Electronic Supplemental Information

Synthesis and Cluster Structure Distortions of Biscarborane Dithiol, Thioether, and Disulfide

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Experimental

All synthetic manipulations were carried out either in a nitrogen-filled VAC drybox or on a dual manifold Schlenk-style vacuum line, unless stated otherwise. The solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å Linde-type molecular sieves. Benzene-d^6 was degassed and stored over activated 4 Å Linde-type molecular sieves. NMR spectra were recorded using Varian spectrometers at 400 (^{1}H) and 128 (^{11}B) MHz, reported in δ (parts per million) and referenced to the residual ^{1}H signals of the deuterated solvent or an external $BF_3(Et_2O)$ (^{11}B(δ): 0.0 ppm) standard.

1,1′-bis(*o*-carborane)[1] was prepared according to the previously reported literature procedure. *Ortho*-carborane $C_2B_{10}H_{12}$ (Boron Specialties) and potassium hexamethyldisilazide (KHMDS, 0.7 M solution in THF) were used as received.

Synthesis of Biscarborane Dithiol $(1\text{-HS-}C_2B_{10}H_{10})_2$ (**2**)

Under a nitrogen atmosphere, biscarborane (50 mg, 0.52 mmol) was dissolved in tetrahydrofuran. Potassium bis(trimethyl silyl) amide (0.7 M in THF, 0.6 mL, 2.4 equiv.) was then added dropwise to the solution and allowed to stir overnight. The solvent was removed, and the resulting potassium salt was washed with hexane to remove excess base and silylamine. The salt was redissolved in THF and sulfur (12 mg, 0.26 equiv.) was then added to the solution, and allowed to stir for 22.5 hours at 60 °C to form the potassium biscarboranyl dithiolate. The solution was exposed to air at this point. The solvent was then removed, and the resulting solid was washed with ether. Dichloromethane (5 mL) was added to dissolve the salt and then the solution was exposed to air and acidified with dilute aqueous hydrochloric acid (5 mL). The solution was stirred until all solids dissolved. The organic layer was extracted to DCM and dried over magnesium sulfate. The solvent was removed under vacuum to obtain an off-white powder. (29 mg, 40%) ^{1}H NMR (300 MHz, $CDCl_3$): 4.192 (s, 1H). ^{11}B NMR (300 MHz, $CDCl_3$): -0.7 (s, 2B), -3.6 (s, 2B), -5.9 (s, 2B), -8.2 (s, 4B). HRMS m/z: 349.309.

Synthesis of Tetrabutylammonium Biscarborane Dithiolate $[NBu_4]_2(S\text{-}C_2B_{10}H_{10})_2$ ($(NBu_4)_2[\mathbf{2}^{2-}]$)

Potassium biscarboranyl dithiolate (50 mg, 0.12 mmol) was dissolved in methanol, and tetrabutyl ammonium bromide (73 mg, 0.25 mmol) was added. The solution was allowed to sit at room temperature overnight. The methanol was removed, and an orange powder formed. This powder was washed with hexane and then redissolved in THF. Single crystals of the product were grown by slow evaporation of the THF solution. ^{11}B NMR (300 MHz, THF): -2.8, -7.1, -11.5, -13.7.

Synthesis of Biscarboranyl Methyl Thioether $(MeS\text{-}C_2B_{10}H_{10})_2$ (**3**)

Under a nitrogen atmosphere, biscarboranyl dithiol **2** (50 mg, 0.14 mmol) was dissolved in benzene and methyl iodide (0.70 mmol, 5 equiv.) was added. The dithiol was then deprotonated by the addition of 1,8-bis(dimethylamino)naphthalene (proton sponge) (2 eq, 0.28 mmol) and allowed to stir overnight. Volatiles were removed under vacuum. The residue was redissolved in ether and filtered through a thin layer of silica gel. Single crystals of product crystallized upon slow evaporation of its ether solution (46 mg, 92%). ^{1}H NMR (C_6D_6): δ 1.56 (s, 6H, $(\text{-S-C}H_3)_2$) ^{11}B{H} NMR (C_6D_6): δ 0.3, -2.7 , -7.1 , -11.1.

Synthesis of Biscarboranyl Disulfide $(S\text{-}C_2B_{10}H_{10})_2$ (**4**)

Biscarboranyl dithiol **2** (50 mg, 0.14 mmol) was dissolved in dichloromethane and a solution of excess iodine in DCM was added. Volatiles were removed under vacuum. Solids were extracted to hexanes and the solution was passed through a thin layer of silica gel. Hexanes was removed under vacuum producing an off-white solid which was redissolved in minimal amount of ether. The product crystallized by slow evaporation (48 mg, 94%). ^{11}B{H} NMR ($CDCl_3$): δ 0.7 , -2.5 , -6.1 , -7.5 , -10.3 , -11.7.

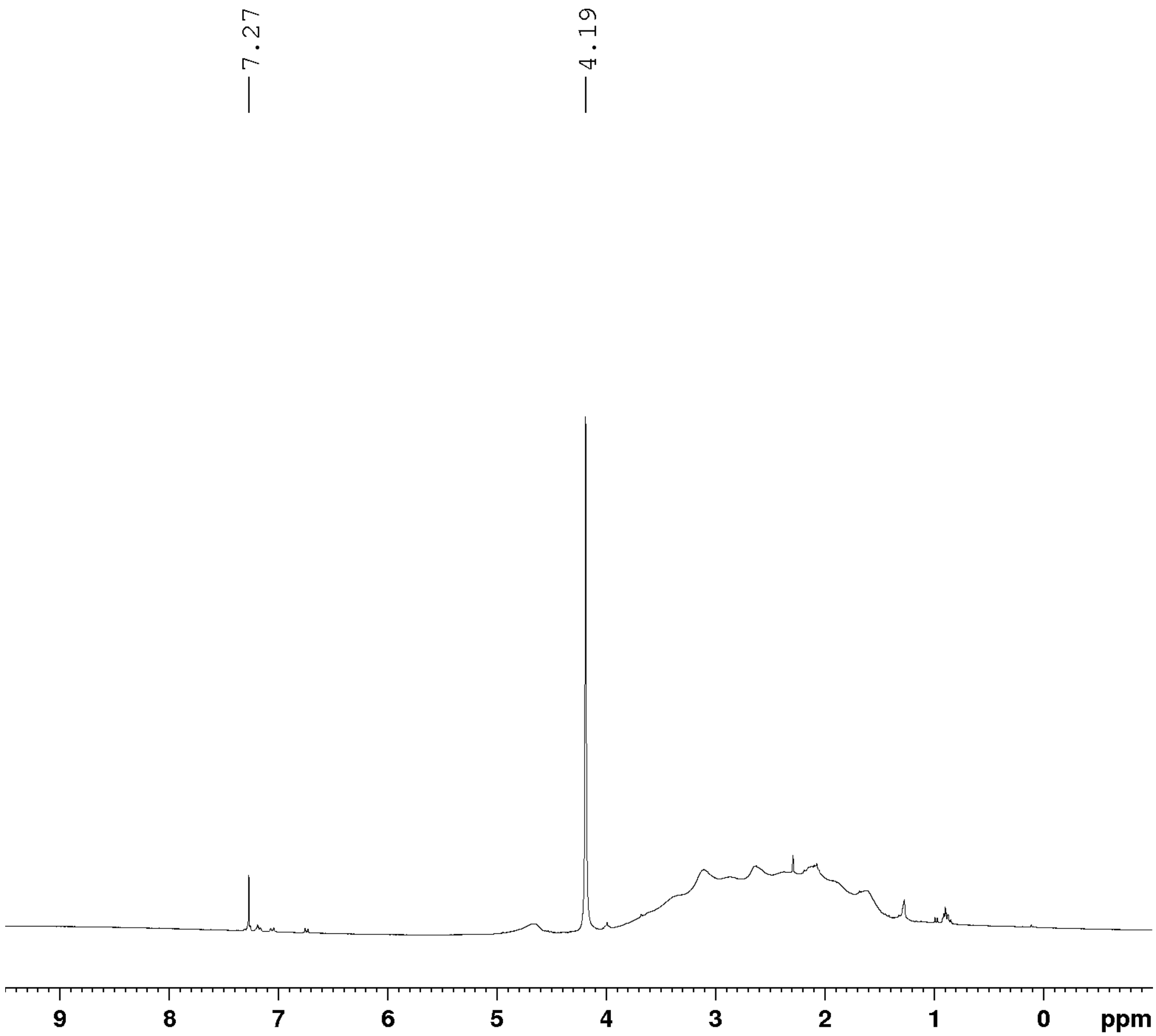

Figure S-1. The ^{1}H NMR spectrum of Biscarborane Dithiol $(1\text{-}HS\text{-}C_2B_{10}H_{10})_2$ (**2**).

