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Synthesis and cluster structure distortions of biscarborane dithiol, thioether, and disulfide†

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The synthesis and structural characterization of the first sulfur-containing derivatives of the C,C-biscarborane (*ortho*-C₂B₁₀)₂ cluster – thiol, thioether, and disulfide – are reported. The biscarboranyl dithiol (1-HS-C₂B₁₀H₁₀)₂ exhibits an exceedingly long intracluster carbon–carbon bond length of 1.858(3) Å, which is attributed to the extensive interaction between the lone pairs of the thiol groups and the unoccupied molecular orbital of the carborane cluster. The structures of the doubly deprotonated biscarboranyl dithiolate anion (1-S-C₂B₁₀H₁₀)₂²⁻ with various counter cations feature an even longer carbon–carbon bond length of 2.062(10) Å within the cluster along with a short carbon–sulfur bond of 1.660(7) Å, both indicative of significant delocalization of electron density from the sulfur atoms into the cluster.

Introduction

The chemistry of boron clusters, such as C₂B₁₀H₁₂, has been actively investigated, with recent expansions into materials science, batteries, ligand design, medicinal chemistry, and catalysis.^{1–13} Among numerous cluster compounds, C₂B₁₀H₁₂ or carboranes, containing two carbon atoms and ten boron atoms in the core, stand out as remarkably robust neutral molecules with a unique electronic delocalization and steric profile. The electronic structure of 3-D aromatic carboranes bears an analogy to that of arenes and features a set of delocalized molecular orbitals within the cluster.^{14–16}

Boron and carbon cluster vertices in carboranes exhibit orthogonal reactivity.¹ The B–H bonds of the cluster are largely non-polarized and exhibit reactivity similar to that of aromatic C–H bonds engaging in electrophilic substitution and oxidative addition to low-valent late transition metal centers.^{17–19} In the derivatives of carboranes, boron atoms of the cluster behave as strong σ -donors for exohedral groups. In contrast, the C–H bonds in carboranes are relatively acidic (pK_a is ca. 23) and can be deprotonated with reagents such as *n*-butyllithium, resulting in the formation of metalated carbanions, which can be derivatized with electrophiles.^{20–22} The carbon atoms of *ortho*-C₂B₁₀H₁₂ form σ -bonds to exohedral substituents with the possibility of electronic communication through π -donation from those groups to the cluster. Thus, the cluster

exhibits electron-withdrawing behavior with respect to a group connected to its carbon atoms.^{23–26}

The donation from the substituents at carbon atoms increases the electron density in the cluster LUMO, which has a $\sigma^*(C-C)$ anti-bonding orbital as a significant component. The population of this σ^* orbital leads to weakening of the intracluster C–C bond and an increase in the C–C interatomic distance. The C–C bond length in the parent unsubstituted cluster is *cf.* 1.624(8) Å,²⁷ which is longer than the “standard” single bond between the sp³-hybridized carbon atoms in ethane (1.54 Å) due to the delocalized bonding in the carborane cage. Extensive computational studies ascribed the trend in lengthening of the cluster carbon–carbon bond and the concomitant shortening of the exohedral bonds to the efficiency of negative hyperconjugation between the lone pairs at the substituent groups and the anti-bonding $\sigma^*(C-C)$ orbital of the *ortho*-carborane cluster.^{28–30} According to calculations, *ortho*-carborane disubstituted with NH₂ or SH groups would have the longest intracluster C–C bonds for the first- and second-row element substituents.³¹ Experimentally, the recently reported diamine derivatives (MesCH₂N(H))₂(C₂B₁₀H₁₀) and (MesN(H))₂(C₂B₁₀H₁₀) exhibit some of the longest C–C bonds (1.931(3) Å and 1.990(4) Å, respectively).^{32–34} Additionally, calculations suggest that negative hyperconjugation is expected to be even more pronounced in the corresponding deprotonated disubstituted clusters with intracluster carbon–carbon distance elongation, which exceeds 2.1 Å, leading to the partial opening of the cluster cage from the *closo*- to the *nido*-form.^{28,31}

