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Additional Information

Synthesis, Structural, Spectroscopic and Electrochemical Studies of Carborane Substituted Naphthyl Selenides

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Abstract

New unsymmetrical selenides bearing an *o*-carborane and a naphthalene ring as the substituents were prepared by the cleavage of the corresponding diselenides. The compounds were characterized by means of spectroscopic and analytical methods. ^{77}Se NMR signals of the selenium atoms attached to the carbon atoms of the carborane cages are shifted downfield in comparison to those bonded only to aromatic rings, indicating electron withdrawing effect of the *o*-carboranyl substituent. Compounds 1-(2-R-1,2-dicarba-*closo*-carboranyl)naphthyl selenides (R = Me, **1**; Ph, **2**) were characterized by means of single crystal X-ray diffraction. The influence of the electronic nature of the substituents attached to the selenium atoms on the structural parameters and packing properties of naphthyl selenides is discussed. Theoretical calculations and cyclic voltammetry (CV) studies were carried out to compare the bonding nature of carboranyl and analogous aryl selenium compounds. Cyclic voltammetry studies of naphthyl carboranyl mono and diselenides have shown that the carboranyl fragment polarizes the Se lone pair making it less prone to generate a Se–Se bond.

Introduction

The rapid advance in organoselenium chemistry during the past decades has been achieved through the discovery of new synthetic methods and the subsequent characterization of an increasing number of compounds.¹ Organoselenides have been shown to play an important role in a number of biochemical transformations² and in materials science as the precursors for metal organic chemical vapour deposition (MOCVD) processes.³ A major factor with an impact on the structure, reactivity, and pharmacological activity of organoselenium compounds is believed to be the inter- and intramolecular interactions involving the *p*-type lone pairs of the selenium atoms. Such interactions can affect the conformational rigidity of the molecules and play a key role, for instance, in chirality transfer^{1b,4} and stabilization of the intermediates in biochemical reactions.⁵

The *p*-type lone pair orbitals of the selenium atoms ($n_p(\text{Se})$), as well as *s*-type lone pair orbitals, will suffer steric compression if they are located at distances shorter than the sum of van der Waals radii. Such steric interactions are usually accompanied by severe exchange repulsions.⁶ However, the steric compression also arises nonbonding interactions involving direct orbital overlap between the atoms placed within such distances, as $\text{S}\cdots\text{S}-\text{O}$ in 1,5-dithiacyclooctane 1-oxide, etc.⁷ $n_p(\text{Se})$ may interact with $\sigma^*(\text{X}-\text{X})$ in $\text{RR}'\text{Se}\cdots\text{X}_2$ ($\text{X} = \text{halogen}$). The resulting unsymmetrical σ -type $n(\text{Se})\cdots\sigma^*(\text{X}-\text{X})$ three center-four electron (3c-4e) interactions⁸ can be attractive, if the exchange repulsions are suitably controlled. The naphthalene 1,8-positions provide a good system to investigate such nonbonding interactions since the distances between the selenium atoms at those positions are close to the sum of van der Waals radii minus 1.0.⁹ It has been demonstrated that such interactions are the factors determining the fine structures of 1-¹⁰ and 1,8-disubstituted¹¹ naphthalene

derivatives. These factors may also affect in the catalyst platforms,¹² proton sponges¹³ and sensors for selective ion recognition¹⁴ in the naphthalene derivatives.

o-Carborane, 1,2-dicarba-*closo*-dodecaborane, is an icosahedral cluster with ten boron atoms and two neighboring carbon atoms¹⁵ and can be formally regarded as a pseudo-sphere with a 0.81 nm outside diameter¹⁶ with a molecular volume similar to that of a hypothetically rotating benzene ring. Some researchers consider that boron clusters have a pseudo-aromatic character which parallels the aromaticity of benzene.¹⁷ The unique properties of carborane molecules, such as thermal stability,¹⁸ electron-withdrawing character,¹⁹ and lipophilicity make them promising candidates as the precursors for liquid crystals,²⁰ NLO (nonlinear optical) materials²¹ or, as boron rich carriers for cancer treatment and diagnosis in Boron Neutron Capture Therapy (BNCT),²² among others.²³

During the past decades the chemistry of carboranyl sulfides, disulfides,²⁴ selenides,²⁵ diselenides,²⁶ and their related metallic complexes has been developed.²⁷ Due to our broad interest in carboranyl chalcogenides, we decided to explore synthetic ways for the preparation of carborane substituted naphthyl selenides and to compare the influence of *o*-carboranyl or aryl groups on the structure and spectroscopic features of the obtained compounds. The results of our investigation are presented in the current paper.

Results and discussion

1. Synthesis and characterization of the species:

Organoselenides can be prepared from diaryl diselenides by reaction with alkali metals²⁸ or alkali hydrides.²⁹ The asymmetric carboranylnaphthyl selenides 1-(2-*R*-1,2-dicarba-*closo*-carboranyl)naphthyl selenides (R = Me, **1**; Ph, **2**), and 1-(phenylselenyl)-8-(2-methyl-1,2-dicarba-*closo*-carboranylselanyl) naphthalene (**3**)

have been prepared by cleavage of organic dinaphthyl diselenide with the corresponding lithiated *o*-carboranes (Scheme 1). Chart 1 . The optimized experimental synthetic conditions as well as the spectroscopic and analytical data for the obtained compounds are given in the experimental section.

It has been established that *closo*-carboranyl groups exert a strong electron-withdrawing effect on the substituent.³⁰ The electron-withdrawing character of the *closo* cluster has been observed for *closo*-carboranylmonophosphines and the effect of the *closo*-carboranyl fragment on the ³¹P NMR chemical shifts was calculated,³¹ as had been done for organic phosphines.³² In order to know the cluster influence on the ⁷⁷Se NMR chemical shifts in *closo*-carboranyl selenides, ⁷⁷Se NMR spectra of compounds **1–3** have been recorded. The ⁷⁷Se NMR chemical shifts and coupling constants for compounds **1–3**, together with selected literature data for naphthyl selenides^{10a,11f} are listed in Table 1. For compounds **1–3**, the ⁷⁷Se NMR resonances appear at δ 480.5, 495.9 and 552.3 ppm, clearly downfield with respect to those of analogous aryl naphthyl selenide or 1-methylselenyl-8-arylselenylnaphthalene derivatives, which appear at δ 356.2, 361.0,^{10a} 379.6, 434.3,^{11f} 427.7^{11f} and 453.9^{11f} ppm (See Table 1). Due to the strong electron withdrawing character of the *o*-carboranyl group,¹⁹ the chemical shift values for **1–3** are shifted downfield with regard to the data found for the selenium atoms bonded to aromatic carbon atoms. Although ⁷⁷Se NMR chemical shifts are due to several factors, in this particular case the chemical shifts correlates well with the stronger electron-withdrawing character of the *o*-carboranyl group in comparison to the phenyl group. Furthermore, the nature of the substituent bonded to the other cluster carbon atom or at the 8 position of the naphthyl group tunes the ⁷⁷Se NMR chemical shift, 480.5 ppm for **1** (R= CH₃), 495.9 ppm for **2** (R= C₆H₅) and 552.3 ppm for **3** (R= SeC₆H₅).