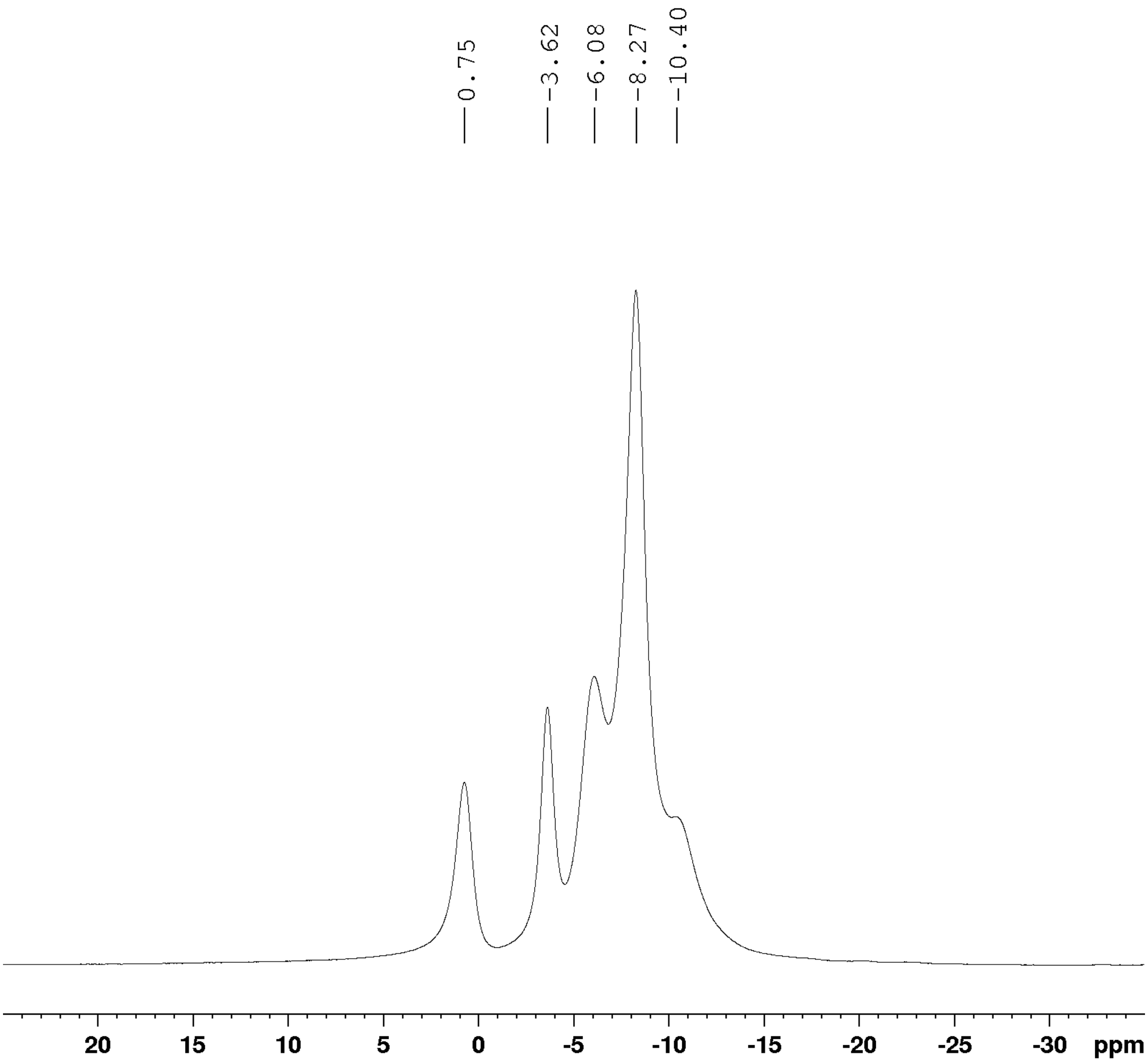

Figure S-2 The $^{11}B\{H\}$ NMR spectrum of Biscarborane Dithiol $(1\text{-}HS\text{-}C_2B_{10}H_{10})_2$ (**2**).

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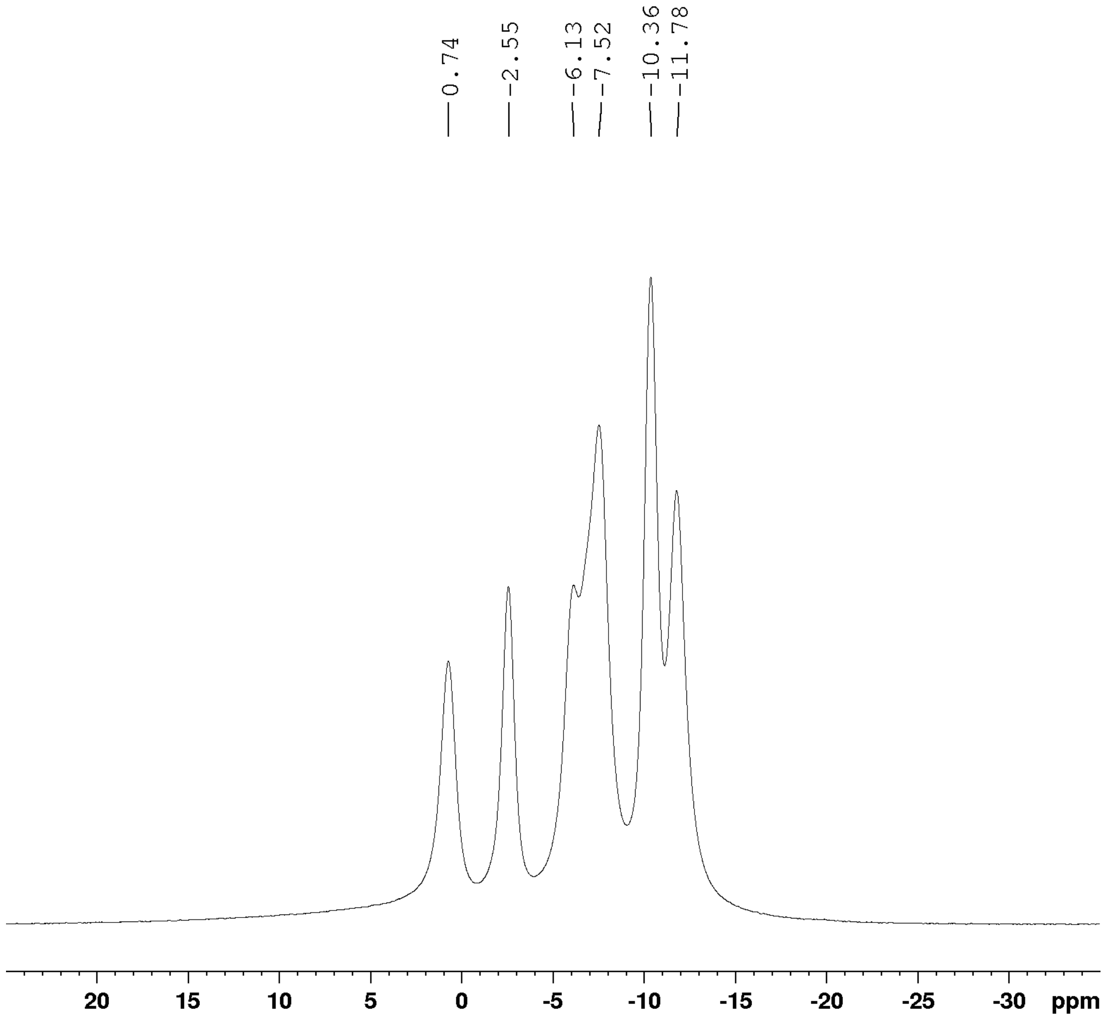


Figure S-3 The $^{11}B\{H\}$ NMR spectrum of Biscarborane Dithiol $(1\text{-HS-}C_2B_{10}H_{10})_2$ (**2**).