In contrast to the increasingly developing chemistry of icosahedral carboranes, its carbon-linked two-cluster derivative, 1,1'-bis(*o*-carborane) (C₂B₁₀H₁₁)(C₂B₁₀H₁₁) (biscarborane), remains relatively unexplored, despite being known for a com-

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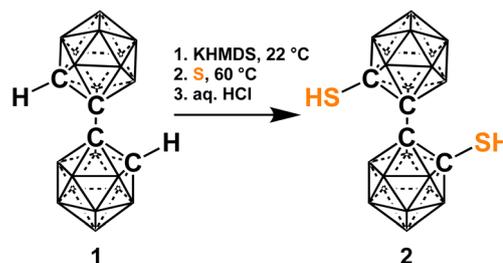
parably long time.^{35–38} The structure of biscarborane can be compared to that of biphenyl where two aromatic rings may exhibit a significant degree of electronic communication. Indeed, the chemical reduction of biscarborane leads to structural changes in both clusters where the individual clusters open with intracuster C–C bonds elongating, accompanied by the shortening of the intercluster C–C bond.^{39–41} Presumably, the presence of two linked electron-accepting clusters in biscarborane will lead to an even more pronounced interaction with exohedral substituents at its remaining carbon atoms with a stronger π -donation of their lone pairs into biscarborane, which will be indicated by the further elongation of intracuster carbon–carbon bonds.

While numerous *C*-substituted derivatives of *closo*-C₂B₁₀H₁₂ clusters have been reported, the derivatization of biscarborane is largely limited to biscarborane acting as a chelating group, *i.e.* the formation of five-member rings with both cluster carbon atoms bound to either a transition metal center or a heteroatom.^{42–49} To the best of our knowledge, there has been only one report in the literature of the attachment of pairs of donor groups (dihydro-1,2-oxazines) to two carbon atoms of biscarborane.⁵⁰ In our previous work, we reported the attempt to install two phosphine groups on both carbon atoms of biscarborane, which, instead of the target diphosphine, led to intramolecular B–H bond activation driven by the reduction of one of the boron clusters.^{51,52} Thiolates represent another large class of donor groups with lone pairs, and single-cage carboranyl thiolates have been utilized in ligand design for catalysis as well as for the decoration of metal surfaces and nanoparticles.^{25,53–64} With the double-cage biscarborane, we sought to functionalize its carbon atoms with thiol groups to obtain an insight into the substituent effects on the cluster structure.

In this work, we report the synthesis and structural characterization of biscarborane dithiol, which exhibits a strikingly long intracuster C–C bond length of 1.858(3) Å. The local distortion of the cluster bonding can be manipulated even further, as we demonstrate by the deprotonation of biscarborane dithiol, which led to partial cluster opening and a remarkably long C–C bond distance of 2.062(10) Å in its anionic dithiolate form. We also report the synthesis and structure of biscarboranyl bis(methylthio)ether and biscarboranyl disulfide.

Results and discussion

Biscarboranyl dithiol was prepared by a procedure similar to that for the synthesis of *ortho*-carboranyl dithiol, which involves deprotonation of cluster carbon vertices and the subsequent reaction with sulfur.^{20,65} However, we found that the more sterically hindered biscarborane requires higher temperature and longer reaction time in comparison with the relatively facile formation of (HS)₂C₂B₁₀H₁₀ at room temperature (Scheme 1). The C–H bonds of 1,1'-bis(*ortho*-carborane) (1) were deprotonated using potassium hexamethyldisilazane (KHMDS) in THF at room temperature.^{21,22,66} The doubly



Scheme 1 The synthesis of biscarboranyl dithiol (HS-C₂B₁₀H₁₀)₂ (2) from biscarborane 1.

C-metalated cluster was isolated and elemental sulfur was added to its THF solution, which then was heated at 60 °C for 24 hours. The reaction mixture was quenched with aqueous HCl, and the biscarboranyl dithiol (HS-C₂B₁₀H₁₀)₂ (2) was isolated after extraction to dichloromethane in 40% yield as a white solid.