The $^{13}\text{C}\{^1\text{H}\}$ chemical shifts of the cage carbon atoms bonded to the selenium atoms, found at 68.12, 73.23 and 71.48 ppm for compounds **1**, **2** and **3** respectively, are shifted upfield in comparison to the values found for the carbon cluster atoms bearing methyl or phenyl substituents, which appear at 78.19, 78.38 and 87.02 ppm for compounds **1**, **3** and **2**, respectively. Upon prolonged acquisition times, two satellite lines due to the $^1J(^{13}\text{C}, ^{77}\text{Se})$ became visible at either side of the signals at chemical shifts 68.12, 73.23 and 71.48 ppm for compounds **1**, **2** and **3**, confirming the presence of the C–Se bond. One-bond couplings, $^1J(^{13}\text{C}, ^{77}\text{Se})$, are negative and strongly depend on the hybridization state, i.e., the *s*-character of the coupled selenium and carbon atoms.³³ The coupling constants $^1J(^{13}\text{C}, ^{77}\text{Se})$ can reach high values ranging from 4 to 249 Hz.³⁴ Typical ranges for $^1J(^{13}\text{C}, ^{77}\text{Se})$ are 10-100 Hz for selenium attached to sp^3 carbon atoms (larger values if heteratoms are attached to C),³⁵ 90-162 Hz for C=C–Se (sp^2 carbon atoms; aromatic or olefinic)^{35b} and 184-193 Hz for C≡C–Se (sp carbon atoms).³⁴ A large $^1J(^{13}\text{C}, ^{77}\text{Se})$ value indicates a strong electron-withdrawing capacity of the substituents attached to the selenium atom,³⁶ and hence a more positively charged Se atom.³⁷ The $^1J(^{13}\text{C}, ^{77}\text{Se})$ values are 167.87 Hz for **1**, 170.65 Hz for **2**, and 178.97 Hz for **3**. The magnitude of $^1J(^{13}\text{C}, ^{77}\text{Se})$ in compounds **1-3** is markedly increased when compared with phenylselenium derivatives (e.g. in diphenylselenide: $^1J(^{13}\text{C}, ^{77}\text{Se})= 103.1$ Hz).³⁸ These high values also support a stronger electron-withdrawing character for the carboranyl as compared to aryl groups. In addition, these values are closer to those reported for selenium atoms bonded to sp -hybridized carbon atoms (187.40 Hz for PhC≡CSeMe) than to the ones for sp^2 -hybridized carbon atoms (115.5 Hz for PhCH=CHSeMe).³⁹

^{77}Se and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra values agree very well with the explanation that when one of the substituents at the selenium becomes more electron-withdrawing,

such as the *o*-carborane cluster, a π -donation from the Se lone pair of electrons to the carbon atom of the cluster may occur. This, in turn, increases the C–Se electron overlap population, thus increasing $^1J(^{13}\text{C}, ^{77}\text{Se})$.

2. X-ray diffraction studies of 1 and 2: The structural studies of the compounds **1** and **2** are of particular interest to establish the general structural peculiarities of selenocarboranyl substituted naphthalenes, compare them to those of 1-(arylselenyl)naphthalenes,^{10a} and study the influence of *o*-carboranyl group on structural parameters and solid state packing of the molecules. Single crystals of **1** and **2** were obtained by slow evaporation of hexane and acetone solutions, respectively. Compound **1** crystallizes in the triclinic *P*-1 space group with two molecules per unit cell, whereas compound **2** crystallizes in the monoclinic *P*2₁/*c* space group with four molecules per unit cell. General views of their molecular structures are shown in Figures 1 and 2. Crystallographic data for **1** and **2** are presented in Table 2. Selected interatomic distances, angles, and torsion angles for **1** and **2** are collected in Table 3.

Earlier X-ray investigations carried out on monosubstituted naphthyl selenides 1-(*p*-YC₆H₄Se)C₁₀H₆ showed that two types of conformers may be adopted by these molecules depending on the Y group: i) the Se–C_{phenyl} bond being almost perpendicular to the naphthyl plane for Y = Cl, Br, CO₂Et and, ii) the Se–C_{phenyl} bond being parallel to the naphthyl plane for Y = OMe.

The corresponding dihedral angles between the C_{cluster}–Se bond and the naphthyl plane (C(1)–Se(1)–C(14)–C(22) in compound **1** and C(1)–Se(1)–C(19)–C(27) in compound **2**, see Figures 1 and 2) were found to be 95.16° and 96.03°, respectively, indicating first structural type (i) for these molecules, being the carboranyl group oriented away from the naphthyl plane in order to reduce the repulsions between the naphthyl group and the carborane cage.

The Se-C_{Naph} bond length for **1** (1.924(5) Å) is close to those previously observed for 1-(*p*-YC₆H₄Se)C₁₀H₇ derivatives^{10a} (1.914(3) Å for Y = OMe, 1.919(4) Å for Y = Cl, 1.922(5) Å for Y = Br and 1.929(4) Å for Y = CO₂Et). The Se-C_{cluster} (Se(1)-C(1)) bond length (1.971(5) Å) is 0.036 Å in average longer than found in (2-Me-1,2-closo-C₂B₁₀H₁₀)₂Se (1.937(3) and 1.933(3) Å).^{24c} The C_{cluster}-Se-C_{Naph} (C(1)-Se(1)-C(14)) angle value (102.7(2)°) is in the range (100–106°) observed for aromatic selenides.⁴⁰ The C_{cluster}-C_{cluster} (C(1)-C(2)) distance is 1.699(3) Å and the C_{cluster}-C_{cluster}-Se (C(2)-C(1)-Se(1)) angle is 110.11(11)°. The Se-C_{naph} (Se(1)-C(19)) (1.924(5) Å), Se-C_{cluster} (Se(1)-C(1)) (1.939(4) Å) bond lengths and C_{cluster}-Se-C_{Naph} (C(19)-Se(1)-C(1)) angle values (101.02(2)°) for **2** are close to those found for compound **1**.

3. Solid state packing of naphthyl selenides: Both compounds, **1** and **2**, form dimers in the solid state via π -stacking of the naphthyl rings, aided by Se $\cdots\pi$ interactions. The motif is similar in both cases (Figure 3), but not identical, since the stacked naphthyl rings in the crystal structure of compound **1** pack facing each other coincidentally and in an inter-digitized fashion, being the selenium atom located above the 5-position (C(18)) of the neighboring naphthyl group, whereas in the case of compound **2** the stacked rings are shifted, so that the selenium atoms interact with the 4-position (C(22)) of the neighboring naphthyl group.

Further differences arise between both crystal lattices. In compound **1**, the dimers form ribbons through C_{naphthyl}-H \cdots H-B interactions (Figure 4), while the methyl group does not seem to participate in any relevant interactions. In contrast, the phenyl group in compound **2** establishes significant contacts, such as C_{phenyl}-H \cdots H-B interactions, yielding a much more complex 3D array of molecules. Nevertheless, in bulk, both crystal structures show layer-type organization of the molecules.

