.6633
H′6	2.0323	0.0	5.1579
H5-H10	0.0	3.0882	3.3097
B1	0.0	1.7070	−1.1025
B2	2.6817	0.0	0.0
B5	1.7830	2.7721	1.5538
B6	3.2088	0.0	3.2611

[a] All coordinates are given in au. B–H bond lengths are those of $B_{10}H_{14}$. The molecular C_2 axis is along z.

Table VII. Average Formal Charges for the Six Types of Three-Center Bond Diagrams[a] of $B_{10}H_{14}^{2-}$ [b]

	I	II	III	IV	V	VI	Av
B1	$^1/_3-$	$^1/_3-$	$^1/_6-$	$^1/_6-$	$^1/_6-$	$^1/_3-$	0.25−
B2	0	0	0	0	$^1/_6-$	$^1/_6-$	0.06−
B5	0	$^1/_{12}-$	$^1/_{12}-$	$^1/_{12}-$	0	0	0.04−
B6	$^2/_3-$	$^1/_2-$	$^2/_3-$	$^2/_3-$	$^2/_3-$	$^1/_2-$	0.61−

[a] Only central three-center BBB bonds are included here. The uniquely symmetrical structure having two open three-center BBB bonds gives charges of $^1/_3-$ at B1 and B2, $^1/_3+$ at B5, and 1− at B6. [b] Because of the extra positive charge on N at positions 6 and 9 in $B_{10}H_{12}L_2$ compounds, structures of types I, III, IV, and V would be more important than types II and VI in this hybrid. Omitting II and VI structure types, the charges are 0.21− at B1, 0.04− at B2 and B5, and 0.667− at B6.

to $B_{10}H_{14}$. Protonation is reversible, yielding[21] $B_{10}H_{15}^-$. Electrochemical interconversion of $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ in acetonitrile occurs as an apparent two-electron step in either direction,[22] but further studies are required to discern possible intermediates and correlation of the electronic step with the hydrogen migration. However, reduction[23] of $B_{10}H_{14}$ in 1,2-dimethoxyethane by electrochemical methods and also reduction by sodium[20,24] appear to involve intermediates and one-electron stages. In 1,2-dimethoxyethane an equimolar mixture of $B_{10}H_{14}$ and $(n\text{-}Bu_4N)_2B_{10}H_{14}$ at −65° yields[22] a radical anion (probably $B_{10}H_{14}^-$), and in either acetonitrile or 1,2-dimethoxyethane this reaction produces[22] an equimolar mixture of $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$.

Unlike $B_9H_{13}NCCH_3$ and $B_9H_{14}^-$, which have different hydrogen arrangements[16,25,26] about a similar B_9 fragment, $B_{10}H_{14}^{2-}$ and 6,9-$B_{10}H_{12}(NCCH_3)_2$ and analogous ligand compounds have a hydrogen arrangement in common within the 2632 topology. Moreover, the ^{11}B nmr spectra[8,27] of $B_{10}H_{12}L_2$ compounds (L is a ligand) and $B_{10}H_{14}^{2-}$ are similar to each other, but very different from the ^{11}B nmr spectrum of $B_{10}H_{14}$.[28] Even for different ligands L, only the B6 (B9) doublet shifted noticeably, moving to higher field as the base strength of the ligand increased. This experimental evidence, along with the similarities of valence structures, leads us to suggest that substitution chemistry may be formally similar in 6,9-$B_{10}H_{12}L_2$ and $B_{10}H_{14}^{2-}$. We exclude formation of $B_{10}H_{12}L_2$ as more indicative of reactivity of $B_{10}H_{14}$ itself, and we exclude ligand displacement reactions[29] which involve only these same 6,9 positions. An intermediate may be 6-$B_{10}H_{13}L^-$, which is most probably analogous to $B_{10}H_{14}^{2-}$ and which reacts with amine hydrochlorides to form $B_{10}H_{12}LL'$.[30] The rate of this reaction depends on the acidity of the amine hydrochloride and hence may be related to proton removal from the 6-$B_{10}H_{13}^-$ ion, but further studies of mechanism are required.

One halogen substitution reaction has been carried out—the bromination in benzene of 6,9-$B_{10}H_{12}[S(CH_3)_2]_2$ to yield the 5-bromo products.[31,32] Probably the reaction is by a free-radical pathway; further kinetic analysis is necessary, although it is possible that electron transfer may be involved from the boron cage to Br during the reaction. In $B_{10}H_{14}^{2-}$ itself B5 is predicted to be least susceptible to electrophilic attack and thus most susceptible to nucleophilic attack.

Registry No. $(NMe_4)_2B_{10}H_{14}$, 37209-64-6.

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