The ¹H NMR spectrum of biscarborane dithiol in CDCl₃ exhibits a characteristic resonance for the S–H proton at 4.19 ppm. Single-crystal X-ray diffraction revealed the molecular structure of the dithiol (Fig. 1). The thiol groups in 2 are arranged in the *trans*-orientation relative to each other. The main structural feature of 2 is the long intracuster C1–C2 bond distance of 1.858(3) Å (*cf.* C1–C2 = 1.690(3) Å for the parent biscarborane).³⁶ This significantly elongated carbon–carbon bond in the cluster can be compared to that in *ortho*-carborane thioethers (1.803(2) Å in 1,2-(SMe)₂-*ortho*-C₂B₁₀H₁₀, and 1.799(3) Å in 1,2-(SPh)₂-*ortho*-C₂B₁₀H₁₀).^{67,68} A summary of the C–C and C–S bond lengths for relevant carboranyl sulfur-containing derivatives and biscarboranyl congeners reported in this work is given in Table 1. Note that the crystal structure of the corresponding dithiol 1,2-(HS)₂-*ortho*-C₂B₁₀H₁₀ has not yet been reported. The significant elongation of the carbon–carbon bond in 2 is due to electronic factors, namely the interaction of the sulfur atom lone pair and the LUMO of the cluster.

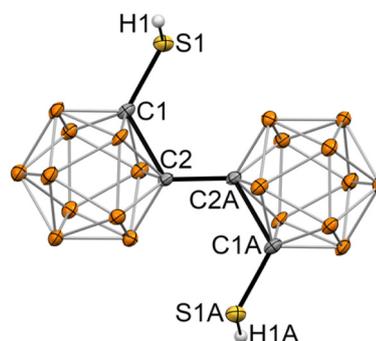


Fig. 1 The displacement ellipsoid plot (50% probability) of biscarboranyl dithiol (HS-C₂B₁₀H₁₀)₂ (2). Hydrogen atoms of the biscarborane cluster are not shown. Selected distances (Å): C1–C2 = 1.858(3), C2–C2A = 1.530(5) and C1–S1 = 1.762(3).

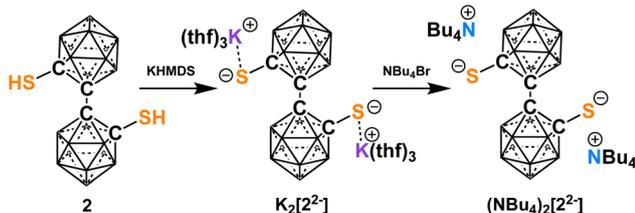
Table 1 Intracuster carbon–carbon and exohedral carbon–sulfur bond lengths in the representative literature examples of *ortho*-carbora-nyl and biscarboranyl (this work) thiols, thiolates, and thioethers

Thiocarborane	C–C distance, Å	C–S distance, Å
Parent <i>ortho</i> -carborene C ₂ B ₁₀ H ₁₂ ²⁷	1.629(5)	—
1-C ₅ H ₅ N-2-SH-C ₂ B ₁₀ H ₁₀ ⁷⁰	1.730(3)	1.775(2)
[H-N,N,N,N-Tetramethylnaphthalene diamine][1-S-2-Ph-C ₂ B ₁₀ H ₁₀] ⁷¹	1.836(5)	1.729(4)
1,2-(SMe) ₂ -C ₂ B ₁₀ H ₁₀ ⁶⁸	1.803(1)	1.761(1)
1,2-SCH ₂ (CH ₂ OCH ₂) ₂ CH ₂ S-C ₂ B ₁₀ H ₁₀ ⁷²	1.858(5)/ 1.826(5)	1.742(4)/ 1.752(4)
Parent biscarborane (C ₂ B ₁₀ H ₁₁) ₂ ³⁶	1.690(3)	—
(HS-C ₂ B ₁₀ H ₁₀) ₂ (2)	1.858(3)	1.762(3)
[K(THF) ₃] ₂ (S-C ₂ B ₁₀ H ₁₀) ₂ (K ₂ [2 ²⁻])	2.022(2)	1.710(1)
[NBu ₄] ₂ (S-C ₂ B ₁₀ H ₁₀) ₂ ((NBu ₄) ₂ [2 ²⁻])	2.030(9)/ 2.062(10)	1.636(8) Å/ 1.660(7) Å
(MeS-C ₂ B ₁₀ H ₁₀) ₂ (3)	1.898(1)	1.756(1)

The intercluster C2–C2A bond length is 1.530(5) Å, which is comparable to that in the parent unsubstituted biscarborane (1.534(1) Å).⁶⁹ The C1–S1 bond length in **2** is 1.762(3) Å, which is comparable to the single carbon–sulfur bonds in aromatic thiols.