Alternative aromatic and carborane 2D domains are observed in the crystal lattices. The layers lay parallel to the crystallographic *ac* and *bc* planes in the case of compounds **1** (Figure 5), and **2** (Figure 6), respectively.

4. Electrochemical study.

Electrochemical oxidation studies carried out on dinaphtho[1,8-*b,c*]-1,5-diselenocin,⁴¹ 3,4-dihydro-2H-naphtho[1,8-*b,c*]-1,5-diselenocine⁴² and 1,8-bis(methylselenyl)naphthalene⁴¹ showed reversible oxidation behaviour for these compounds, as an evidence for the stabilization of the cation-radicals by the lone pair of the neighbouring chalcogen atom. For the monosubstituted 1-methylselenylnaphthalene, irreversible oxidation at the potential of +0.82 V was reported.⁴¹ Therefore, the electrochemical reversibility appears to be associated with the existence of two atoms, geometrically very close, having lone pairs. When only one selenium atom is present in the molecule, the anodic electrochemical response is irreversible.

In order to study the influence of the *o*-carboranyl group on the electrochemical properties of 1-monosubstituted naphthyl selenides and to explore the possible stabilization of oxidized species by the participation of the lone pair of the neighbouring selenium atom at the 8-position we, have performed an electrochemical study of compounds **1** and **3**.

The cyclic voltammogram recorded for **1** is presented in Figure 7a. This voltammogram exhibits an irreversible oxidation process +1.75 V (peak A), and an irreversible oxidation (peak C) at +2.5V, both *vs* Ag/AgCl. Similar studies carried out on 1-(2-Me-1,2-dicarba-*closo*-carboranyl)naphthyl sulfide, isostructural to **1**, showed irreversible oxidation at potentials higher than + 2.3 V *vs* Ag/AgCl, as can be seen in Figure 7b. This value is very close to the peak C in Figure 7a.

Normally, organic selenides having alkyl and/or aryl groups show the irreversible electrochemical oxidation behaviour.

In comparison to compound **1**, **3** oxidises even at a higher potential (the oxidation wave starts at about +1.45 V vs. Ag,AgCl). The corresponding reduction wave is also shifted toward more negative values (about 0.3 – 0.4 V vs. Ag,AgCl).

These data are consistent with the electron-polarizing ability of the carborane cluster, so that the electron pairs on the selenium, or sulfur, are less likely to be removed (oxidized) and therefore less able to generate new Se–Se bonds, for example. This is true both for **1** with one Se, or for **3** with two Se. The difficulty of oxidation is even higher for 1-(2-Me-1,2-dicarba-closo-carboranyl)naphthyl sulfide. Most likely in these cases Se-O or S-O bonds are generated causing the irreversibility of the system.

5. Theoretical approach: Why do the molecular structures of **1** and **2** appear as shown in Figures 1 and 2, respectively? Which factor would operate to determine the structure of **3**, although it is not analyzed, yet? The structures of **1** and its 8-methylselanyl derivative (**4**) have been optimized employing the 6-311+G(d) basis sets for Se and the 6-31+G(d) basis sets for C, B, and H of the Gaussian 03 program.⁴³ Calculations are performed at the density functional theory (DFT) level of the Becke three parameter hybrid functionals with the Lee-Yang-Parr correlation functional (B3LYP). Two conformers are optimized to be stable, which are called **1 (A₁)** and **1 (A₂)**. The structures are shown in Figure 8.⁴⁴ **1 (A₁)** is the global minimum and **1 (A₂)** is a local one. The observed structure is consistent with the global minimum, **1 (A₁)**. However, we must be careful since the energy difference is very small. It is only 1.3 kJ mol⁻¹, which corresponds to [**1 (A₂)**]/[**1 (A₁)**] = 0.59 in a non-polar solvent at 298 K, although thermal and solvent effects are not considered in the calculations. Why is the **1 (A₁)** conformer the one observed in the crystals? The **1 (A₁)** structure of the

extended form would be more suitable for the π -stacking of the naphthyl planes in crystals than **1** (**A₂**), in addition to the global minimum nature of **1** (**A₁**) by 1.3 kJ mol⁻¹, as compared to **1** (**A₂**).

The structure of **4** has also been optimized with the same method as used for **1**, where the partial structure of **1** (**A₁**) is assumed for the naphthyl selenylcarborane moiety. Two structures have been optimized. They are **4** (**A_{1A}**) and **4** (**A_{1B}**), where the Me–Se bond is perpendicular to the naphthyl plane in **4** (**A_{1A}**) and it is almost on the plane in **4** (**A_{1B}**), respectively. **4** (**A_{1B}**) is predicted to be more stable than **4** (**A_{1A}**) by 12.6 kJ mol⁻¹. The structure of **3** would be close to that optimized in **4** (**A_{1B}**), although the SeMe group in **4** should be replaced by the SePh group in **3**.

The $n_p(\text{Se})$ of the selenylcarborane group in **4** lies on the naphthyl plane, since the Se–C(carborane) bond is fixed perpendicular to the naphthyl plane due to the bulkiness of the carborane group. Therefore, the conformation of the SeMe group in **4** is limited to the cases where it is also perpendicular to the naphthyl plane (**4** (**A_{1A}**)) or on the plane (**4** (**A_{1B}**)). Whereas **4** (**A_{1B}**) is stabilized by the $n_p(\text{Se})\cdots\sigma^*(\text{Se}-\text{C})$ 3c–4e interaction, **4** (**A_{1A}**) must be destabilized by the $n_p(\text{Se})\cdots n_p(\text{Se})$ 2c–4e interaction. The energy difference between **4** (**A_{1B}**) and **4** (**A_{1A}**) ($E(\mathbf{4}(\mathbf{A}_{1A})) - E(\mathbf{4}(\mathbf{A}_{1B})) = 12.6$ kJ mol⁻¹) seems smaller than expected based on the above discussion. It must be due to the 0.243 Å longer Se \cdots Se nonbonding distance in **4** (**A_{1A}**) as compared to that in **4** (**A_{1B}**). The longer distance must avoid the disadvantageous exchange energy due to the $n_p(\text{Se})\cdots n_p(\text{Se})$ 2c–4e interaction in **4** (**A_{1A}**). The torsional angles between the C_{cluster}–Se or C_{methyl}–Se bond and the naphthyl plane (ϕ) (see Figure 8, bottom, for a clear illustration of such angles) in **4** (**A_{1A}**) are predicted to be 84.3° and 70.0°, respectively. The smaller ϕ (see Figure 8, bottom) 70.0° directs $n_p(\text{Se})$ of the SeMe

group away from the Se atom at the 1-position in **4** (**A₁A**), which also avoids the disadvantageous exchange energy.

