SYNTHESIS, CHARACTERIZATION, AND CHEMISTRY OF DIMETHYL SULFIDE DERIVATIVES OF *closo*-$B_{10}H_{10}^{2-}$

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Dedicated to Professor Jaromír Plešek, a scholar and a gentleman, on the occasion of his 75th birthday in recognition of his outstanding contributions to the area of boron chemistry.

The reaction of $Cs_2[B_{10}H_{10}]$ with DMSO in acid produces the disubstituted 1,10-, 1,6-, and 2,7(8)-isomers of $(Me_2S)_2B_{10}H_8$ as well as the monosubstituted $[(Me_2S)B_{10}H_9]^-$ anion. Through a modified procedure, the trisubstituted compound 1,10-$(Me_2S)_2$-2-$(MeS)B_{10}H_7$ was prepared and characterized. The 1,10-$(Me_2S)_2B_{10}H_8$ isomer was converted to the enantiomers 2,7-$(Me_2S)_2B_{10}H_8$ and 2,8-$(Me_2S)_2B_{10}H_8$ which were separated on a chiral column. The 1,6-$(Me_2S)_2B_{10}H_8$ isomer was converted to a mixture of 1,10-$(Me_2S)_2B_{10}H_8$ and 2,3-$(Me_2S)_2B_{10}H_8$. These polyhedral rearrangements are believed to occur through the diamond-square-diamond mechanism. The 1,6- and 1,10-$(Me_2S)_2B_{10}H_8$ isomers were reduced with alkali metal in liquid ammonia to produce the dianions $[1,6\text{-}(MeS)_2B_{10}H_8]^{2-}$ and $[1,10\text{-}(MeS)_2B_{10}H_8]^{2-}$, respectively. Sodium ethanethiolate was used for the reduction of $[1\text{-}(Me_2S)B_{10}H_9]^-$ and 1,10-$(Me_2S)_2B_{10}H_8$ to form $[1\text{-}(MeS)B_{10}H_9]^{2-}$ and [1-(MeS)-10-$(Me_2S)B_{10}H_8]^-$, respectively. The structures of 1,10-$(Me_2S)_2B_{10}H_8$, 1,6-$(Me_2S)_2B_{10}H_8$, 2,8-$(Me_2S)_2B_{10}H_8$, 2,3-$(Me_2S)_2B_{10}H_8$, 1,10-$(Me_2S)_2$-2-$(MeS)B_{10}H_7$, [1-(MeS)-10-$(Me_2S)B_{10}H_8]^-$, and $[1,6\text{-}(MeS)_2B_{10}H_8]^{2-}$ were determined by single-crystal X-ray diffraction analysis.

Keywords: Boranes; Decaborane; Rearrangements; Reductions; Dimethyl sulfide; X-Ray diffraction; Crystal structure.

The boron cluster $[B_{10}H_{10}]^{2-}$ was first reported by Hawthorne in 1959 and shortly thereafter by Muetterties[1]. This dianion has a *closo*-B_{10} core that is a bicapped square antiprismatic polyhedron. It possesses excellent thermal stability, and it is stable in acidic and basic media[2]. Through the years salts of this anion have been the subject of many investigations. Derivatives such

as halogen[3], carboxyl[4], azide[4], isocyanate[4], nitrile[4], acyl[5], hydroxy[5], and amine[4,6] have been synthesized. Although the chemistry of the $[B_{10}H_{10}]^{2-}$ cage has been studied extensively, its derivatives continue to attract interest. Possible applications considered are in the areas of nonlinear optics[7], burn rate propellants[8], and boron neutron capture therapy (BNCT) for the treatment of tumors[9].

The electrophilic substitution reaction of dimethyl sulfoxide onto the boron cage was first published in 1965 by Knoth, Hertler, and Muetterties[10]. They reported the formation of the neutral isomeric species 1,6-, 1,10-, and 2,7(8)-$(Me_2S)_2B_{10}H_8$ as well as the monoanions, $[Me_2SB_{10}H_8SMe]^-$ and $[Me_2SB_{10}H_9]^-$. Halogenated derivatives of $(Me_2S)_2B_{10}H_8$ and the halogenated, diazonium, deuterio, hydroxy, benzoyl, and amine derivatives of $[Me_2SB_{10}H_9]^-$ were also reported[10]. Recent studies of the rich chemistry of the related icosahedral dimethyl sulfide derivatives $(Me_2S)_2B_{12}H_{10}$ [11], prompted us to reexamine the reactivity of the $(Me_2S)_2B_{10}H_8$ system.

The present investigation is concerned with the preparation and study of the neutral isomers of $(Me_2S)_2B_{10}H_8$ and the anions that are derived from them by removal of CH_3^+. During the course of this study, two new neutral complexes, 2,3-$(Me_2S)_2B_{10}H_8$ and 1,10-$(Me_2S)_2$-2-$(MeS)B_{10}H_7$, and the dianions $[1\text{-}(MeS)B_{10}H_9]^{2-}$, $[1,10\text{-}(MeS)_2B_{10}H_8]^{2-}$, and $[1,6\text{-}(MeS)_2B_{10}H_8]^{2-}$ were synthesized and characterized. Compounds were characterized using several spectroscopic techniques including single-crystal X-ray diffraction analysis when suitable single crystals could be obtained. Chart 1 depicts the dimethyl sulfide derivatives of *closo*-$[B_{10}H_{10}]^{2-}$ prepared and studied in this investigation.

EXPERIMENTAL

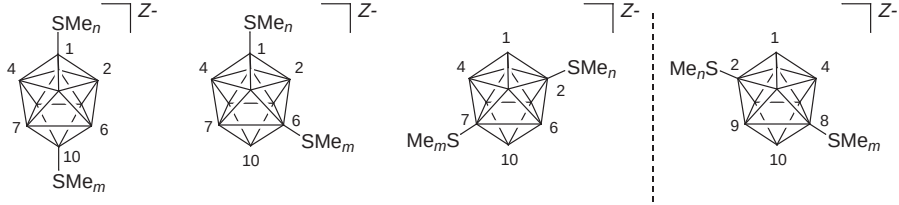
General Data

DMSO was dried over BaO and distilled under vacuum. The distilled DMSO was then placed under nitrogen and stored in a glovebox. ^{11}B, ^1H, and ^{13}C NMR spectra were obtained using one of three instruments, a Bruker AM-250 (^{11}B, 80.25 MHz; ^{13}C, 62.9 MHz; ^1H, 250.1 MHz), a Bruker DPX-400 (^{11}B, 128.3 MHz; ^{13}C, 100.6, MHz; ^1H, 400.1 MHz), or a Bruker DRX-500 (^{11}B, 160.5 MHz; ^{13}C, 125.76 MHz; ^1H, 500.1 MHz). Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Infrared spectra (wavenumbers in cm^{-1}) were collected on a Mattson Polaris FTIR spectrometer. Samples were prepared as KBr pellets. Mass spectra were obtained by The Ohio State University Campus Chemical Instrumentation Center. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

X-Ray Structure Determination

Single-crystal X-ray diffraction data were collected on one of two instruments, an Enraf–Nonius CAD4 diffractometer or an Enraf–Nonius Kappa CCD diffraction instrument. Both instruments employ graphite-monochromated MoKα radiation. The Enraf–Nonius CAD4 diffractometer was used to obtain structural data from **3b** and **5** at –60 °C. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in the 2θ range of 24–30°. Diffraction data were corrected for Lorentz and polarization effects and empirical absorption (empirically from Q-scan data).