Deprotonation of dithiol **2** can be expected to lead to an even larger increase in the exohedral π -bonding of the cluster. We examined the structures of several thiolate salts derived from **2** that differ in the coordinating ability of the counter cation: K₂[2²⁻], (HNET₃)₂[2²⁻], and (NBu₄)₂[2²⁻]. Their synthesis and structures are described below (Scheme 2).

Potassium dithiolate K₂[2²⁻] was prepared by deprotonation of dithiol **2** with KHMDS in THF. The single crystals of [K(THF)₃]₂[2²⁻] were grown from THF solution. The biscarboranyl dithiolate anion adopted the *trans*-orientation of thiol fragments with two potassium cations coordinated to each sulfur atom (K⋯S distances are 3.137(1) Å and 3.242(1) Å). The intracuster C1–C2 bond distance is exceptionally long at 2.022(2) Å. This distance is comparable with that of the related deprotonated hydroxycarborane anions 1-O⁻-2-Ph-C₂B₁₀H₁₀ with either protonated “proton sponge” or triphenylmethyl-phosphonium counter cations (2.001(3) Å and 2.065(7) Å, respectively).²⁸ The substantial degree of delocalization of the negative charge from sulfur into the cluster is also manifested by the short exohedral C1–S1 bond of 1.710(1) Å. This bond length is shorter than that in the parent neutral **2** (1.762(3) Å). The electronic conjugation of two clusters in the biscarborane



Scheme 2 Deprotonation of biscarborane dithiol and the formation of the potassium salt [K(THF)₃]₂(S-C₂B₁₀H₁₀)₂ (K₂[2²⁻]) and tetrabutylammonium salt [NBu₄]₂(S-C₂B₁₀H₁₀)₂ ((NBu₄)₂[2²⁻]).

core of K₂[2²⁻] is demonstrated by the shortening of the intercluster C2–C2A bond to 1.507(2) Å (Fig. 2).

The effect of weak counter cation coordination can be demonstrated by the crystal structure of the tetraalkylammonium salt (NBu₄)₂[2²⁻], which was obtained by the ion exchange from K₂[2²⁻] (Fig. 3). The structure of (NBu₄)₂[2²⁻] similarly features the *trans*-orientation of the sulfur atoms on the biscarborane scaffold. The C1–C2/C3–C4 bond distances are also similarly long at 2.030(9) and 2.062(10) Å. The absence of coordination of the sulfur atoms to the cation results in drastic shortening of the carbon–sulfur distances to 1.636(8) Å and 1.660(7) Å in (NBu₄)₂[2²⁻]. These bond lengths are within the range of carbon–sulfur double bonds in thioketones. Furthermore, the intercluster C–C bond is shortened to 1.459(8) Å. These structural distortions of the *closo*-biscarborane cluster in (NBu₄)₂[2²⁻] draw nearer to those of the biscarboranyl dianion (*nido*-C₂B₁₀H₁₁)₂²⁻ obtained by Hawthorne and co-workers in the chemical reduction of biscarborane with sodium metal, where the intracuster C–C distance is 2.414(4) Å and intercluster C=C double bond length is 1.377(4) Å. The structure of (NBu₄)₂[2²⁻] also features two close S⋯H–C contacts between the thiolate and alkylammonium cation (2.523(2) Å and 2.634(2) Å) that correspond to the S⋯C distances (3.384(9) Å and 3.420(9) Å), which are shorter than the van der Waals radii sum for sulfur and carbon.