Conclusions

The preparation, spectroscopic, structural and electrochemical properties of unsymmetrical selenides bearing naphthyl and *o*-carboranyl substituents have been described. It has been shown that the introduction of a *o*-carboranyl cage leads to a downfield shift of the selenium atom bonded to the naphthalene ring in ⁷⁷Se NMR spectra as compared to analogous aryl derivatives, due to the electron withdrawing properties of the *o*-carborane cage. The X-ray structural analyses of molecules **1** and **2** have shown conformations with the carboranyl groups oriented away from the naphthyl plane. Both **1** and **2**, form dimers in the solid state via π -stacking of the naphthyl rings, aided by Se $\cdots\pi$ interactions. Cyclic voltammetry investigations of **1** and **3** reveal that the carboranyl fragment, in agreement with the ⁷⁷Se NMR chemical shifts, polarizes the Se lone pair making it less prone to generate an Se–Se bond.

Supporting Information Available:

"CCDC 802312 & 802313 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033."

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Experimental section

Materials and Methods. All reactions were performed in nitrogen atmosphere using Schlenk techniques. Solvents were freshly distilled over sodium benzophenone prior to use. The purity of the starting materials was controlled by NMR spectroscopy and thin layer chromatography. 1-Methyl-*o*-carborane and 1-phenyl-*o*-carborane were purchased from Katchem Ltd. (Prague). The dinaphthyl 1,1'-diselenide and bis(8-phenylselenyl)-1,1'-diselenide were prepared according to the methods described in literature.⁴⁵ *n*-Butyl lithium (1.6 M solution of in hexanes) was purchased from Fluka, diluted in dry hexane, and titrated using double Gilman titration method.⁴⁶ AgNO₃, LiClO₄, Et₄NCl (all Aldrich), and acetonitrile (Merk, dried over molecular sieves) were used in the electrochemical studies.

¹H-NMR (300.13 MHz), ¹³C{¹H} NMR (75.47 MHz), ⁷⁷Se (75.48 Hz), and ¹¹B-NMR (96.29 MHz) spectra were recorded using a Bruker ARX-300 instrument. Chemical shift values for ¹H and ¹³C{¹H}, ¹¹B, and ⁷⁷Se were referenced relative to Si(CH₃)₄, BF₃·O(C₂H₅)₂, and Se(CH₃)₂ respectively. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz. MALDI-TOF mass spectra were recorded using a Bruker Biflex instrument (N₂ laser, λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)). Electrospray were recorded using a Bruker Esquire 3000 instrument by the direct insertion method. IR spectra were obtained from KBr pellets on a Nicolet 710-FT spectrophotometer. Melting points were measured using a Stuart Scientific SMP10 apparatus. Microanalyses were performed using a Perkin-Elmer 240B microanalyser.

Voltammograms were acquired using three electrode cells. A 0.5 mm Φ Pt wire embedded in PTFE, a home-made Ag/AgCl (0.1 M Et₄NCl in acetonitrile), and a Pt sheet (~ 1 cm² area) were the working, reference, and counter electrodes, respectively. The reference electrode (RE) was checked with ferrocene solutions in acetonitrile, as recommended by IUPAC.⁴⁷ In this way, we have found that the potential of the used reference electrode is 0.72 ± 0.01 V more cathodic than that of Ag/Ag⁺ (0.1 M AgNO₃ in acetonitrile). The latter electrode represented the reference for any other electrochemical data cited in the present paper from literature.

Synthesis of compound 1. To a solution of 1-CH₃-1,2-C₂B₁₀H₁₁ (0.0384 g, 0.2430 mmol) in diethyl ether (3 mL) was added at 25 °C 0.42 mL of a 0.57 M solution of *n*-BuLi in hexanes (0.2430 mmol). The resulting solution was stirred for 0.5 h at ambient conditions, and dinaphthyl 1,1'-diselenide (0.1000 g, 0.2430 mmol) in diethyl ether (10 mL) was added dropwise at the same temperature. The reaction mixture was stirred for an additional 1 h at ambient conditions, neutralized by 0.1 M HCl, and washed with a saturated aqueous solution of NaCl (10 mL). Ether layer was separated and evaporated in vacuum. The pure product was isolated by silica gel chromatography using graduate elution from CHCl₃/hexane (1 % CHCl₃) to CHCl₃/hexane (50 % CHCl₃) mixture as an eluent. Yield: 0.0679 g (77 %). Pale yellow solid. M.p. 162 °C. NMR ¹H (CDCl₃): δ 1.00 – 3.20 (br, BH), 2.28 (s, 3H, CH₃), 7.46 – 7.66 (m, 3H, C_{aryl}-H), 7.89 (d, 1H, $J(\text{HH}) = 8.16$, C_{aryl}-H), 7.96 (d, 1H, $J(\text{HH}) = 7.32$, C_{aryl}-H), 8.02 (d, 1H, $J(\text{HH}) = 8.13$, C_{aryl}-H), 8.46 (d, 1H, $J(\text{HH}) = 8.13$, C_{aryl}-H). NMR ¹³C{¹H} (CDCl₃): δ 25.49 (CH₃), 68.12 [C_c, ¹ $J(^{13}\text{C}, ^{77}\text{Se}) = 167.87$], 78.19 (C_c), 125.60, 126.85, 127.10, 127.75, 127.88, 128.78, 132.60, 134.16, 135.06, 139.29. NMR ¹H [(CD₃)₂CO]: δ 0.80 – 3.40 (br, BH), 2.38 (s, 3H, CH₃), 7.57

– 7.73 (m, 3H, C_{aryl}-H), 8.02 (d, 1H, $J(\text{HH}) = 7.77$, C_{aryl}-H), 8.10 (d, 1H, $J(\text{HH}) = 6.84$, C_{aryl}-H), 8.17 (d, 1H, $J(\text{HH}) = 8.07$, C_{aryl}-H), 8.50 (d, 1H, $J(\text{HH}) = 8.10$, C_{aryl}-H). NMR ⁷⁷Se (CDCl₃): δ 480.48. NMR ¹¹B{¹H}(CDCl₃): –8.13, –3.64, –1.83. IR (KBr): $\nu(\text{cm}^{-1})$ 2592 (B–H). MALDI-TOF-MS (negative ions), (m/z): 363 (M[–]; 2 %, 157 ([C₃B₁₀H₁₃][–]; 19 %). Anal. Calcd for C₁₃H₂₀B₁₀Se: C, 42.97; H, 5.55. Found: C, 43.01; H, 5.56.