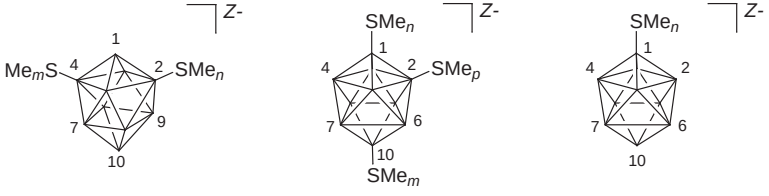
All remaining structures were determined using the Enraf–Nonius Kappa CCD system. A single crystal was mounted on the tip of a glass fiber coated with Fomblin oil (a pentafluoropolyether) and crystallographic data were collected at 150 K. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the Denzo-SMN package (Nonius BV, 1999)[12]. Absorption correction was applied using the SORTAV program[13] provided by MaXus software. All of the structures were solved by direct methods and refined using SHELXTL97 (difference electron density calculation, full matrix least-squares refinements) structure solution package[14]. Data merging was performed using the data preparation program supplied by SHELXTL97. All non-hydrogen atoms were located and refined anisotropically.



1, $n = m = 2$, $Z = 0$ **2**, $n = m = 2$, $Z = 0$ **3**, $n = m = 2$, $Z = 0$

1^{1-}, $n = 1$, $m = 2$, $Z = 1$ **2**$^{2-}$, $n = m = 1$, $Z = 2$

1^{2-}, $n = m = 1$, $Z = 2$



4, $n = m = 2$, $Z = 0$ **5**, $n = m = 2$, $p = 1$, $Z = 0$ **6**$^{1-}$, $n = 2$, $Z = 1$

6^{2-}, $n = 1$, $Z = 2$

CHART 1

Crystal data are given in Table I and average B–B and B–S bond distances are given in Table II. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe D-76344 Eggenstein–Leopoldshafen (Germany), e-mail: crysdata@fiz-karlsruhe.de on quoting the depository numbers CSD-412501, CSD-412503, CSD-412504, CSD-412505, CSD-412506, CSD-412502, and CSD-412500 for compounds **1**, **2**, **3b**, **4**, **5**, $\mathbf{2}^{2-}$, and $\mathbf{1}^{1-}$, respectively.

Preparation of 1,10- (**1**), 1,6- (**2**), and 2,7(8)-$(Me_2S)_2B_{10}H_8$ (**3**)

The method of Knoth, Hertler, and Muetterties[10] was used. $Cs_2B_{10}H_{10}$ (2.993 g, 7.794 mmol), 50 ml of glacial acetic acid, and 2 ml of DMSO were used. The product was vacuum filtered, washed with distilled water, and placed in a drying oven at 55 °C overnight (1.576 g, 84%).

Separation of 1,10- (**1**), 1,6- (**2**), and 2,7(8)-$(Me_2S)_2B_{10}H_8$ (**3**)

A column was prepared using 230–400 mesh silica gel and toluene–1,2-dichloroethane (1 : 1) as the eluent. The crude product containing **1**–**3** was dissolved in 6 ml of hot dichloromethane and placed on the column for separation. Isomers **1** and **3** eluted together, followed by **2**. The solvent was then removed from the products using a rotary evaporator resulting in **1** and **3** (0.966 g, 51%) and **2** (0.408 g, 22%). The mixture of **1** and **3** was dissolved in hot benzene–cyclohexane (1 : 1). The solvent was allowed to slowly evaporate over a period of days in which **1** preferentially crystallized. Following removal of **1** crystals and successive recrystallizations, the mother liquor contained an increasing amount of **3**. Crystals of **1** and **3** may be visually distinguished by their different crystalline habits. Crystals of **1** are small and cubic whereas those of **3** are long and needle-like.

1,10-$(Me_2S)_2B_{10}H_8$ (**1**): $^1H\{^{11}B\}$ NMR (500.1 MHz, CD_2Cl_2): 3.00 s, 12 H ($S(CH_3)_2$); 0.85 s, 8 H (H2-9). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2): 29.2 s ($S(CH_3)_2$). ^{11}B NMR (160.5 MHz, CD_2Cl_2): 9.3 s (B1, B10); –24.5 d, J_{B-H} = 135 (B2-B9). IR (KBr): 3 015 (w), 2 507 (s), 1 422 (m), 1 329 (w), 1 037 (m), 997 (m), 872 (w), 690 (w). MS (EI), *m/z*: calculated for $C_4H_{20}B_{10}S_2$ 240.444, found 240.200.

1,6-$(Me_2S)_2B_{10}H_8$ (**2**): $^1H\{^{11}B\}$ NMR (500.1 MHz, CD_2Cl_2): 3.86 s, 1 H (H10); 2.93 s, 6 H (axial $S(CH_3)_2$); 2.25 s, 6 H (equatorial $S(CH_3)_2$); 0.99 s, 2 H (H4, H5); 0.94 s, 2 H (either H2, H3, H7, H9); 0.84 s, 2 H (either H2, H3, H7, H9); 0.53 s, 1 H (H8). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2): 29.3 s (axial $S(CH_3)_2$); 26.7 s, equatorial ($S(CH_3)_2$). ^{11}B NMR (160.5 MHz, CD_2Cl_2): 2.6 s and d (B(1,10)); –17.2 s (B6); –22.6 d, J_{B-H} = 138 (B(4,5)); –26.6 d, J_{B-H} = 137 (B(2,3,7,8,9)). IR (KBr): 3 022 (w), 2 498 (s), 1 424 (m), 1 038 (w), 1 000 (w), 953 (w). MS (EI), *m/z*: calculated for $C_4H_{20}B_{10}S_2$ 240.444, found 240.200.

2,7(8)-$(Me_2S)_2B_{10}H_8$ (**3**): ^1H NMR (500.1 MHz, CD_2Cl_2): 2.3 s, 12 H. ^{11}B NMR (160.5 MHz, CD_2Cl_2): –2.4 s (B(1,10)); –15.6 s (B(2,7)); –24.9 d, J_{B-H} = 141 (B(3,6)); –29.2 d, J_{B-H} = 141 (B(4,5,8,9)). IR (KBr): 3 024 (w), 2 498 (s), 1 424 (m), 1 037 (w), 991 (w), 837 (w).