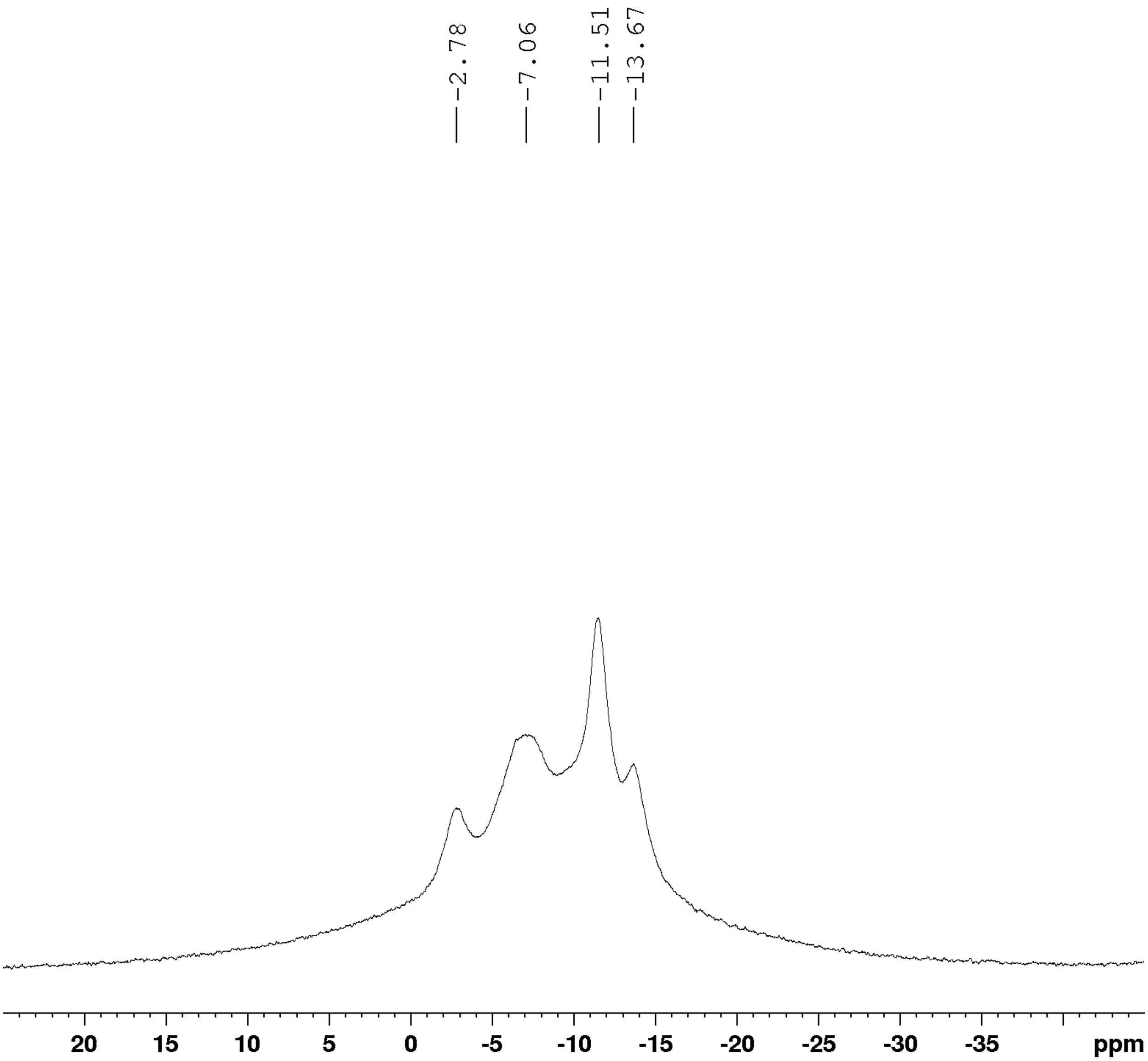


Figure S-4. The ^{11}B{H} NMR spectrum of Biscarborane Thiolate $(NBu_4)_2(1\text{-}S\text{-}C_2B_{10}H_{10})_2$ (**$(NBu_4)_2[2^{2-}]$**).

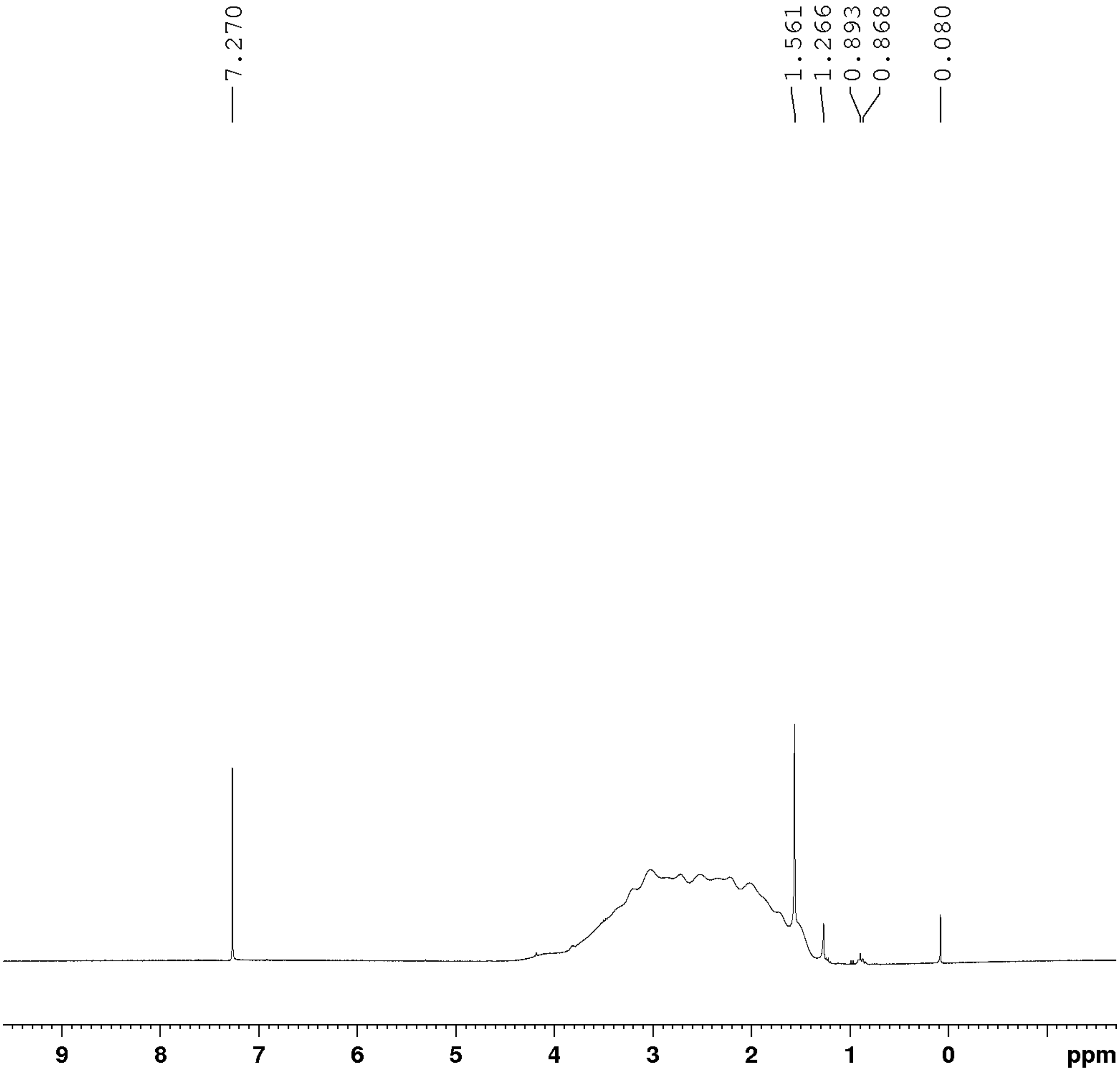


Figure S-5 The ^{1}H NMR spectrum of Biscarboranyl Disulfide (**4**).