Synthesis of compound 2. To a solution of 1-C₆H₅-1,2-C₂B₁₀H₁₁ (0.0530 g, 0.2430 mmol) in diethyl ether (3 mL) was added at 0 °C 0.48 mL of 0.51 M solution of *n*-BuLi in hexanes (0.2430 mmol). The resulting solution was stirred for 0.5 h at 0 °C, 0.5 h at room temperature, and cooled down again to 0 °C, followed by the slow addition of dinaphthyl 1,1'-diselenide (0.1000 g, 0.2430 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 0.5 h at 0 °C, warmed up to room temperature, and stirred for an additional week at ambient conditions. Precipitate was filtered off, filtrate diluted by diethyl ether (30 mL), washed with saturated water solution of Na₂CO₃ (50 mL), and NaCl (50 mL). Ether layer was separated, dried over MgSO₄ and evaporated in vacuum. The pure product was isolated by two chromatographic separations using CHCl₃/hexane (10 % CHCl₃) and finally THF/hexane (5 % THF) mixture as an eluent. Yield: 0.0816 g (79 %). Pale yellow solid. M.p. 146 °C. NMR ¹H (CDCl₃): δ 0.80 – 4.00 (br, BH), 7.29 – 7.64 (m, 9H, C_{aryl}-H), 7.82 (d, 1H, $J(\text{HH}) = 8.13$, C_{aryl}-H), 7.86 (d, 1H, $J(\text{HH}) = 8.52$, C_{aryl}-H), 7.93 (d, 1H, $J(\text{HH}) = 7.74$, C_{aryl}-H). NMR ¹³C{¹H} (CDCl₃): δ 73.23 (C_c, $J(^{13}\text{C}, ^{77}\text{Se}) = 170.65$), 87.02 (C_c), 125.34, 126.59, 126.81, 127.47, 128.00, 128.43, 128.57, 130.72, 131.99, 132.31, 133.87, 134.84, 138.92. NMR ⁷⁷Se (CDCl₃): δ 495.94. NMR ¹¹B{¹H} (CDCl₃): δ –10.54, –8.52, –1.79. IR (KBr): $\nu(\text{cm}^{-1})$ 2602 (B–H). MALDI-TOF-MS

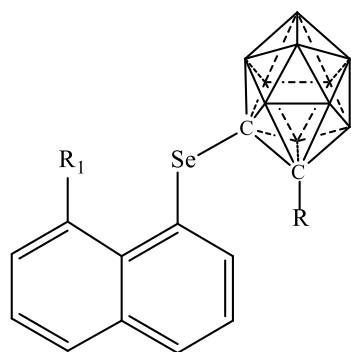
(negative ions), (m/z): 425 (M^- ; 2 %, 220 ($[C_8B_{10}H_{15}]^-$; 27 %). Anal. Calcd for $C_{18}H_{22}B_{10}Se$: C, 50.82; H, 5.21. Found: C, 50.89; H, 5.20.

Synthesis of compound 3. To a solution of 1- CH_3 -1,2- $C_2B_{10}H_{11}$ (0.0103 g, 0.0652 mmol) in diethyl ether (1 mL) was added at 25 °C 0.11 mL of 0.62 M solution of *n*-BuLi in hexanes (0.0652 mmol). The reaction mixture was stirred for 0.5 h at ambient conditions, followed by the slow addition of suspension of diselenide (0.0471 g, 0.0652 mmol) in diethyl ether (20 mL). The slurry was stirred for 4 h at 25 °C, and refluxed for 2 h. The reaction mixture was neutralized by 0.1 M HCl, and washed with saturated solution of NaCl (10 mL). Ether layer was separated and evaporated in vacuum. The pure product was isolated by silica gel chromatography using graduate elution from $CHCl_3$ /hexane (10 % $CHCl_3$) to $CHCl_3$ /hexane (50 % $CHCl_3$) mixture as an eluent. Yield: 0.0140 g (41 %). Pale yellow oil. NMR 1H ($CDCl_3$): δ 1.10 – 3.10 (br, BH), 2.03 (3H, CH_3), 7.26 – 7.54 (m, 8H, C_{aryl-H}), 7.73 (d, 1H, $J(HH) = 7.74$, C_{aryl-H}), 7.99 (d, 1H, $J(HH) = 8.13$, C_{aryl-H}), 8.14 (d, 1H, $J(HH) = 7.35$, C_{aryl-H}). NMR $^{13}C\{^1H\}$ ($CDCl_3$): δ 25.18 (CH_3), 71.48 (C_c , $^1J(^{13}C, ^{77}Se) = 178.97$ Hz), 78.38 (C_c), 125.91, 126.17, 126.66, 128.17, 128.28, 129.55, 133.08, 133.23, 134.03, 134.49, 134.82, 135.34, 136.17, 141.26. NMR ^{77}Se ($CDCl_3$): δ 431.50 ($Se-C_6H_5$), 552.26 ($Se-C_2(CH_3)B_{10}H_{10}$, $^8J(^{1}Se, ^8Se) = 329.69$ Hz). NMR $^{11}B\{^1H\}$ ($CDCl_3$): δ -8.25, -3.69, -1.77. ES-MS in $CHCl_3$ /MeOH (1:1), (m/z): 550 ($M^+ + CH_3OH$, 17 %).

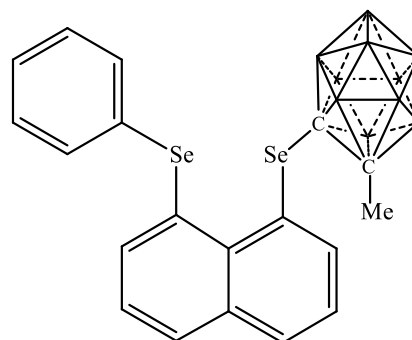
X-ray Structural Determination of 1 and 2: Colorless crystals of **1** and colorless crystals of **2** were grown by slow evaporation of hexane and acetone solutions, respectively. The intensity data were collected on a Rigaku AFC5R four-circle diffractometer with graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71069$ Å) for **1** and **2**. The structures of **1** and **2** were solved by heavy-atom Patterson methods,

PATTY,⁴⁸ and expanded using Fourier techniques, DIRDIF94.⁴⁹ All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on a total of 2678 reflections for **1** and on 2659 for **2** with 218 observed reflections [$I > 1.50\sigma(I)$] for **1** and 262 [$I > 1.50\sigma(I)$] for **2**, respectively. Variable parameters and converged with unweighted and weighted agreement factors of $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = \{\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2\}^{1/2}$ were used. For least squares, the function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$, where $w = (\sigma_c^2|F_o| + p^2|F_o|^2/4)^{-1}$.

Chart 1.- Graphical representation of the carboranyl naphthyl selenides (compounds **1-3**).



- 1:** R = Me, R₁ = H
2: R = Ph, R₁ = H



3

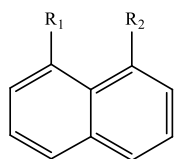
TABLES CAPTION

Table 1. ^{77}Se NMR chemical shifts^[a] and $^4J(^1\text{Se}, ^8\text{Se})$ coupling constants for 1-R¹-8-R²-C₁₀H₆.

Table 2. Crystallographic data for **1** and **2**.

Table 3. Selected bond distances (Å), angles (°), and torsional angles (°) around the selenium atom in compounds **1** and **2**.

Table 1. ^{77}Se NMR chemical shifts^[a] and $^4J(^1\text{Se}, ^8\text{Se})$ coupling constants for 1- R^1 -8- R^2 - C_{10}H_6 .