Preparation of additional 2,7(8)-$(Me_2S)_2B_{10}H_8$ (**3**) *via* the Dowtherm Process

A portion of the **1** and **3** mixture (0.201 g, 0.834 mmol) was added, along with biphenyl (4.086 g, 26.495 mmol) and diphenyl ether (11.65 ml), to a 250 ml round bottom flask with a magnetic stirbar. The flask was attached to a reflux condenser and placed in a sand bath. A thermometer was placed in the sand bath and the flask was wrapped with glass wool for insulation. The flask was heated while stirring the reaction mixture at 220–230 °C for

TABLE I
Crystallographic data for compounds **1**, **2**, **3b**, **4**, **5**, $\mathbf{1}^{1-}$, and $\mathbf{2}^{2-}$

Parameter	**1**	**2**	**3**	**4**	**5**	$\mathbf{1}^{1-}$	$\mathbf{2}^{2-}$
Empirical formula	$C_4H_{20}B_{10}S_2 \cdot C_6H_6$	$C_4H_{20}B_{10}S_2$	$C_4H_{20}B_{10}S_2$	$C_4H_{20}B_{10}S_2$	$C_5H_{22}B_{10}S_3$	$C_7H_{29}B_{10}NS_2$	$C_{10}H_{38}B_{10}N_2S_2$
M	318.53	240.42	120.21	240.42	286.51	299.53	358.64
Crystal system	monoclinic	monoclinic	trigonal	orthorhombic	monoclinic	orthorhombic	tetragonal
Space group	$P2_1/c$	$P2_1/n$	$P3_221$	$Pca2_1$	$P2_1/c$	*Pnma*	$P4_32_12$
Crystal color	white	white	white	white	white	white	white
a, Å	7.961(1)	7.611(2)	15.182(4)	25.898(1)	12.100(1)	16.049(1)	14.351(2)
b, Å	20.030(1)	38.10(2)	15.182(4)	12.547(1)	9.504(1)	9.432(1)	14.351(2)
c, Å	12.040(1)	14.778(3)	7.418(3)	8.761(1)	13.759(1)	11.901(1)	23.785(5)
α, °	90	90	90	90	90	90	90
β, °	101.53(1)	100.52(3)	90	90	93.21(1)	90	90
γ, °	90	90	120	90	90	90	90
V, Å^3	1 881.0(3)	4 213(2)	1 480.6(9)	2 846.9(4)	1 579.9(2)	1 801.4(3)	4 899(1)
Z	4	12	6	8	4	4	8
Final R_1 indices $[I > 2\sigma(I)]^a$	0.0328	0.0508	0.0520	0.0505	0.0366	0.0360	0.0573
wR_2 (all data)^b	0.0872	0.1199	0.1704	0.0963	0.0984	0.0873	0.1373
GOF	1.032	1.015	1.246	1.013	1.065	1.001	1.103

^{a} $R_1 = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$. ^{b} $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]\}^{1/2}$.

40 min and then the flask was allowed to cool. The product precipitated from solution when 125 ml pentane was added. It was vacuum filtered, washed with additional pentane, and placed in a drying oven at 55 °C overnight (0.160 g, 80%). The ratio of **1** to **3** changed from 61 : 1 to 6 : 1 (based upon ^{1}H NMR spectra).

Optical Rotation of 2,7(8)-$(Me_2S)_2B_{10}H_8$ (**3**)

A 0.022 g sample of a mixture of **1** and **3** (1.4 : 1) was dissolved in 2.273 g of toluene–1,2-dichloroethane (1 : 1) and placed in a Perkin–Elmer 241 MC Polarimeter using a 1 mm slit width and the 589.5 nm sodium line. Readings were taken after 5, 7, 10, 30, and 40 min and compared to readings taken of the solvent.

Separation of 2,7-$(Me_2S)_2B_{10}H_8$ (**3a**) from 2,8-$(Me_2S)_2B_{10}H_8$ (**3b**)

A concentrated sample of **1** and **3** in THF was placed in a 1.0 cm cuvette in a Perkin–Elmer Lambda 6 UV/VIS absorption spectrometer. A background scan of THF was taken prior to introducing the sample. The sample displayed a strong absorption in the 220–280 nm range. A 3 mg sample of **3** was dissolved in 2 ml of distilled THF. A 1.0 µl injection of this sample was introduced to a 4.6 mm × 25 cm Chiracel OD column on a Spectra Physics Analytical LC. The solvent system consisted of 40% isopropanol and 60% hexanes with a flow rate of 0.5 ml/min. A UV/VIS absorption detector was used, operating at 254 nm.

1,10-$(Me_2S)_2B_{10}H_8$ (**1**) and 2,3-$(Me_2S)_2B_{10}H_8$ (**4**) from 1,6-$(Me_2S)_2B_{10}H_8$ (**2**) *via* the Dowtherm Process

A portion of **2** (0.067 g, 0.28 mmol) was added, along with biphenyl (4.076 g, 26.43 mmol) and diphenyl ether (11.65 ml), to a 100 ml round bottom flask with a magnetic stirbar. The flask was attached to a reflux condenser and placed in a sand bath. A thermometer was placed in the sand bath and the flask was wrapped with glass wool for insulation. The flask was heated while stirring at 250–260 °C for 40 min and then allowed to cool. The product

TABLE II
Average bond distances (in Å) from single-crystal X-ray diffraction data

Compound	Apical B–S	Equatorial B–S	Apical-equatorial B–B	Equatorial-equatorial B–B	Interequatorial B–B
1	1.866(3)		1.682(7)	1.859(8)	1.810(8)
2	1.862(5)	1.886(5)	1.69(2)	1.84(2)	1.81(2)
3		1.885(5)	1.69(1)	1.82(2)	
4		1.883(8)	1.70(2)	1.83(1)	1.81(2)
5	1.854(2)	1.866(3)	1.678(8)	1.86(1)	1.810(9)
$\mathbf{1}^{1-}$	1.861(4)		1.688(8)	1.848(5)	1.811(6)
$\mathbf{2}^{2-}$	1.860(3)	1.871(3)	1.69(1)	1.83(1)	1.81(1)

precipitated from solution upon addition of 100 ml pentane. It was vacuum filtered, washed with additional pentane, and dried at 55 °C overnight (0.049 g, 74%). The crude mixture was separated using a Chromatotron (a centrifugal TLC separator) with 1 mm thick silica gel and toluene–dichloromethane (1 : 4) as the elutant. The product contained primarily **1** and **2**, along with a low yield of **4**.

2,3-(Me$_2$S)$_2$B$_{10}$H$_8$ (**4**): ^{11}B NMR (160.5 MHz, CD_2Cl_2): 4.9 d, J_{B-H} = 140 (B10); –8.2 d, J_{B-H} = 152 (B1); –15.6 s (B(2,3)); –24.0 d, $J_{B-H} \approx 160$ (B6); –25.5 d, J_{B-H} = 139 (B(4,5)); –27.7 d, J_{B-H} = 138 (B(7,9)); –32.0 d, J_{B-H} = 139 (B8).