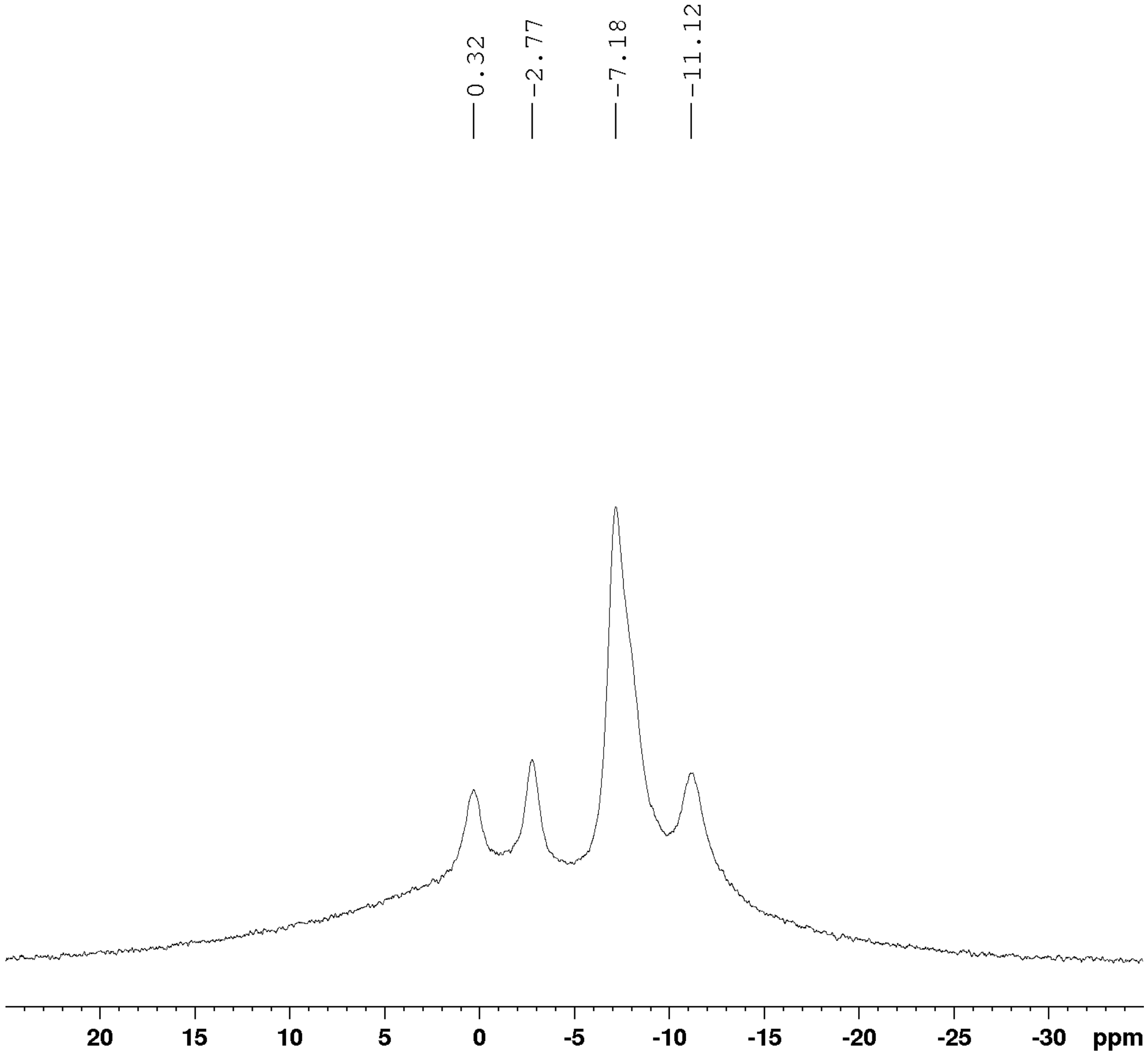


Figure S-6. The $^{11}B\{H\}$ NMR Biscarboranyl Methyl Thioether $(MeS\text{-}C_2B_{10}H_{10})_2$ (**3**)

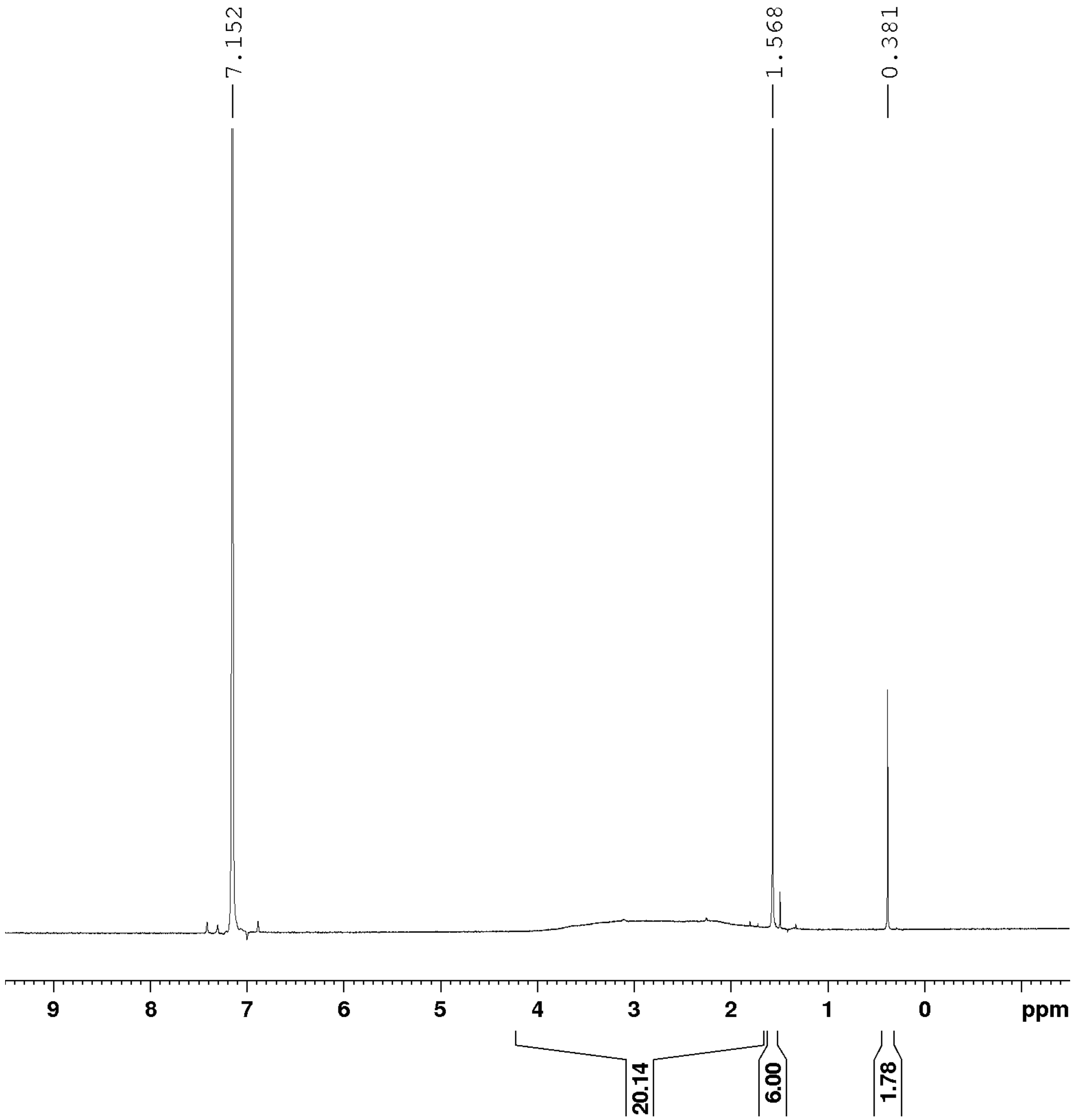


Figure S-7. The ^{1}H NMR Biscarboranyl Methyl Thioether $(MeS-C_2B_{10}H_{10})_2$ (**3**)

X-Ray Structure Determination, Biscarborane Dithiol (1-HS-$C_2B_{10}H_{10}$)$_2$ (2)

X-ray intensity data from a colorless plate were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å). The raw area detector data frames were reduced and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.[1,2] The structure was solved with SHELXT.[3] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018[3] using OLEX2.[4]

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was uniquely consistent with the space group $P2_1/n$, which was confirmed by structure solution. The asymmetric unit consists of half of one molecule, which is located on a crystallographic inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and freely refined. The largest residual electron density peak in the final difference map is 0.38 $e^-/Å^3$, located 1.06 Å from S1.

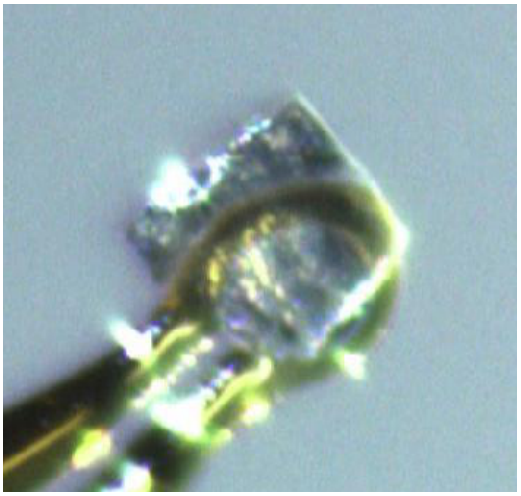


Image of data crystal

(1) **APEX3** Version 2018.1-0 and **SAINT+** Version 8.38A. Bruker AXS, Inc., Madison, Wisconsin, USA, 2016.

(2) **SADABS**-2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. and Stalke D. *J. Appl. Cryst.* **2015**, *48*, 3-10.

(3) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8. (b) **SHELXL:** Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.