The crystal structure of the triethylammonium salt (HNET₃)₂[2²⁻] provides another case of cluster bond distortions in the series of deprotonated 2²⁻ anions (see the ESI† for details). The intracuster C–C bond is similarly long at 2.046(2) Å, the intercluster C–C bond is relatively short at 1.502(1) Å, and the exohedral C–S bond length is 1.713(1) Å. Each HNET₃ cation is hydrogen-bonded to thiolate sulfur atoms with an S⋯N distance of 3.161(2) Å and a nearly linear N–H⋯S angle of 176(2)°.

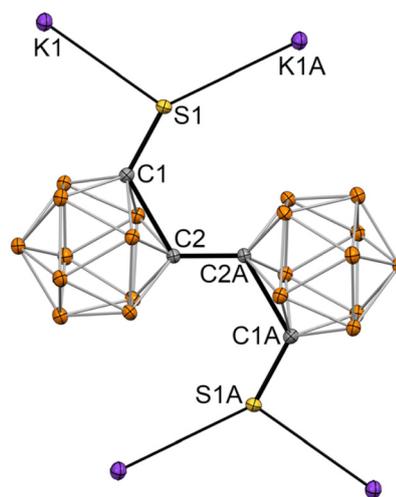


Fig. 2 The displacement ellipsoid plot (50% probability) of [K(THF)₃]₂(S-C₂B₁₀H₁₀)₂ (K₂[2²⁻]). Hydrogen atoms of the biscarborane cluster are not shown. THF molecules coordinated to the potassium cations are not shown. Selected distances (Å): C1–C2 = 2.022(2), C1–S1 = 1.710(1), C2–C2A = 1.507(2), S1–K1 = 3.137(1) and S1–K1A = 3.242(1).

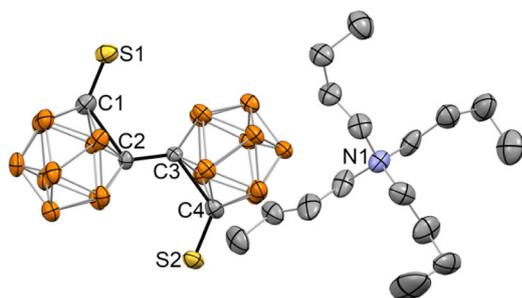
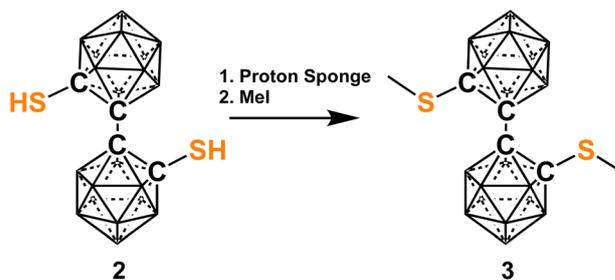


Fig. 3 The displacement ellipsoid plot (50% probability) of $[\text{NBu}_4]_2(\text{S-C}_2\text{B}_{10}\text{H}_{10})_2$ ($[\text{NBu}_4]_2[2^{2-}]$). Hydrogen atoms of the biscarborane cluster are not shown. Only one cation–anion pair present in the asymmetric unit is shown. Selected distances (Å): C1–C2 = 2.030(9), C3–C4 = 2.062(10), C1–S1 = 1.660(7), C4–S2 = 1.636(8) and C2–C3 = 1.459(8).

Deprotonation of the dithiol **2** in THF led to a color change from colorless to yellow/orange. The spectrum of **2** contains only the absorption band below 300 nm in the UV region of the spectrum. In contrast, the spectrum of $[2^{2-}]$ contains an additional broad band spanning from 300 to 450 nm with a maximum at 340 nm that is consistent with its orange color. The density functional theory calculations of the electronic structure using ADF⁷³ with the hybrid PBE0 functional and the TZP basis set for **2** and ATZP basis set⁷⁴ for $[2^{2-}]$ demonstrated the difference between the magnitude of the HOMO–LUMO energy gap for neutral **2** (5.45 eV) and its free deprotonated anion $[2^{2-}]$ (3.48 eV). Notably, for both **2** and $[2^{2-}]$ the HOMO represents lone pairs at sulfur atoms, and LUMO is mostly localized within the biscarborane cluster with the lobes corresponding to the anti-bonding interactions for the intracuster carbon–carbon bonds and π -bonding interactions with respect to the intercluster carbon–carbon bonds and exohedral carbon–sulfur bonds (see the ESI† for details). In addition, HOMO–3 for $[2^{2-}]$ dianion consists of lobes representing π -bonding interactions between cluster carbon and sulfur atoms as well as the intercluster carbon–carbon bond indicating a significant thioketone characteristic of its carbon–sulfur bonds.