1,10-(Me$_2$S)$_2$-2-(MeS)B$_{10}$H$_7$ (**5**)

A stream of gaseous hydrogen chloride was passed through a mixture of $Cs_2[B_{10}H_{10}]$ (5.206 g, 13.6 mmol) and 50 ml of dry DMSO for one hour with stirring. The temperature of the reaction mixture spiked quickly in excess of 150 °C. After the initial peak, the temperature was prevented from rising above 60 °C by occasional use of an ice bath. The reaction mixture was then added to approximately 150 ml of water with stirring. The yellow, oily solid was filtered and dissolved in acetone. The remaining water–DMSO solution was extracted with dichloromethane to remove any additional product. The acetone solution and dichloromethane solutions were added together and allowed to stand at room temperature for two days in which the color changed from yellow to pink. The solvent was then removed using a rotary evaporator. The product was passed through a chromatography column consisting of 230–400 mesh silica gel using ethyl acetate–hexane (4 : 1) as the eluent, resulting in **5** (0.563 g, 14%) along with an oily unidentifiable product after solvent removal. ^{1}H{^{11}B} NMR (500.1 MHz, CD_2Cl_2): 2.96 s, 6 H ($S(CH_3)_2$); 2.94 s, 6 H ($S(CH_3)_2$); 1.61 s, 3 H (SCH_3); 1.35 s, 2 H (H3, H5); 1.07 s, 2 H (H7, H8); 1.02 s, 2 H (H6, H9); 0.76 s, 1 H (H4). ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): 29.0 s ($S(CH_3)_2$ on B1); 27.8 s ($S(CH_3)_2$ on B10); 16.1 s (SCH_3). ^{11}B NMR (160.5 MHz, CD_2Cl_2): 9.1 s (B10); 5.4 s (B1); –11.5 s (B2); –20.2 d, J_{B-H} = 147 (B3, B5); –21.9 d, J_{B-H} = 175 (B7, B8); –23.2 d, J_{B-H} = 164 (B6, B9); –25.0 d, J_{B-H} = 167 (B4). IR (KBr): 3 011 (w), 2 918 (w), 2 501 (s), 1 422 (w), 1 038 (w), 1 001 (w). MS (EI), *m/z*: calculated for $C_5H_{22}B_{10}S_3$ 286.500, found 286.189.

[Me$_4$N]$_2$[1,10-(MeS)$_2$B$_{10}$H$_8$] ((Me$_4$N)$_2^+$**1**$^{2-}$) and [Me$_4$N]$_2$[1,6-(MeS)$_2$B$_{10}$H$_8$] ((Me$_4$N)$_2^+$**2**$^{2-}$)

Compound **1** (0.521 g, 2.16 mmol) was placed in a 100 ml round bottom flask equipped with a stirbar. In a glovebox, potassium (0.516 g, 13.19 mmol) was added and the flask was attached to a vacuum line and evacuated. Ammonia, dried over sodium metal (10–15 ml), was condensed into the flask using an ethanol–dry ice cold bath at –76 °C. Once all of the ammonia was transferred, the temperature of the cold bath was allowed to warm to –40 °C and the solution was stirred for 30 min at this temperature. When the ammonia melted, a blue color appeared and a non-condensable gas evolved. After 30 min, the solvent was removed, the residue re-dissolved in ethanol, and the anion precipitated by addition of [Me$_4$N]OH·5H$_2$O in minimal MeOH (0.566 g, 73%). Pure [Me$_4$N]$_2$[1,10-(MeS)$_2$B$_{10}$H$_8$] ((Me$_4$N)$_2^+$**1**$^{2-}$) was obtained after recrystallization from methanol–1-propanol. The crystals were washed with 5 ml of cold ethanol followed by 10 ml of pentane and dried at 70 °C overnight. ^{1}H{^{11}B} NMR (500.1 MHz, CD_3CN): 3.13 s, 24 H ($N(CH_3)_4$); 2.29 br s, 6 H (SCH_3); 0.29 s, 8 H (H(2-8)). ^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN): 56.4 t, 4 C ($N(CH_3)_4$); 18.5 s (SCH_3). ^{11}B NMR (160.5 MHz, CD_3CN): 7.3 s (B(1,10)); –27.5 d, J_{B-H} = 117 (B(2-9)). IR (KBr): 3 581 (w), 3 452 (w), 3 023 (w), 2 968 (w), 2 913 (w), 2 465 (s), 1 483 (s), 1 286 (w),

1 125 (w), 997 (w), 949 (m), 875 (w), 464 (w). For $C_{10}H_{38}B_{10}N_2S_2$ (358.6) calculated: 33.49% C, 10.67% H, 7.80% N; found: 32.28% C, 11.11% H, 7.34% N.

The same procedure was employed for the preparation of $(Me_4N)_2^+\mathbf{2}^{2-}$ from **2** (0.332 g, 75%). $^1H\{^{11}B\}$ NMR (500.1 MHz, CD_3CN): 3.14 s, 24 H ($N(CH_3)_4$); 2.99 s, 1 H (H10); 2.15 br s, 3 H (apical SCH_3); 0.58 s, 2 H (H(2,3)); 0.50 s, 2 H (H(7,9)); 0.42 s, 2 H (H(4,5)); 0.01 s, 1 H (H8). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): 56.4 t, 4 C ($N(CH_3)_4$); 18.2 s (SCH_3 apical); 17.53 s (SCH_3 equatorial). ^{11}B NMR (160.5 MHz, CD_3CN): 8.2 s (B1); –5.1 d, J_{B-H} = 137 (B10); –16.2 s (B6); –24.1 d, J_{B-H} = 133 (B(2,3)); –25.1 d, J_{B-H} = 147 (B(7,9)); –26.3 d, J_{B-H} = 158 (B(4,5)); 29.7 d, J_{B-H} = 130 (B8). IR (KBr): 3 485 (w), 3 021 (w), 2 911 (w), 2 464 (s), 1 484 (m), 949 (w), 807 (w), 479 (w). For $C_{10}H_{38}B_{10}N_2S_2$ (358.6) calculated: 33.49% C, 10.67% H, 7.80% N; found: 33.21% C, 11.05% H, 7.72% N.