R^1	R^2	$\delta(^1\text{Se})$	$\delta(^8\text{Se})$	$^4J(^1\text{Se}, ^8\text{Se})$
H	$\text{C}_6\text{H}_5\text{Se}^{[10a]}$	—	361.0	—
H	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{Se}^{[10a]}$	—	356.2	—
H	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{Se}^{[10a]}$	—	379.6	—
H	(1) 1-Se-2- CH_3 -1,2- $\text{C}_{10}\text{H}_{10}$	—	480.5	—
H	(2) 1-Se-2- C_6H_5 -1,2- $\text{C}_{10}\text{H}_{10}$	—	495.9	—
CH_3Se	$\text{C}_6\text{H}_5\text{Se}^{[11f]}$	235.4	434.3	322.4
CH_3Se	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{Se}^{[11f]}$	234.5	427.7	330.9
CH_3Se	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{Se}^{[11f]}$	240.1	453.9	272.5
$\text{C}_6\text{H}_5\text{Se}$	(3) 1-Se-2- CH_3 -1,2- $\text{C}_{10}\text{H}_{10}$	431.5	552.3	329.7

^[a] Relative to $(\text{CH}_3)_2\text{Se}$ in CDCl_3 .

Table 2. Crystallographic data for **1** and **2**.

	1	2
Chemical formula	C ₁₃ H ₂₀ B ₁₀ Se	C ₁₈ H ₂₂ B ₁₀ Se
fw	363.36	425.43
temp (K)	298(1)	298(1)
cryst system	triclinic	monoclinic
space group	<i>P</i> 1_ (#2)	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>a</i> (Å)	7.589(2)	10.759(4)
<i>b</i> (Å)	16.898(4)	14.445(3)
<i>c</i> (Å)	7.614(2)	13.734(4)
α (deg)	84.03(2)	
β (deg)	113.26(2)	99.32(2)
γ (deg)	85.61(2)	
<i>V</i> (Å ³)	884.8(5)	2106.2(9)
<i>Z</i>	2	4
<i>D</i> _{calcd} (g cm ⁻³)	1.364	1.342
<i>F</i> (000)	364	856
no. of reflns collected	2678	2659
no. of parameters	218	262
R1 [<i>I</i> > 1.5 σ (<i>I</i>)] ^[a]	0.052	0.045
wR2 [<i>I</i> > 1.5 σ (<i>I</i>)] ^[b]	0.040	0.032
GOF	2.95	1.97

^[a] $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$. ^[b] $R_w = \{ \sum \omega (|F_o| - |F_c|)^2 / \sum \omega F_o^2 \}^{1/2}$.

Table 3. Selected bond distances (Å), angles (°), and torsional angles (°) around the selenium atom in compounds **1** and **2**.

Compound 1		Compound 2	
Bond distances (Å)			
Se(1)-C(1)	1.970(5)	Se(1)-C(1)	1.940(4)
Se(1)-C(14)	1.921(5)	Se(1)-C(19)	1.924(4)
C(1)-C(2)	1.697(7)	C(1)-C(2)	1.734(5)
Angles (°)			
C(1)-Se(1)-C(14)	102.7(2)	C(1)-Se(1)-C(19)	101.0(2)
Se(1)-C(1)-C(2)	118.3(3)	Se(1)-C(1)-C(2)	117.3(2)
Se(1)-C(14)-C(15)	118.0(4)	Se(1)-C(19)-C(20)	118.2(4)
Se(1)-C(14)-C(22)	121.0(4)	Se(1)-C(19)-C(27)	121.5(4)
Torsional angles (°)			
Se(1)-C(1)-C(2)-C(13)	-6.0(7)	Se(1)-C(1)-C(2)-C(13)	-4.6(5)
C(2)-C(1)-Se(1)-C(14)	90.0(4)	C(2)-C(1)-Se(1)-C(19)	103.8(3)
C(1)-Se(1)-C(14)-C(15)	-94.0(4)	C(1)-Se(1)-C(19)-C(20)	-88.2(4)
C(1)-Se(1)-C(14)-C(22)	95.1(4)	C(1)-Se(1)-C(19)-C(27)	96.0(3)
Se(1)-C(14)-C(15)-C(16)	-173.5(4)	Se(1)-C(19)-C(20)-C(21)	-177.8(4)
Se(1)-C(14)-C(22)-C(23)	171.7(3)	Se(1)-C(19)-C(27)-C(28)	176.5(3)

Scheme 1. General reaction of compounds synthesis.

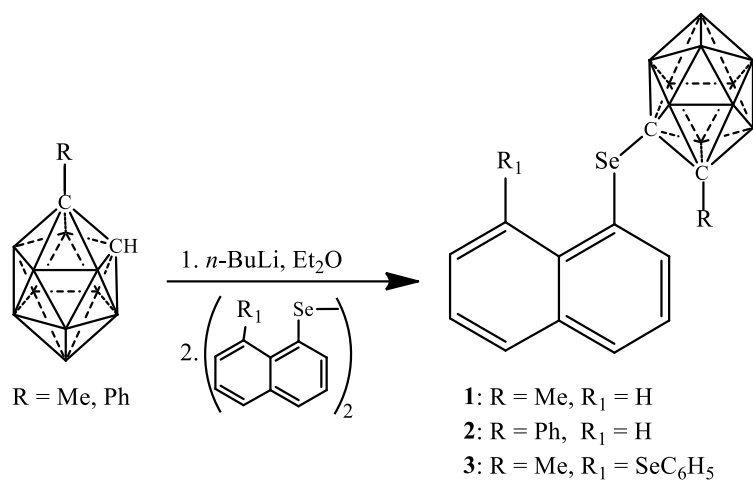


FIGURE CAPTIONS

Figure 1. Structure of **1** with displacement ellipsoids shown at the 50 % probability level.

Figure 2. Structure of **2** with displacement ellipsoids shown at the 50 % probability level.

Figure 3. Representation of the dimers formed in the crystal structures of compounds **1** (top) and **2** (bottom). Se $\cdots\pi$ interactions are depicted as dotted blue lines. White = H, pink = B, grey = C, purple = Se.

Figure 4. A perspective of the ribbons established *via* C_{naphthyl}-H \cdots H-B contacts between dimers in the crystal structure of compound **1**. The interactions of importance are depicted as dotted blue lines. White = H, pink = B, grey = C, purple = Se.

Figure 5. A perspective of the packing in the crystal lattice of compound **1**, showing the alternate layers formed parallel to the crystallographic *ac* plane. White = H, pink = B, grey = C, purple = Se.

Figure 6. A perspective of the packing in the crystal lattice of compound **2**, showing the alternate layers formed parallel to the crystallographic *bc* plane. White = H, pink = B, grey = C, purple = Se.

Figure 7. Cyclic voltammograms acquired at 500 mV/s scan rates for: (a) 10 mM 1-(2-Me-1,2-dicarba-*closo*-carboranyl)naphthyl selenide (**1**) dissolved in a 0.1 M LiClO₄ acetonitrile solution; and (b) 10 mM 1-(2-Me-1,2-dicarba-*closo*-carboranyl)naphthyl sulfide dissolved in a 0.1 M LiClO₄ acetonitrile solution.

Figure 8. Predicted structures of **1** and **4**, together with the energies.

Figure 1. Structure of **1** with displacement ellipsoids shown at the 50 % probability level.