(4) **OLEX2**: a complete structure solution, refinement and analysis program. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table S-1 Crystal data and structure refinement for Biscarborane Dithiol (1-HS-$C_2B_{10}H_{10}$)$_2$ (2)

Identification code	th01065a
Empirical formula	$C_4H_{22}B_{20}S_2$
Formula weight	350.53
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.6040(16)
b/Å	9.2193(19)
c/Å	13.110(3)
α/°	90
β/°	95.532(5)
γ/°	90
Volume/Å^3	914.8(3)
Z	2
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	0.275
F(000)	356.0
Crystal size/mm^3	0.2 × 0.14 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.41 to 52.9
Index ranges	$-9 \leq h \leq 8$, $-11 \leq k \leq 11$, $-16 \leq l \leq 16$
Reflections collected	8991
Independent reflections	1859 [R_{int} = 0.0630, R_{sigma} = 0.0471]
Data/restraints/parameters	1859/0/162
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.1187
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1340
Largest diff. peak/hole / e Å^{-3}	0.38/-0.44

X-Ray Structure Determination, Biscarborane Disulfide $(S\text{-}C_2B_{10}H_{10})_2$ (4)

X-ray intensity data from a colorless block were collected at 300(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo Kα radiation, $\lambda = 0.71073$ Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.[1,2] The structure was solved with SHELXT.[3] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018[3] using OLEX2.[4]

The compound crystallizes in the orthorhombic system. The pattern of systematic absences in the intensity data was consistent with the space groups $Pna2_1$ and $Pnma$; intensity statistics were consistent with an acentric structure. The acentric group $Pna2_1$ was confirmed by obtaining a reasonable and stable solution, and was further verified with ADDSYM.[5] The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in Fourier difference maps and refined freely. The largest residual electron density peak in the final difference map is 0.14 $e^-/Å^3$, located 0.73 Å from C2. The absolute structure (Flack) parameter after the last refinement cycle was -0.01(3).

(1) **APEX3** Version 2019.11-0 and **SAINT+** Version 8.40B. Bruker Nano, Inc., Madison, WI, USA, 2019.

(2) **SADABS**-2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. and Stalke D. *J. Appl. Cryst.* **2015**, *48*, 3-10.

(3) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8. (b) **SHELXL:** Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.

(4) **OLEX2**: a complete structure solution, refinement and analysis program. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(5) (a) LePage, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264-269. (b) Spek, A. L. *J. Appl. Crystallogr.*, **1988**, *21*, 578-579. (c) Spek, A. L. *Acta Crystallogr., Sect A* **1990**, *46*, C34. (d) **PLATON**: Spek, A.L. *Acta Cryst.,* **2009**, *D65*, 148-155.

Table S-2. Crystal data and structure refinement for Biscarborane Disulfide ($(S-C_2B_{10}H_{10})_2$) (4)

Identification code	jrxr01177a
Empirical formula	$C_4H_{20}B_{20}S_2$
Formula weight	348.52
Temperature/K	300(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	21.2698(8)
b/Å	6.9867(2)
c/Å	12.5238(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1861.11(11)
Z	4
$\rho_{calc}g/cm^3$	1.244
μ/mm^{-1}	0.270
F(000)	704.0
Crystal size/mm^3	0.38 × 0.22 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.138 to 56.584
Index ranges	$-28 \leq h \leq 28, -8 \leq k \leq 9, -16 \leq l \leq 16$
Reflections collected	44313
Independent reflections	4612 [R_{int} = 0.0614, R_{sigma} = 0.0319]
Data/restraints/parameters	4612/1/315
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0747
Final R indexes [all data]	R_1 = 0.0432, wR_2 = 0.0799
Largest diff. peak/hole / e $Å^{-3}$	0.14/-0.15
Flack parameter	-0.01(3)

X-Ray Structure Determination, Biscarboranyl Methyl Thioether $(MeS\text{-}C_2B_{10}H_{10})_2$ (3)

X-ray intensity data from a colorless plate were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo Kα radiation, $\lambda = 0.71073$ Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.[1,2] The structure was solved with SHELXT.[3] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018[3] using OLEX2.[4]

The compound crystallizes in the triclinic system. The space group *P*-1 (No. 2) was confirmed by structure solution. The asymmetric unit consists of half of one molecule, which is located on a crystallographic inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. Those bonded to boron atoms were refined freely. The methyl hydrogens were placed in geometrically idealized positions with *d*(C-H) = 0.98 Å, allowed to rotate as a rigid group to the orientation of maximum observed electron density and refined with isotropic displacement parameters. The largest residual electron density peak in the final difference map is 0.39 $e^-/\text{Å}^3$, located 0.76 Å from C2.

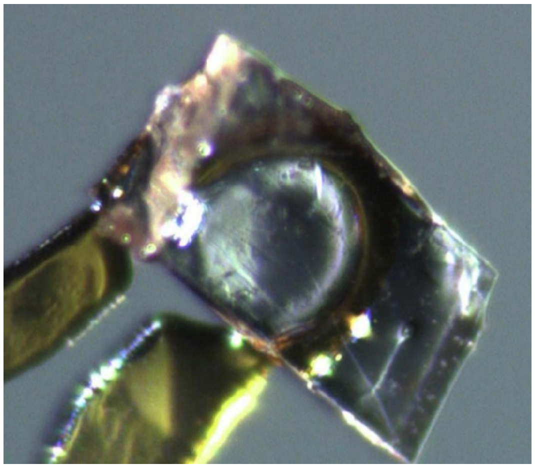


Image of crystal used for data collection

(1) **APEX3** Version 2019.11-0 and **SAINT+** Version 8.40B. Bruker Nano, Inc., Madison, WI, USA, 2019.

(2) **SADABS**-2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. and Stalke D. *J. Appl. Cryst.* **2015**, *48*, 3-10.

(3) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8. (b) **SHELXL:** Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.

(4) **OLEX2**: a complete structure solution, refinement and analysis program. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table S-3 Crystal data and structure refinement for Biscarboranyl Methyl Thioether (MeS-$C_2B_{10}H_{10})_2$ (3)

Identification code	jrxr_02_soa
Empirical formula	$C_6H_{26}B_{20}S_2$
Formula weight	378.59
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.9280(5)
b/Å	8.0128(6)
c/Å	10.0978(7)
α/°	79.295(2)
β/°	70.057(2)
γ/°	70.854(2)
Volume/$Å^3$	496.07(6)
Z	1
ρcalcg/cm^3	1.267
μ/mm^{-1}	0.258
F(000)	194.0
Crystal size/mm^3	0.54 × 0.24 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.4 to 70.136
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$
Reflections collected	25076
Independent reflections	4378 [R_{int} = 0.0443, R_{sigma} = 0.0273]
Data/restraints/parameters	4378/0/171
Goodness-of-fit on F^2	1.101
Final R indexes [I>=2σ (I)]	R_1 = 0.0269, wR_2 = 0.0756
Final R indexes [all data]	R_1 = 0.0337, wR_2 = 0.0784
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.33

X-Ray Structure Determination, $[HNEt_3]_2(S\text{-}C_2B_{10}H_{10})_2$ ($(HNEt_3)_2[2^{2-}]$)

X-ray intensity data from a yellow needle were collected at 300(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.[1,2] The structure was solved with SHELXT.[3] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018[3] using OLEX2.[4]

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space groups *Ia* and *I*2/*a*, the latter of which was confirmed by structure solution. The *I*-centered monoclinic cell is the conventional cell in this case, as it gives shorter *a* and *c* axes than *C*-centered and also avoids a large beta angle of 121°. The asymmetric unit in *I*2/*a* consists of one $[HN(CH_2CH_3)_3]^+$ cation and half of one $[C_4B_{20}H_{20}S_2]^-$ anion, which is located on a crystallographic inversion center. The $[HN(CH_2CH_3)_3]^+$ cation is disordered over two positions with a major component occupancy of 0.885(3). The geometry of the minor component was restrained to be similar to that of the major using a SHELX SAME instruction. All non-hydrogen atoms were refined with anisotropic displacement parameters except for most atoms of the minor disorder component (isotropic). Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms with d(C-H) = 0.97 Å and Uiso(H) = 1.2Ueq(C) for methylene hydrogen atoms and d(C-H) = 0.96 Å and Uiso(H) = 1.5Ueq(C) for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. Hydrogen atoms bonded to nitrogen and boron were located in difference Fourier maps and refined freely. The largest residual electron density peak in the final difference map is 0.21 $e^-/Å^3$, located 0.89 Å from H13D.

(1) **APEX3** Version 2019.11-0 and **SAINT+** Version 8.40B. Bruker Nano, Inc., Madison, WI, USA, 2019.

(2) **SADABS**-2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. and Stalke D. *J. Appl. Cryst.* **2015**, *48*, 3-10.