$[Me_4N][1\text{-}(Me_2S)B_{10}H_9]$ ($(Me_4N)^+\mathbf{6}^{1-}$)

This procedure is based upon that of Knoth, Hertler, and Muetterties[10]. A stream of hydrogen chloride gas was passed into a solution of $(Me_4N)_2B_{10}H_{10}$ (1.197 g, 4.50 mmol) in 50 ml of dry DMSO for 5 min at a rate such that the temperature was maintained between 50 and 60 °C with cooling from an ice water bath. The solution was then poured with stirring into 100 ml of water and filtered through a glass frit to remove a small amount of $(Me_2S)_2B_{10}H_8$. Excess $[Me_4N]Cl$ was then added to precipitate $(Me_4N)^+\mathbf{6}^{1-}$ (0.677 g, 59%). $^1H\{^{11}B\}$ NMR (500.1 MHz, DMSO-d_6): 3.08 s, 12 H ($N(CH_3)_4$); 2.87 s, 6 H (SMe_2); 0.53 s, 4 H (H(2-5)); 0.11 s, 4 H (H(6-9)). $^{13}C\{^1H\}$ NMR (125.76 MHz, DMSO-d_6): 54.4 t ($N(CH_3)_4$); 28.7 s (SMe_2). ^{11}B NMR (160.5 MHz, DMSO-d_6): 8.0 d, J_{B-H} = 143 (B10); 0.9 s (B1); –25.2 d, J_{B-H} = 127 (B(2-5)); –27.8 d, J_{B-H} = 126 (B(6-9)). IR (KBr): 3 025 (w), 2 473 (s), 1 482 (m), 1 417 (w), 1 034 (w), 985 (w), 950 (w).

$[Me_4N]_2[1\text{-}(MeS)B_{10}H_9]$ ($(Me_4N)_2^+\mathbf{6}^{2-}$) and $[Me_4N][1\text{-}(MeS)\text{-}10\text{-}(Me_2S)B_{10}H_8$ ($(Me_4N)^+\mathbf{1}^{1-}$)

A 25 ml three-neck round bottom flask equipped with a condenser and stirbar was charged with 0.081 g (3.4 mmol) of 95% NaH in a glovebox. About 3 ml of ethanol was added and the resulting pressure released through a bubbler. After the gas evolution ceased, 0.16 ml of 97% EtSH (2.2 mmol) was added to the flask by a syringe *via* a rubber septum. Under nitrogen, 0.416 g (1.64 mmol) of $(Me_4N)^+\mathbf{6}^{1-}$ was added through one of the necks along with 10–12 ml of dry CH_3CN. The mixture was refluxed for 2 h. The resulting solution was transferred into a 100 ml round bottom flask and the volatiles were removed by rotary evaporation. About 30 ml of distilled water was added to the residue. Solid $[Me_4N]Cl$ was added until complete precipitation of $(Me_4N)_2^+\mathbf{6}^{2-}$ as a white solid. The solid was filtered, washed with 2–3 ml of distilled water, 4 ml of cold ethanol, 15 ml of pentane and dried at 70 °C overnight (0.241 g, 47%). $^1H\{^{11}B\}$ NMR (500.1 MHz, DMSO-d_6): 3.09 s, 24 H ($N(CH_3)_4$); 2.14 s, 3 H (SCH_3); 0.17 s, 4 H (H(2-5)); –0.18 s (H(6-9)). $^{13}C\{^1H\}$ NMR (125.76 MHz, DMSO-d_6): 54.4 t ($N(CH_3)_4$); 18.0 s (SCH_3). ^{11}B NMR (160.5 MHz, DMSO-d_6): 8.0 s (B1); –3.1 d, J_{B-H} = 112 (B10); –27.6 d, J_{B-H} = 95 (B(2-5)); –29.4 d, J_{B-H} = 100 (B(6-9)). IR (KBr): 2 915 (w), 2 485 (s), 1 482 (w), 1 322 (br), 1 019 (w), 948 (w).

The same procedure was employed for the preparation of $(Me_4N)^+\mathbf{1}^{1-}$ from **1** (0.303 g, 56%). $^1H\{^{11}B\}$ NMR (500.1 MHz, DMSO-d_6): 3.09 s, 12 H ($N(CH_3)_4$); 2.88 s, 6 H ($S(CH_3)_2$); 2.19 s, 3 H (SCH_3); 0.56 s, 4 H (H(2-5)); 0.37 s, 4 H (H(6-9)). $^{13}C\{^1H\}$ NMR (125.76 MHz, DMSO-d_6): 54.4 t, 4 C ($N(CH_3)_4$); 28.7 s ($S(CH_3)_2$); 17.7 s (SCH_3). ^{11}B NMR (160.5 MHz,

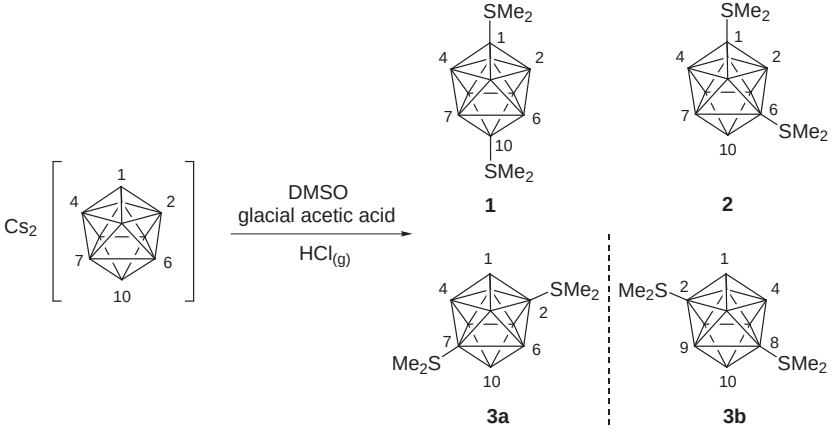
DMSO-d_6): 17.4 s (B1); –0.4 s (B10); –26.2 d, $J_{B\text{-}H}$ = 90 (B(2-5)); –26.9 d, $J_{B\text{-}H}$ = 85 (B(6-9)). IR (KBr): 3 033 (w), 2 913 (w), 2 481 (s), 2 341 (w), 1 482 (w), 1 323 (br), 945 (w).

RESULTS AND DISCUSSION

*Preparation and Separation of Neutral Disubstituted Isomers of the Form $(Me_2S)_2B_{10}H_8$ (**1–4**)*

The disubstituted inner sulfonium salts 1,10-$(Me_2S)_2B_{10}H_8$ (**1**), 1,6-$(Me_2S)_2B_{10}H_8$ (**2**) and the enantiomers 2,7-$(Me_2S)_2B_{10}H_8$ (**3a**) and 2,8-$(Me_2S)_2B_{10}H_8$ (**3b**) were first prepared and isolated by Knoth, Hertler, and Muetterties[10]. However, NMR instrumentation at that time (1964) was not adequate to fully assign boron signals. Molecular structures were not determined, but the correct structures were deduced. We prepared these compounds (Scheme 1) in order to obtain starting materials for new derivative chemistry. They were characterized with respect to molecular structure (Figs 1 and 2, Tables I and II) and spectroscopic data was obtained employing modern instrumentation.