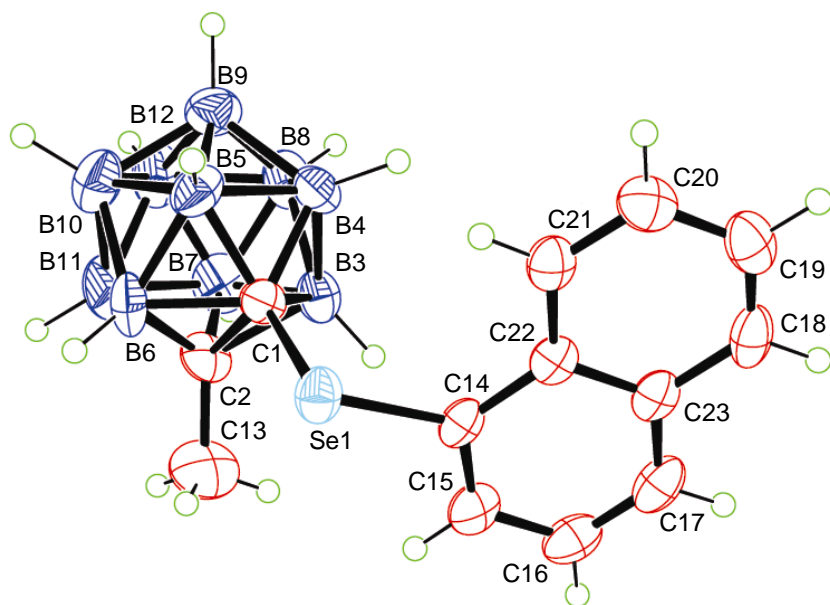


Figure 2. Structure of **2** with displacement ellipsoids shown at the 50 % probability level.

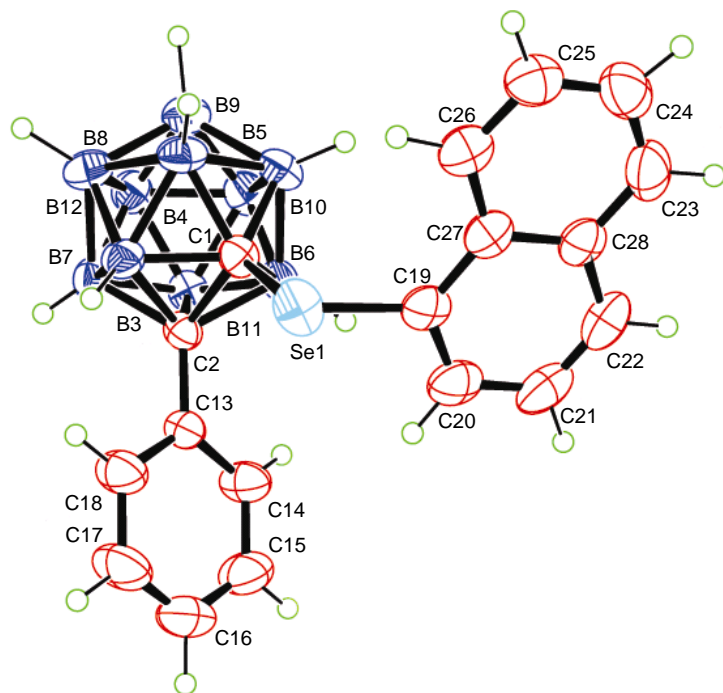


Figure 3. Representation of the dimers formed in the crystal structures of compounds **1** (top) and **2** (bottom). Se $\cdots\pi$ interactions are depicted as dotted blue lines. White = H, pink = B, grey = C, purple = Se.

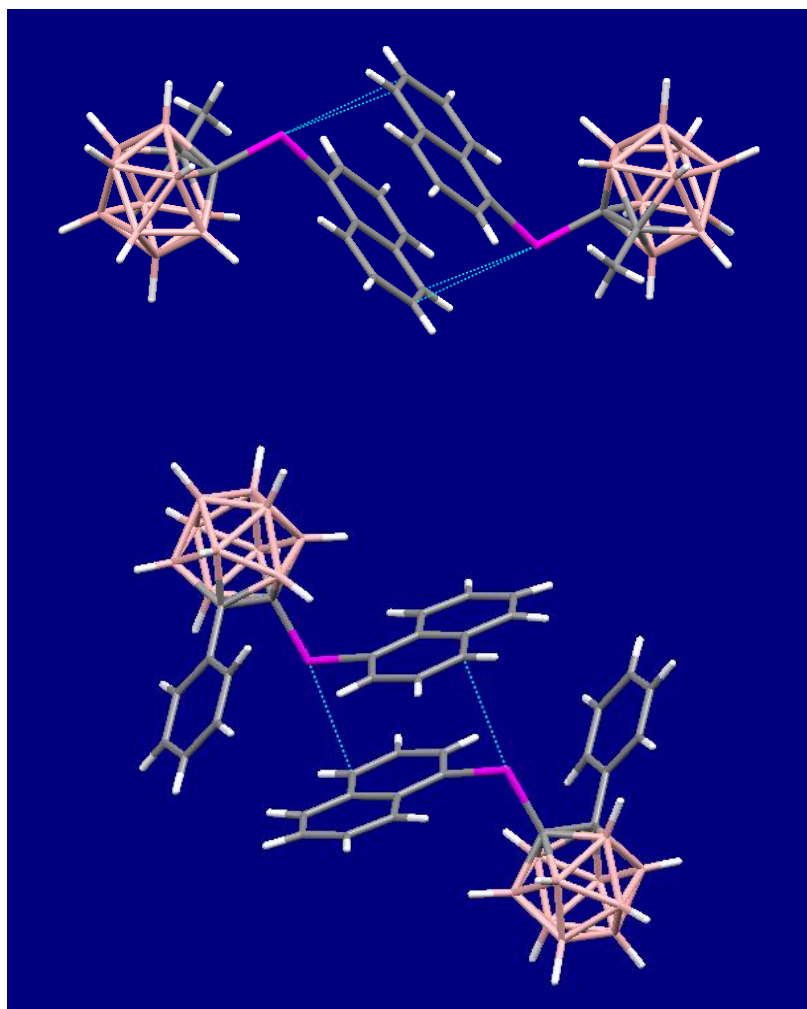


Figure 4. A perspective of the ribbons established *via* $C_{\text{naphthyl}}\text{-H}\cdots\text{H-B}$ contacts between dimers in the crystal structure of compound **1**. The interactions of importance are depicted as dotted blue lines. White = H, pink = B, grey = C, purple = Se.