(3) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst.* **2015**, *A71*, 3-8. (b) **SHELXL:** Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.

(4) **OLEX2**: a complete structure solution, refinement and analysis program. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table S-4. Crystal data and structure refinement for $[HNEt_3]_2(S\text{-}C_2B_{10}H_{10})_2$ ($(HNEt_3)_2[2^{2-}]$)

Identification code	jrxr01186y
Empirical formula	$C_{16}H_{52}B_{20}N_2S_2$
Formula weight	552.91
Temperature/K	300(2)
Crystal system	monoclinic
Space group	I2/a
a/Å	20.5322(6)
b/Å	7.1970(2)
c/Å	23.6579(10)
α/°	90
β/°	106.9640(10)
γ/°	90
Volume/Å^3	3343.8(2)
Z	4
ρcalcg/cm^3	1.098
μ/mm^{-1}	0.174
F(000)	1176.0
Crystal size/mm^3	0.4 × 0.18 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.632 to 55.044
Index ranges	$-26 \leq h \leq 26$, $-9 \leq k \leq 9$, $-30 \leq l \leq 30$
Reflections collected	61183
Independent reflections	3842 [R_{int} = 0.0547, R_{sigma} = 0.0191]
Data/restraints/parameters	3842/12/258
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.1064
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1131
Largest diff. peak/hole / e Å^{-3}	0.21/-0.16

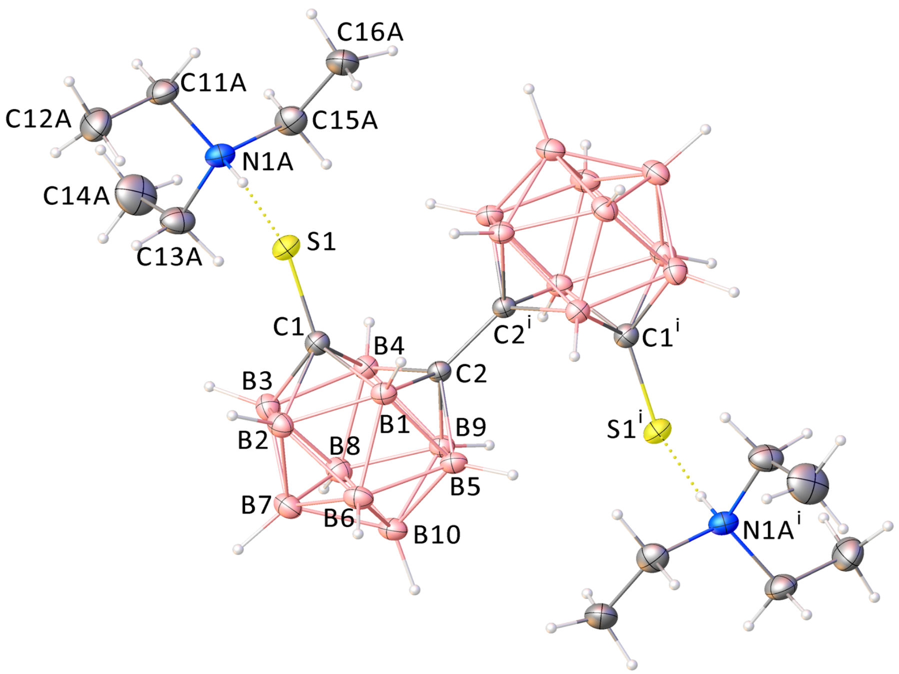
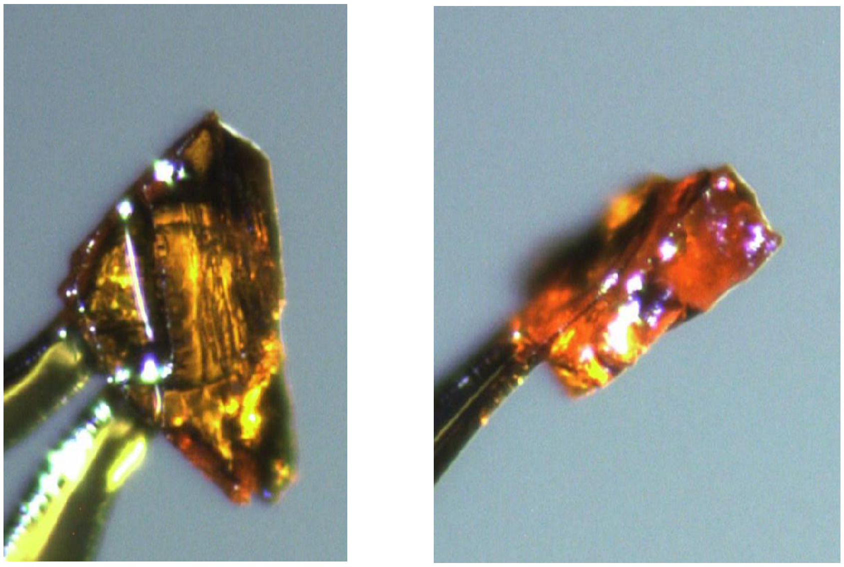


Figure S-8. Displacement ellipsoids of [HNEt$_3$]$_2$(S-C$_2$B$_{10}$H$_{10}$)$_2$ (**(HNEt$_3$)$_2$[2^{2-}]**) drawn at the 20% probability level. The anion is located on a crystallographic inversion center and only half is present per HNEt$_3$ cation. The HNEt$_3$ cation is positionally disordered, major occupancy is 0.885(3). Superscripts denote symmetry-equivalent atoms.

X-Ray Structure Determination, Tetrabutylammonium Biscarborane Dithiolate $[NBu_4]_2(S\text{-}C_2B_{10}H_{10})_2$ ($(NBu_4)_2[2^{2-}]$)

X-ray intensity data from an orange plate were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, $\lambda = 0.71073$ Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.[1,2] The structure was solved with SHELXT.[3] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018[3] using OLEX2.[4]

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space groups *Cc* and *C*2/*c*; intensity statistics were consistent with an acentric structure. The solution program XT found *Cc*; the subsequent stable refinement model obtained in *Cc* was checked with ADDSYM, which found no missed symmetry elements. The asymmetric unit in *Cc* consists of two crystallographically independent $[C_4B_{20}H_{20}S_2]^{2-}$ anions and four independent $N(CH_2CH_2CH_2CH_3)^{4+}$ (NBu_4^+) cations. Three of the four NBu_4^+ cations (N2, N3, N4) are disordered, affecting the ethyl or propyl ends of the butyl groups (cations N2 and N3) or the entire cation (N4). The occupancies of each disordered butyl group were refined independently but were constrained to sum to one. Like C-C bond distances between disordered atoms in the cations were restrained to be similar (SHELX SADI). 1,3- distances of disordered groups were restrained to 2.50(2) Å. A SHELX SAME instruction was applied to cation N4, restraining its 1,2- and 1,3- distances to be similar to those in cation N1. All non-hydrogen atoms were refined with anisotropic displacement parameters except for some disordered atoms (isotropic). All hydrogen atoms were placed in geometrically idealized positions and included as riding atoms with d(B-H) = 1.120 Å and Uiso(H) = 1.2Ueq(B) for hydrogen atoms of the carborane cage, d(C-H) = 0.99 Å and Uiso(H) = 1.2Ueq(C) for methylene hydrogen atoms and d(C-H) = 0.98 Å and Uiso(H) = 1.5Ueq(C) for methyl hydrogens. The largest residual electron density peak in the final difference map is 0.76 $e^-/Å^3$, located 1.50 Å from H41B.



Images of the data crystal

(1) **APEX3** Version 2016.5-0 and **SAINT+** Version 8.37A. Bruker AXS, Inc., Madison, Wisconsin, USA, 2016.

(2) **SADABS**-2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. and Stalke D. *J. Appl. Cryst.* **2015**, *48*, 3-10.

(3) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8. (b) **SHELXL:** Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.