Since **3a** and **3b** are formed in low yield, a more efficient route to form these enantiomers was explored. The mixture of **1** and **3a**, **3b**, obtained from the procedure indicated in Scheme 1, was dissolved in Dowtherm A [10,15,16] (a mixture of diphenyl ether and biphenyl) and heated under reflux at 230 °C. At the temperature of reflux **1** rearranges to **3a**, **3b** presumably through the polyhedral diamond-square-diamond mechanism[1b,16] to give a



SCHEME 1
Synthesis of **1**, **2**, **3a**, and **3b** from $Cs_2[B_{10}H_{10}]$

ten-fold increase of **3a**, **3b** relative to the original ratio. The original mixture contained a 61 : 1 ratio of **1** to **3a**, **3b** and after heating the ratio was 6 : 1. Ratios are based on integration of the proton resonances of the dimethyl sulfide substituents on **1** and **3a**, **3b** . Lower temperatures did not promote conversion and higher temperatures caused decomposition.

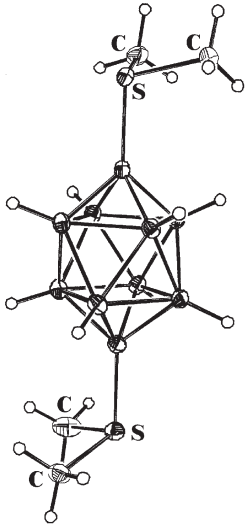


FIG. 1
Molecular structure of 1,10-$(Me_2S)_2B_{10}H_8$ (**1**)

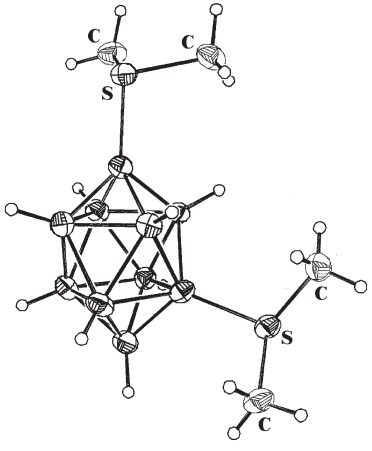


FIG. 2
Molecular structure of 1,6-$(Me_2S)_2B_{10}H_8$ (**2**)

An analytical chiral column separated the **3a**, **3b** enantiomers to produce two bands on the column, of approximately equal area, that were observed by means of a UV detector (Fig. 3). However, we were unable to separate sufficient amounts of the separated enantiomers to measure their optical rotation. It should be noted that Hertler earlier[15] separated the related enantiomers 2,7-$(Me_3N)_2B_{10}H_8$ and 2,8-$(Me_3N)_2B_{10}H_8$. Also, for a review of HPLC separation of chiral boranes see Plešek[17] and included references.

The molecular structure of 2,8-$(Me_2S)_2B_{10}H_8$ was determined by single-crystal X-ray analysis (Fig. 4, Tables I and II). It is of interest that the 2,7- and 2,8-isomers of $(Me_2S)_2B_{10}H_8$ crystallize separately but only the 2,8-$(Me_2S)_2B_{10}H_8$ crystals suitable for X-ray analysis could be successfully

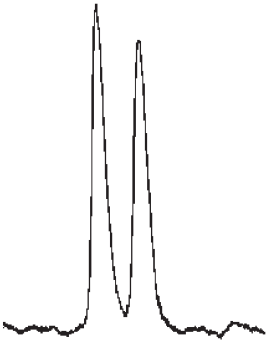


FIG. 3
Resolved enantiomers 2,7-$(Me_2S)_2B_{10}H_8$ (**3a**) and 2,8-$(Me_2S)_2B_{10}H_8$ (**3b**) using an analytical chiral column (retention times are 31.69 and 34.92 min)

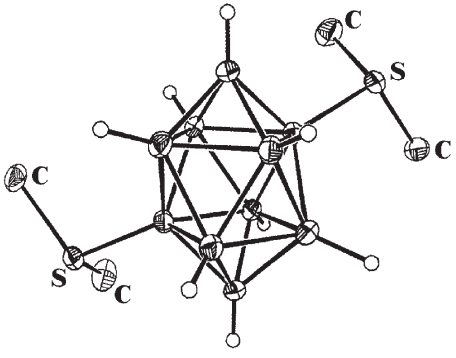


FIG. 4
Molecular structure of 2,8-$(Me_2S)_2B_{10}H_8$ (**3b**) (methyl hydrogen atoms omitted for clairity)

grown. No evidence for a 2,7-$(Me_2S)_2B_{10}H_8$ crystal was found. Jasper, Jones, Mattern, Huffman, and Todd[18] reported a similar result concerning the separation of the 2,7(8)-enantiomers of $(Me_2PPh)_2B_{10}H_8$ upon crystallization, in which the 2,8-isomer was chosen for structure determination.

In Dowtherm A, compound **2** was converted to **1** and the previously unreported isomer 2,3-$(Me_2S)_2B_{10}H_8$ (**4**) (Fig. 5, Tables I and II). This conversion is believed to proceed through a diamond-square-diamond mechanism[1b,16] (Fig. 6). For unknown reasons the conversion **2** to **1** and **4** was not always reproducible. The reaction was attempted in separate experiments at time intervals ranging from 5–40 min and at temperatures ranging from 245–260 °C. Each time, the major components of the reaction mixture were **2** (remaining starting material) and **1**, with the former being present in greater amount, and **4** as a very minor product.

The ^1H and ^{11}B NMR chemical shifts agree well with those reported earlier[10] for **1**. The $^{11}B\{^1H\}$ NMR spectrum reflects the high symmetry (D_{4d}) of

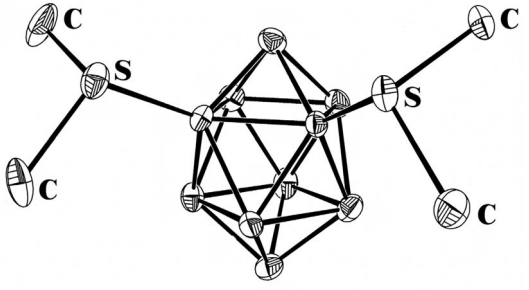


FIG. 5
Molecular structure of 2,3-$(Me_2S)_2B_{10}H_8$ (**4**) (methyl hydrogen atoms and boron cage hydrogen atoms omitted for clarity)