Carboranyl thiols are known to be readily converted to the corresponding thioethers.^{67,68} We found that deprotonation of **2** with “proton sponge” (1,8-bis(dimethylamino)naphthalene) and the subsequent addition of iodomethane resulted in the formation of biscarboranyl bis(methylthio)ether **3** (Scheme 3). The ¹H NMR spectrum exhibited the presence of the characteristic resonance at 1.56 ppm for the S–CH₃ group and the absence of the signal from the S–H group of the parent dithiol. Single-crystal X-ray diffraction study revealed the elongation of the intracuster C1–C2 bond length at 1.898(1) Å, which is even more pronounced than that of the corresponding bond in the dithiol **2** at 1.858(3) Å (Fig. 4). Notably, the C1–C2 bond in **3** is longer than the intracuster carbon–carbon bonds in the previously reported carboranyl thioethers 1,2-(SMe)₂-C₂B₁₀H₁₀ (1.803(2) Å) and 1,2-(SPh)₂-C₂B₁₀H₁₀ (1.799(3) Å),^{67,68} which



Scheme 3 The synthesis of biscarboranyl bis(methylthio)ether ($\text{MeS-C}_2\text{B}_{10}\text{H}_{10})_2$ (**3**).

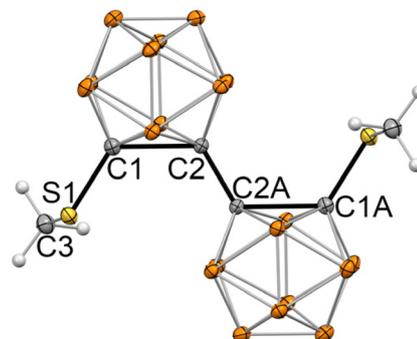
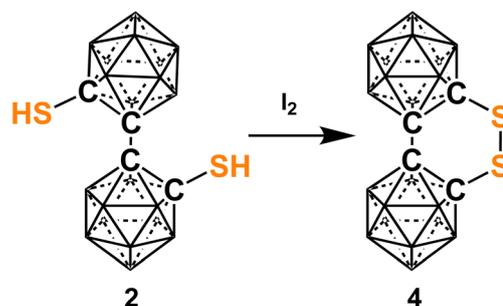


Fig. 4 The displacement ellipsoid plot (50% probability) of $(\text{MeS-C}_2\text{B}_{10}\text{H}_{10})_2$ (**3**). Hydrogen atoms of the biscarborane cluster are not shown. Selected distances (Å): C1–C2 = 1.898(1), C1–S1 = 1.756(1) and C2–C2A = 1.522(1).

can be attributed to the stronger electron-accepting properties of the biscarborane cluster in comparison with the parent single-cage carborane. The C1–S1 bond length in **3** is 1.756(1) Å, which is comparable with that in 1,2-(SMe)₂-C₂B₁₀H₁₀ (1.761(1) Å).

During the synthesis of **2**, we also isolated biscarboranyl disulfide **4** as a minor side product. The disulfide **4** was also produced in quantitative yield by oxidation of dithiol **2** with iodine (Scheme 4). The crystal structure of **4** features an intracuster bond length (C1–C2) of 1.676(3) Å, which is significantly shorter than that in dithiol **2** (1.858(3) Å), and similar to that in the parent biscarborane (1.690(3) Å). The intercluster



Scheme 4 The synthesis of biscarboranyl disulfide ($\text{S-C}_2\text{B}_{10}\text{H}_{10})_2$ (**4**).

C2–C3 distance is 1.535(3) Å, which is comparable to that in the parent biscarborane and dithiol 2. The C1–S1 distance in the disulfide (1.790(2) Å) is longer than that in the biscarboranyl dithiol (1.762(3) Å).