(4) **OLEX2**: a complete structure solution, refinement and analysis program. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table S-5. Crystal data for Tetrabutylammonium Biscarborane Dithiolate $[NBu_4]_2(S\text{-}C_2B_{10}H_{10})_2$ $((NBu_4)_2[2^{2-}])$

Identification code	th01085b
Empirical formula	$C_{36}H_{92}B_{20}N_2S_2$
Formula weight	833.43
Temperature/K	100(2)
Crystal system	monoclinic
Space group	Cc
a/Å	43.403(10)
b/Å	11.311(3)
c/Å	20.644(5)
α/°	90
β/°	103.059(7)
γ/°	90
Volume/Å^3	9873(4)
Z	8
ρ_{calc}g/cm^3	1.121
μ/mm^{-1}	0.138
F(000)	3632.0
Crystal size/mm^3	0.38 × 0.28 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.05 to 50.054
Index ranges	$-51 \leq h \leq 51$, $-13 \leq k \leq 13$, $-24 \leq l \leq 24$
Reflections collected	70274
Independent reflections	17370 [R_{int} = 0.0613, R_{sigma} = 0.0493]
Data/restraints/parameters	17370/219/1095
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0964, wR_2 = 0.2530
Final R indexes [all data]	R_1 = 0.1161, wR_2 = 0.2733
Largest diff. peak/hole / e Å^{-3}	0.76/-0.44
Flack parameter	0.09(2)

X-Ray Structure Determination, $[K(THF)_3]_2(S\text{-}C_2B_{10}H_{10})_2$ ($K_2[2^{2-}]$)

X-ray intensity data from a colorless needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.[1,2] Final unit cell parameters were determined by least-squares refinement of 9978 reflections taken from the data set. The structure was solved with SHELXT.[3] Subsequent difference Fourier calculations and full-matrix least-squares refinement against *F*2 were performed with SHELXL-2018[3] using OLEX2.4

The compound crystallizes in the triclinic system. The space group *P*-1 (No. 2) was confirmed by structure solution. The asymmetric unit consists of one potassium ion, three independent tetrahydrofuran (THF) molecules and half of one $C_4B_{20}H_{20}S_2^{2-}$ ligand, which is located on a crystallographic inversion center. One THF molecule (O3, C31–C34) is disordered over two conformations. Two atoms (C32, C33) are affected and were refined with split positions. The major disorder component fractional occupancy refined to 0.61(1). 1,2- and 1,3- distances in the disordered THF were restrained to be similar to those in an ordered THF (O1/C11-C14) using SHELX SAME restraints. All non-hydrogen atoms were refined with anisotropic displacement parameters. The THF methylene hydrogen atoms were located in Fourier difference maps before being placed in geometrically idealized positions and included as riding atoms with *d*(C-H) = 0.99 Å and *U*iso(H) = 1.2*U*eq(C). All hydrogen atoms bonded to boron of the carborane cage were located and refined freely. The largest residual electron density peak in the final difference map is 0.31 e-/Å3, located 0.79 Å from C24.

(1) **APEX3** Version 2016.5-0 and **SAINT+** Version 8.37A. Bruker AXS, Inc., Madison, Wisconsin, USA, 2016.

(2) **SADABS**-2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. and Stalke D. *J. Appl. Cryst.* **2015**, *48*, 3-10.

(3) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst.* **2015**, *A71*, 3-8. (b) **SHELXL:** Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.

(4) **OLEX2**: a complete structure solution, refinement and analysis program. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table S-6. $[K(THF)_3]_2(S\text{-}C_2B_{10}H_{10})_2$ ($K_2[2^{2-}]$).

Identification code	th01083a
Empirical formula	C28H68B20K2O6S2
Formula weight	859.34
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.8304(3)
b/Å	10.2692(4)
c/Å	12.8148(4)
α/°	95.495(2)
β/°	106.1310(10)
γ/°	107.5560(10)
Volume/Å3	1161.85(7)
Z	1
ρcalcg/cm3	1.228
μ/mm-1	0.332
F(000)	454.0
Crystal size/mm3	0.22 × 0.09 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.592 to 61.298
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	28320
Independent reflections	7111 [Rint = 0.0394, Rsigma = 0.0417]
Data/restraints/parameters	7111/30/316
Goodness-of-fit on F2	1.020
Final R indexes [I>=2σ (I)]	R1 = 0.0372, wR2 = 0.0803
Final R indexes [all data]	R1 = 0.0566, wR2 = 0.0879
Largest diff. peak/hole / e Å-3	0.31/-0.29

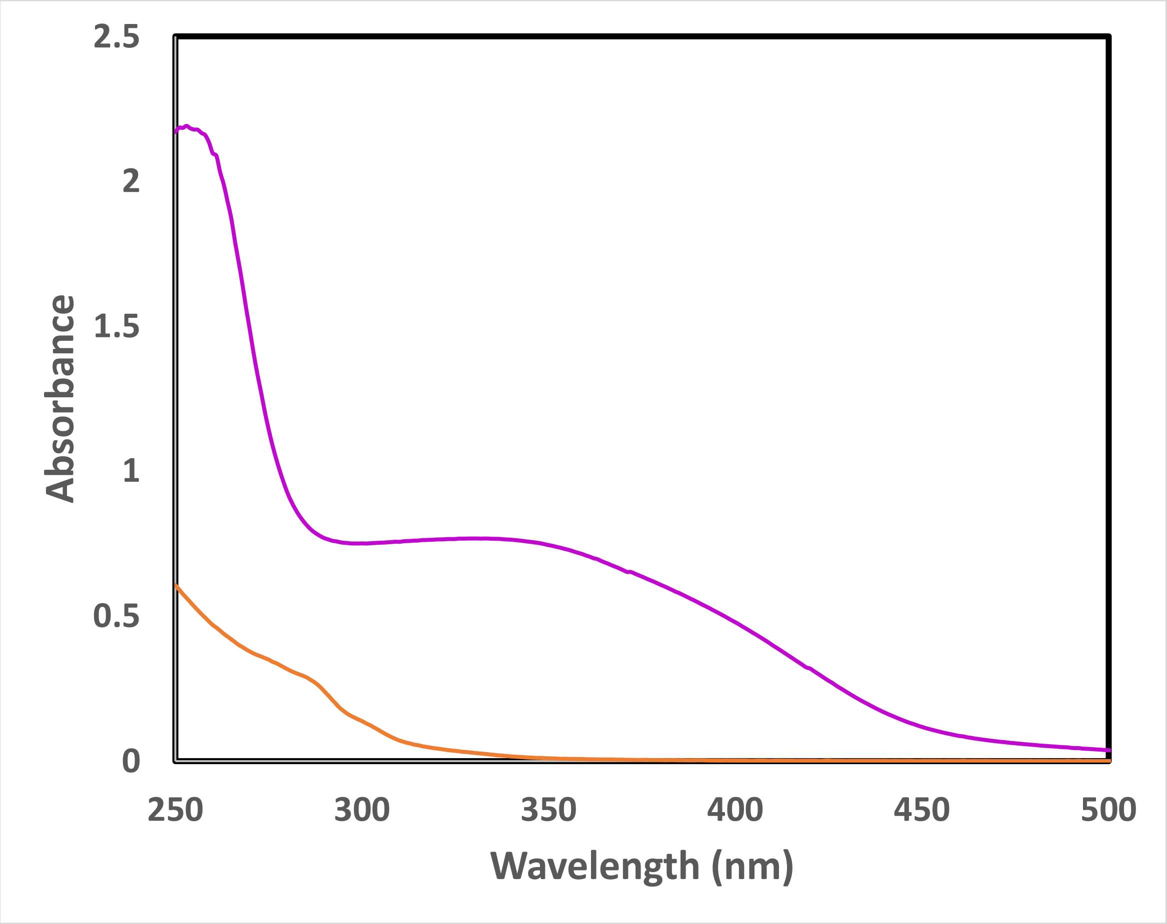


Figure S-9. UV-vis absorption spectra of biscarboranyl dithiol **2** (0.5 mM in dichloromethane, orange line) and deprotonated biscarboranyl dithiolate (**$(HNEt_3)_2[2^{2-}]$**) (0.2 mM in dichloromethane, purple line).