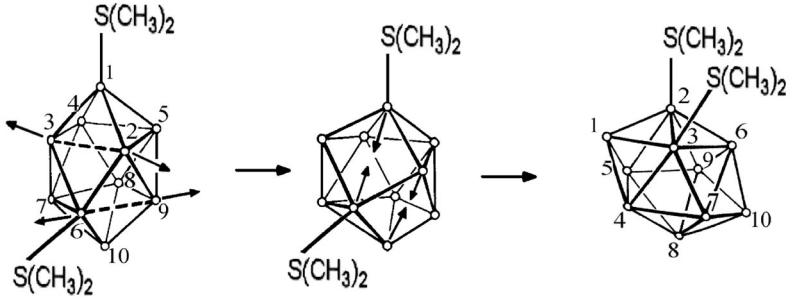


FIG. 6
Diamond-square-diamond mechanism for formation of 2,3-$(Me_2S)_2B_{10}H_8$ (**4**) from 1,6-$(Me_2S)_2B_{10}H_8$ (**2**)

the molecule with two resonances appearing at 9.3 and –25.3 ppm for the apical and equatorial boron nuclei, respectively. The ^1H NMR spectrum of **2** contains two singlets at 3.00 and 2.30 ppm corresponding to the apical and equatorial dimethyl sulfide substituents, respectively. A ^1H-$^{11}B\{^1H\}$ 2D HETCOR experiment was used to assign the protons of the boron cage. One noticeable feature of the $^1H\{^{11}B\}$ NMR spectrum of **2** is the downfield signal (3.86 ppm) of the proton on boron 10 relative to the equatorial protons (0.99–0.53 ppm), which was also noted by Muetterties, Balthis, Chia, Knoth, and Miller[2]. A ^{11}B-$^{11}B\{^1H\}$ 2D COSY NMR experiment was utilized to assign each of the boron resonances of **2**. Surprisingly, the substituted and unsubstituted apical boron signals overlap. Only a single resonance at 2.30 ppm is observed for the equatorial dimethyl sulfide protons of **3**. A ^{11}B-$^{11}B\{^1H\}$ 2D COSY was employed in assigning the ^{11}B resonances of **3**. The ^{11}B-$^{11}B\{^1H\}$ 2D COSY of **4** was also employed in assigning the ^{11}B resonances of **4**. The ^{11}B NMR spectrum does not contain any extraordinary features.

*Neutral Trisubstituted Isomer, 1,10-$(Me_2S)_2$-2-(MeS)$B_{10}H_7$ (**5**)*

Knoth and Muetterties speculated that the formation of the trisubstituted cation, $[(Me_2S)_3B_{10}H_7]^+$, is possible[1b]. Using the same procedure as that for the syntheses of the neutral disubstituted isomers of $(Me_2S)_2B_{10}H_8$ but allowing the temperature to initially spike to over 150 °C, the neutral trisubstituted, 1,10-$(Me_2S)_2$-2-(MeS)$B_{10}H_7$ (**5**) compound (Fig. 7, Tables I and II), was synthesized and isolated in 14% yield. The ^1H NMR spectrum contains three resonances at 2.95 and 2.94 ppm for the apical dimethyl sulfide groups and 1.62 ppm for the equatorial methylthio group. The $^1H\{^{11}B\}$ NMR spectrum of **5** parallels its $^{11}B\{^1H\}$ NMR spectrum in the sense that the order of assignments is the same. The ^{11}B and $^{11}B\{^1H\}$ NMR spectra contain three singlets for the substituted boron nuclei. Assignments of these resonances are based upon the ^{11}B-$^{11}B\{^1H\}$ 2D COSY NMR spectrum. Presumably **5** formed as a result of decomposition of $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]^+$. Single-crystal X-ray diffraction analysis confirmed the structure of **5**. See Table II for average bond distances.

*The Monosubstituted $[1\text{-}(Me_2S)B_{10}H_9]^-$ (**6**$^{1-}$)*

Knoth, Hertler, and Muetterties[10] produced salts of the monosubstituted anions $[1\text{-}(Me_2S)B_{10}H_9]^-$ (**6**$^{1-}$) and $[2\text{-}(Me_2S)B_{10}H_9]^-$. We obtained the tetramethylammonium salt of **6**$^{1-}$ in 59.4% yield.

The dimethyl sulfide proton signal appears at 2.87 ppm in the ^1H NMR spectrum of $\mathbf{6}^{1-}$. In the $^1H\{^{11}B\}$ spectrum, the resonance that corresponds to the protons on borons 2–5 have a chemical shift of 0.53 ppm and the protons on borons 6–9 have a shift of 0.11 ppm. Assignments were based upon a ^1H-$^{11}B\{^1H\}$ HETCOR experiment.

*Sodium Ethanethiolate Reduction of [1-(Me_2S)$B_{10}H_9$]$^-$ ($\mathbf{6}^{1-}$) and 1,10-(Me_2S)$_2B_{10}H_8$ (**1**). Formation of [1-(MeS)$B_{10}H_9$]$^{2-}$ ($\mathbf{6}^{2-}$) and [1-(MeS)-10-(Me_2S)$B_{10}H_8$]$^-$ ($\mathbf{1}^{1-}$)*

Knoth, Hertler, and Muetterties used potassium phthalimide and tributylphosphine as a method for generating [(MeS)(Me_2S)$B_{10}H_8$]$^-$ and [(MeS)$_2B_{10}H_2Cl_6$]$^{2-}$, respectively[10]. Here, an alternate nucleophilic reagent, sodium ethanethiolate[11c], was used due to the ease of workup and high yield. Sodium ethanethiolate, which is created *in situ* from EtSH and EtONa, reacts at the carbon site to cause demethylation. Reduction by an alkali metal in liquid ammonia achieves the same result, but higher yields were obtained using EtSNa.

Demethylation of $\mathbf{6}^{1-}$ and **1** with sodium ethanethiolate produced $\mathbf{6}^{2-}$ and $\mathbf{1}^{1-}$ (Eqs (*1*) and (*2*)).

$$[Me_4N][1\text{-}(Me_2S)B_{10}H_9] \xrightarrow[CH_3CN\text{–}EtOH]{EtSNa} Na_2[1\text{-}(MeS)B_{10}H_9] + EtSMe \qquad (1)$$

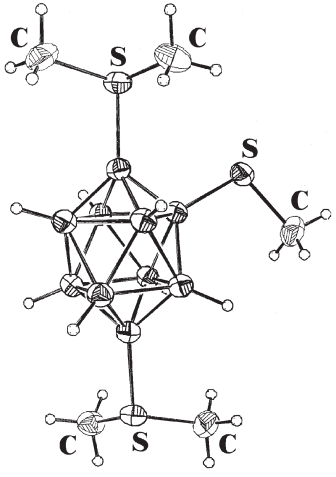


FIG. 7
Molecular structure of 1,10-(Me_2S)$_2$-2-(MeS)$B_{10}H_8$ (**5**)

$$1,10\text{-}(Me_2S)_2B_{10}H_8 \xrightarrow[CH_3CN\text{–}EtOH]{EtSNa} Na[1\text{-}(MeS)\text{-}10\text{-}(Me_2S)B_{10}H_8] + EtSMe \quad (2)$$

The $[Me_4N]$ salts of $\mathbf{6}^{2-}$ and $\mathbf{1}^{1-}$ were isolated in 47 and 56% yields, respectively.