Given the similarities between aromatic carborane clusters and arenes, the structure of the biscarboranyl disulfide 4 can be compared with the reported structure of 2,2'-biphenyl disulfide (Fig. 5).⁷⁵ The carbon–sulfur distances in these compounds are virtually identical. However, there is a slightly shorter S–S bond in biscarboranyl disulfide at 2.034(1) Å than in biphenyl disulfide (2.066(1) Å). The longer C–S bonds and shorter intracenter C–C bonds in the biscarboranyl disulfide indicate that there is no longer as large an impact from the sulfur lone pairs on cluster bonding in this molecule. The torsion angle C1–C2–C3–C4 is smaller in the case of the biscarboranyl disulfide at 25.2(3)° than the same angle in biphenyl disulfide C1–C2–C3–C4 at 36.7(2)°. This decrease in the torsion angle is attributed to the longer biscarborane C–C bonds and shorter S–S bond.

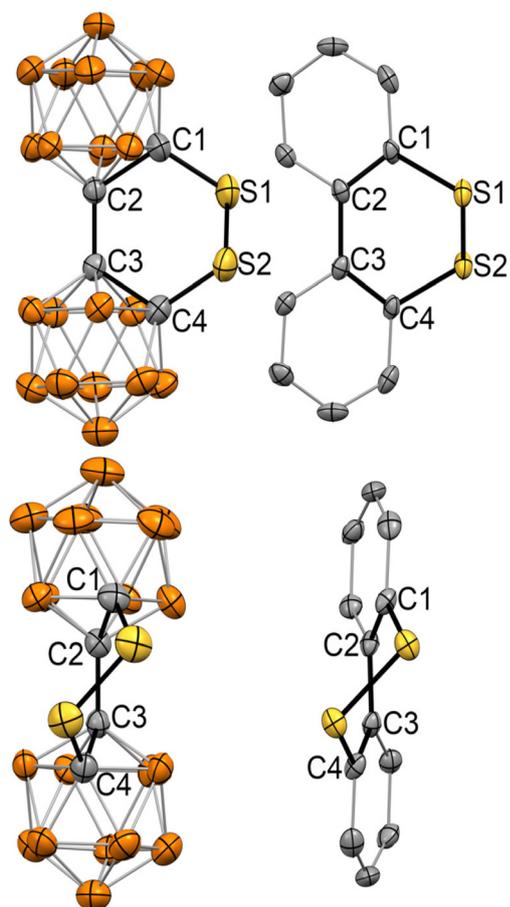


Fig. 5 The displacement ellipsoid plots (50% probability) of biscarboranyl disulfide ($S-C_2B_{10}H_{10}$)₂ (4, left) and biphenyl disulfide⁷⁵ (right). Hydrogen atoms are not shown. Selected distances (Å) and angles (°) in biscarboranyl disulfide: C1–C2 = 1.676(3), C1–S1 = 1.790(2), S1–S2 = 2.034(1), C1–C2–C3–C4 = 25.2(3); and in biphenyl disulfide: S1–S2 = 2.066(1), C1–C2–C3–C4 = 36.7(2).

Conclusions

In conclusion, we synthesized a series of sulfur-functionalized biscarborane clusters that serve as the first examples of biscarborane clusters bearing independent donor groups at both carbon atoms. Biscarborane dithiol, deprotonated dithiolate, and bis(methyl)thioether feature exceedingly long intracenter C–C bond lengths, consistent with the increased π -donation of sulfur atom lone pairs into the electron-accepting boron cluster. These distortions of the boron cage bonding are more significantly pronounced in these biscarborane-based derivatives than in the analogous single cluster carborane examples, likely due to the stronger electron-withdrawing nature of the two linked clusters in comparison with only one. For example, the tetrabutylammonium salt of the deprotonated biscarborane thiol $[NBu_4]_2(S-C_2B_{10}H_{10})_2$ exhibits the longest cluster C–C bond length of 2.030(9) Å and the shortest C–S bond of 1.660(7) Å, indicative of a double bond. The exploration of the coordination chemistry of the potentially redox- and proton-responsive biscarboranyl dithiol ligand is underway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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