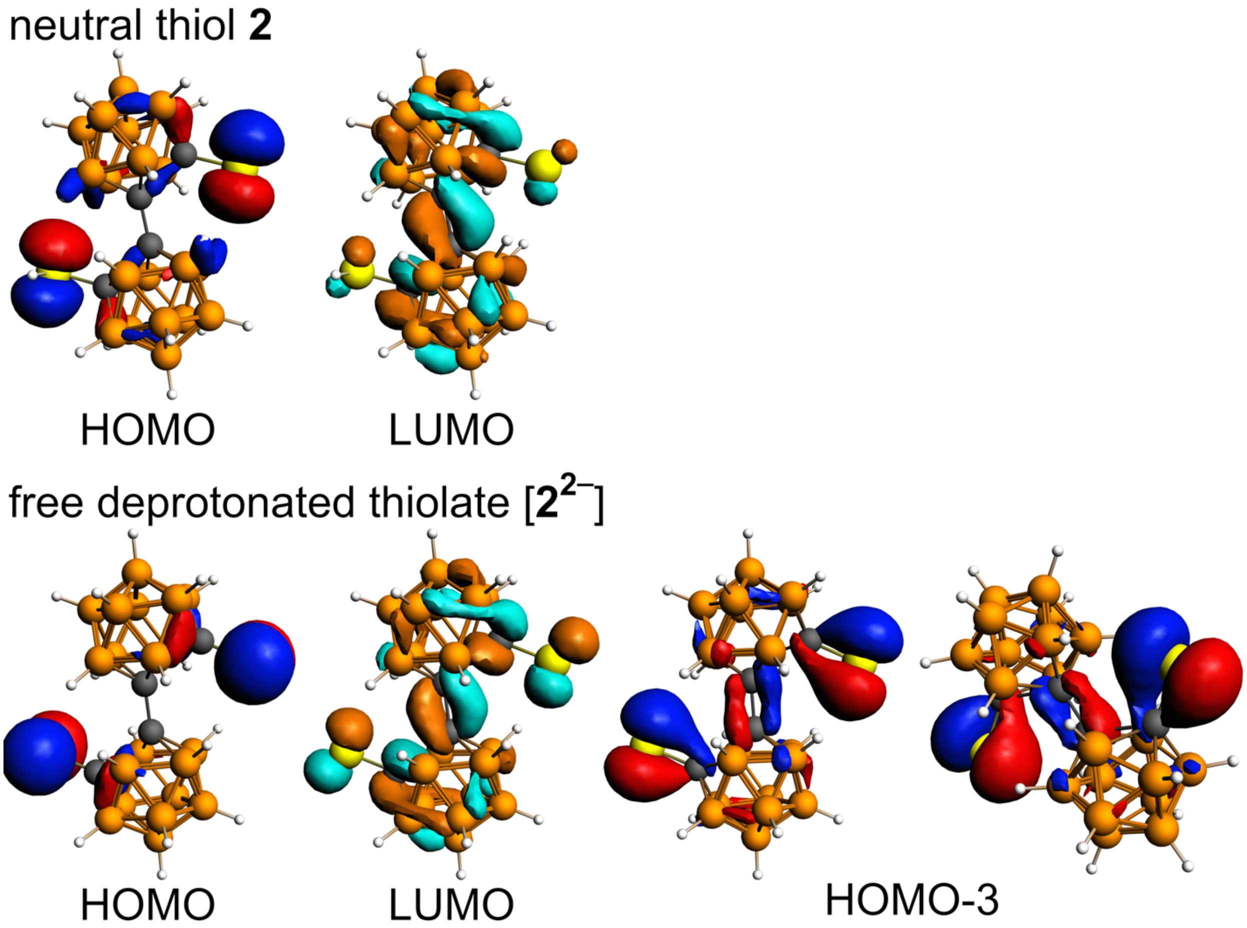
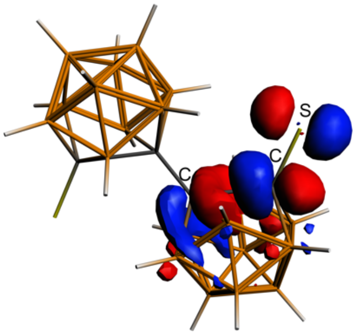


Figure S-10. Plots of the frontier molecular orbitals for the dithiol **2** and the free deprotonated anion **[2^{2-}]** at the isosurface value of 0.035.



NLMO 94

Figure S-11. Plot of the natural localized molecular orbital NLMO 94 demonstrating the negative hyperconjugation between the lone pair of the sulfur atom and the antibonding σ*(C–C) orbital in **[2^{2-}]**.

Computational details.

The density functional theory calculations were carried out utilizing SCM ADF software package.[3] Molecular geometries were optimized using the hybrid PBE0 functional and the TZP basic set for neutral **2** and the augmented by diffuse functions ATZP basis set for dianion [$\mathbf{2}^{2-}$] with scalar relativistic effects considered using the ZORA formalism. Frequency calculations were carried out to confirm the local minimum results. Solvent effects (dichloromethane) were considered within COSMO model.

Table S-7. The optimized geometry coordinates for 2.

Atom	X	Y	Z (Angstrom)
1.S	-2.416966	-2.245920	0.032246
2.H	-1.839165	-3.158429	0.834267
3.C	-0.958971	-1.915395	-0.912843
4.C	0.148058	-0.466807	-0.582560
5.B	0.609817	-2.088171	-0.237864
6.H	0.708119	-2.418016	0.891104
7.B	-0.019839	-3.167875	-1.513246
8.H	-0.343507	-4.258704	-1.187076
9.B	-1.021646	-2.166690	-2.575261
10.H	-2.060165	-2.546572	-2.994355
11.B	-0.972744	-0.517444	-1.895794
12.H	-1.915300	0.191549	-1.857056
13.B	1.704458	-0.921848	-1.011926
14.H	2.594973	-0.505495	-0.362545
15.B	1.634885	-2.580634	-1.604523
16.H	2.547499	-3.315103	-1.422421
17.B	0.625966	-2.598667	-3.066547
18.H	0.796344	-3.365145	-3.954979
19.B	0.004753	-0.952782	-3.319381
20.H	-0.263813	-0.500925	-4.381861
21.B	0.693213	0.083198	-2.068414
22.H	0.834721	1.245694	-2.201930
23.B	1.674510	-1.218952	-2.755890
24.H	2.625108	-0.961754	-3.416699
25.S	2.416966	2.245920	-0.032246
26.H	1.839165	3.158429	-0.834267
27.C	0.958971	1.915395	0.912843
28.C	-0.148058	0.466807	0.582560
29.B	-0.609817	2.088171	0.237864
30.H	-0.708119	2.418016	-0.891104

31.B	0.019839	3.167875	1.513246
32.H	0.343507	4.258704	1.187076
33.B	1.021646	2.166690	2.575261
34.H	2.060165	2.546572	2.994355
35.B	0.972744	0.517444	1.895794
36.H	1.915300	-0.191549	1.857056
37.B	-1.704458	0.921848	1.011926
38.H	-2.594973	0.505495	0.362545
39.B	-1.634885	2.580634	1.604523
40.H	-2.547499	3.315103	1.422421
41.B	-0.625966	2.598667	3.066547
42.H	-0.796344	3.365145	3.954979
43.B	-0.004753	0.952782	3.319381
44.H	0.263813	0.500925	4.381861
45.B	-0.693213	-0.083198	2.068414
46.H	-0.834721	-1.245694	2.201930
47.B	-1.674510	1.218952	2.755890
48.H	-2.625108	0.961754	3.416699

Table S-8. The optimized geometry coordinates for $[2^{2-}]$.

Atom	X	Y	Z (Angstrom)
1.S	-2.484886	-2.407203	0.011619
2.B	-1.670840	1.225921	2.728434
3.C	-1.120956	-2.079750	-0.952014
4.C	0.146678	-0.455906	-0.573837
5.B	0.511752	-2.088700	-0.254320
6.H	0.620903	-2.447756	0.866505
7.B	-0.052007	-3.200279	-1.532647
8.H	-0.301286	-4.330239	-1.272284
9.B	-1.047674	-2.171819	-2.602587
10.H	-2.040512	-2.531549	-3.142208
11.B	-0.973891	-0.554363	-1.852053
12.H	-1.909526	0.167734	-1.856379
13.B	1.680923	-0.938031	-0.982020
14.H	2.577922	-0.539840	-0.325242
15.B	1.596094	-2.586632	-1.586120
16.H	2.503408	-3.337640	-1.411044
17.B	0.619168	-2.592924	-3.064433
18.H	0.813439	-3.344981	-3.968173
19.B	0.007780	-0.945728	-3.294250
20.H	-0.243704	-0.496232	-4.367845
21.B	0.693402	0.082461	-2.045022
22.H	0.852682	1.244428	-2.182366
23.B	1.670840	-1.225921	-2.728434
24.H	2.633039	-0.981866	-3.386938

25.S	2.484886	2.407203	-0.011619
26.H	-2.633039	0.981866	3.386938
27.C	1.120956	2.079750	0.952014
28.C	-0.146678	0.455906	0.573837
29.B	-0.511752	2.088700	0.254320
30.H	-0.620903	2.447756	-0.866505
31.B	0.052007	3.200279	1.532647
32.H	0.301286	4.330239	1.272284
33.B	1.047674	2.171819	2.602587
34.H	2.040512	2.531549	3.142208
35.B	0.973891	0.554363	1.852053
36.H	1.909526	-0.167734	1.856379
37.B	-1.680923	0.938031	0.982020
38.H	-2.577922	0.539840	0.325242
39.B	-1.596094	2.586632	1.586120
40.H	-2.503408	3.337640	1.411044
41.B	-0.619168	2.592924	3.064433
42.H	-0.813439	3.344981	3.968173
43.B	-0.007780	0.945728	3.294250
44.H	0.243704	0.496232	4.367845
45.B	-0.693402	-0.082461	2.045022
46.H	-0.852682	-1.244428	2.182366