In the ^1H NMR spectrum of $\mathbf{6}^{2-}$, there is an upfield shift of the methyl protons from 2.87 ppm for $\mathbf{6}^{1-}$ to 2.14 ppm. The $^1H\{^{11}B\}$ NMR spectrum contains two resonances for the different equatorial protons at 0.12 ppm corresponding to protons on B2–B5 and –0.13 ppm for those on B6–B9. This again is an upfield shift relative to the parent compound. The ^{11}B NMR spectrum of $\mathbf{6}^{2-}$ is significantly different from that of the parent compound, $\mathbf{6}^{1-}$. The chemical shift of B1 for $\mathbf{6}^{1-}$ resides at 0.8 ppm whereas for $\mathbf{6}^{2-}$ it is at 8.0 ppm. B10 has a chemical shift of 7.4 ppm for $\mathbf{6}^{1-}$ and a chemical shift of –3.5 ppm for $\mathbf{6}^{2-}$.

The ^1H NMR spectrum of $\mathbf{1}^{1-}$ contains a resonance at 2.88 ppm due to the SMe_2 substituent and another signal at 2.19 ppm that is assigned to the SMe substituent. These chemical shifts are upfield from the single resonance found at 3.00 ppm for the dimethyl sulfide groups of the parent compound, **1**. The protons on the cage appear at 0.56 ppm for protons on B2–B5 and 0.37 ppm for those bonded to B6–B9. The ^{11}B NMR chemical shifts of B1 and B10 are at 17.4 and –0.4 ppm, respectively for $\mathbf{1}^{1-}$, compared to 9.3 ppm for the apical borons of neutral **1**. A single-crystal X-ray diffraction analysis of $\mathbf{1}^{1-}$ confirmed the structure (Fig. 8, Tables I and II).

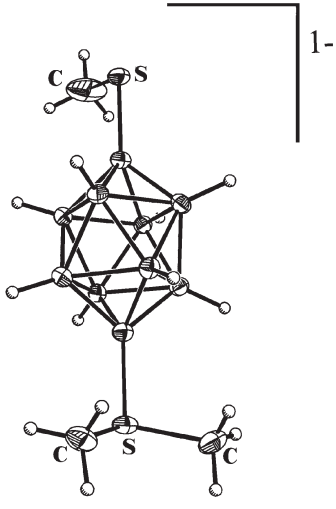


FIG. 8
Molecular structure of $[1\text{-}(MeS)\text{-}10\text{-}(Me_2S)B_{10}H_8]^-$ ($\mathbf{1}^{1-}$)

*Alkali Metal Reduction of and 1,10-$(Me_2S)_2B_{10}H_8$ (**1**) and 1,6-$(Me_2S)_2B_{10}H_8$ (**2**). Formation of the Bissulfide Dianions, $[1,10\text{-}(MeS)_2B_{10}H_8]^{2-}$ ($\mathbf{1}^{2-}$) and $[1,6\text{-}(MeS)_2B_{10}H_8]^{2-}$ ($\mathbf{2}^{2-}$)*

The inner sulfonium salts, **1** and **2**, were reduced with an excess of alkali metal according to Eq. (*3*).

$$(Me_2S)_2B_{10}H_8 \xrightarrow[-40\ °C,\ M = Na,\ K]{M,\ NH_3} M_2[(Me_2S)_2B_{10}H_8] + 2\ CH_4 + \text{other produsts} \quad (3)$$

The reaction proceeded quickly with the evolution of methane and exclusive formation of the new dianions, $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$. We expect that reduction proceeds *via* a radical pathway suggested[11c] earlier for $(Me_2S)_2B_{12}H_{10}$. The tetramethylammonium salts of $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ were isolated in 73 and 75% yields, respectively.

The ^1H NMR spectrum of $(Me_4N)_2\mathbf{1}^{2-}$ contains a broad resonance for the sulfur methyl protons at 2.25 ppm, which is shifted upfield from the sharp singlet of **1**. A similar shift is apparent when comparing $[(MeS)_2B_{12}H_{10}]^{2-}$ to $(Me_2S)_2B_{12}H_{10}$ [11c]. Additionally, the ^{11}B and ^{13}C NMR spectra of $\mathbf{1}^{2-}$ display an upfield shift in the boron and carbon resonances relative to **1**. The same effect is evident in the ^1H, ^{11}B, and ^{13}C NMR spectra of $(Me_4N)_2\mathbf{2}^{2-}$.

Single-crystal X-ray diffraction analysis confirms that compound $\mathbf{2}^{2-}$ is the dianion derived from neutral **2** (Fig. 9, Tables I and II).

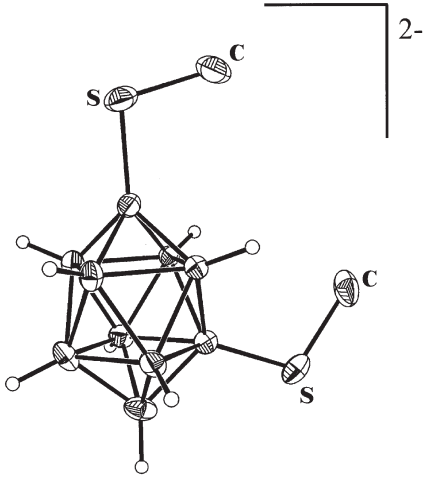


FIG. 9
Molecular structure of $[1,6\text{-}(MeS)_2B_{10}H_8]^{2-}$ ($\mathbf{2}^{2-}$) (methyl hydrogen atoms omitted for clarity)

In summary, dimethyl sulfide derivatives of *closo*-$B_{10}H_{10}^{2-}$, 1,10-$(Me_2S)_2B_{10}H_8$ and 1,6-$(Me_2S)_2B_{10}H_8$ were revisited with the discovery of two new neutral compounds, 2,3-$(Me_2S)_2B_{10}H_8$ and 1,10-$(Me_2S)_2$-2-$(MeS)B_{10}H_7$, a trisubstituted complex. The 1,10-$(Me_2S)_2B_{10}H_8$ isomer was converted to the 2,7-$(Me_2S)_2B_{10}H_8$ and 2,8-$(Me_2S)_2B_{10}H_8$ enantiomers and the 1,6-$(Me_2S)_2B_{10}H_8$ isomer was converted to a mixture of 1,10-$(Me_2S)_2B_{10}H_8$ and 2,3-$(Me_2S)_2B_{10}H_8$. Sodium ethanolate reduced [1-$(Me_2S)B_{10}H_9]^-$ and 1,10-$(Me_2S)B_{10}H_8$ to the new dianion [1-$(MeS)B_{10}H_9]^{2-}$ and the monoanion [1-(MeS)-10-$(Me_2S)B_{10}H_8]^-$ while 1,6-$(Me_2S)_2B_{10}H_8$ and 1,10-$(Me_2S)_2B_{10}H_8$ were reduced by alkali metal in liquid ammonia to produce the new dianions [1,6-$(MeS)_2B_{10}H_8]^{2-}$ and [1,10-$(MeS)_2B_{10}H_8]^{2-}$.

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