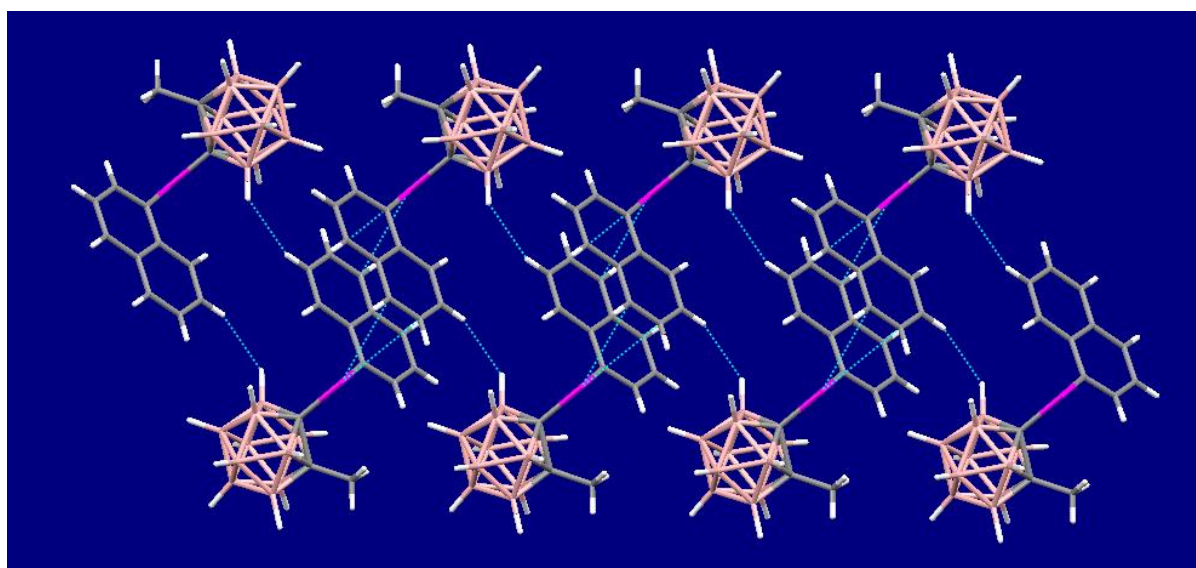


Figure 5. A perspective of the packing in the crystal lattice of compound **1**, showing the alternate layers formed parallel to the crystallographic ac plane. White = H, pink = B, grey = C, purple = Se.

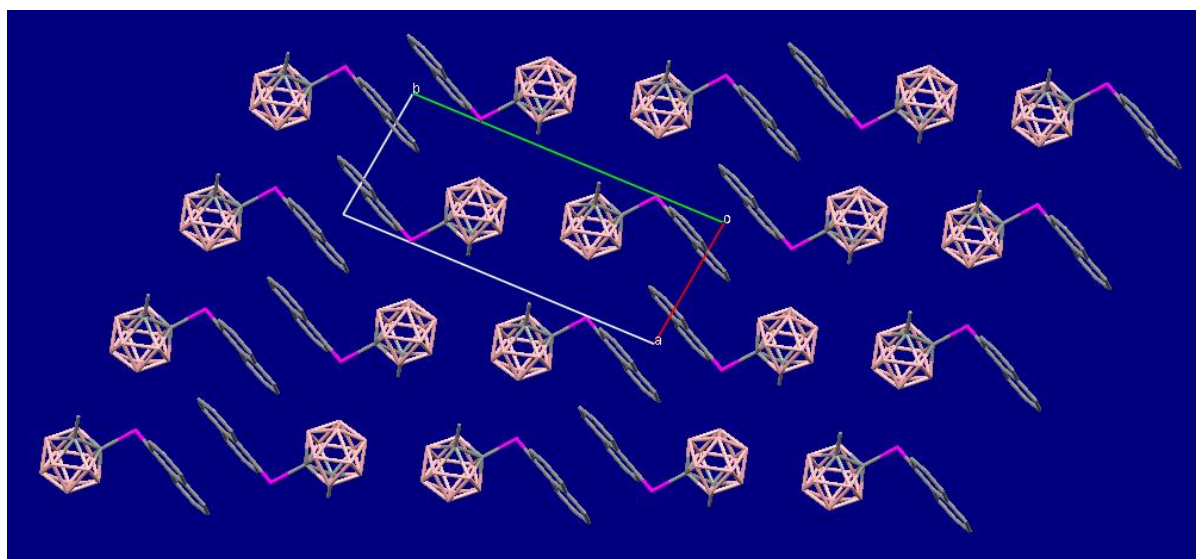


Figure 6. A perspective of the packing in the crystal lattice of compound **2**, showing the alternate layers formed parallel to the crystallographic bc plane. White = H, pink = B, grey = C, purple = Se.

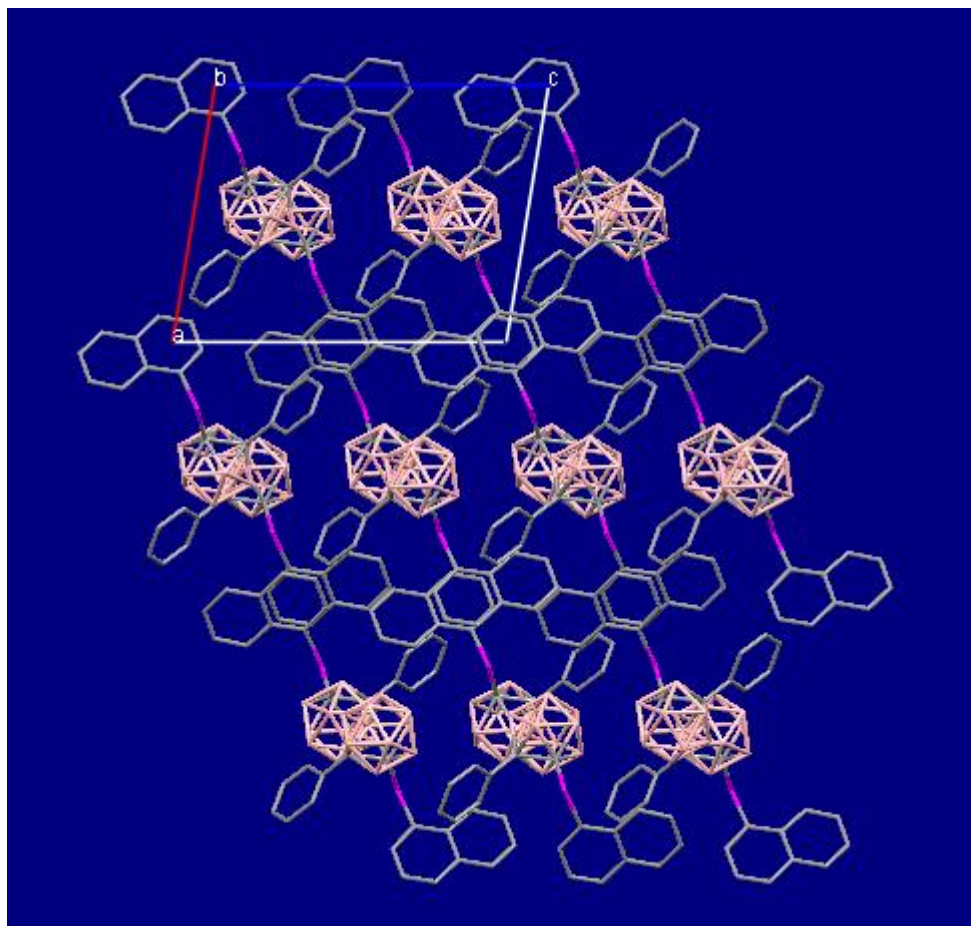


Figure 7. Cyclic voltammograms acquired at 500 mV/s scan rates for: (a) 10 mM 1-(2-Me-1,2-dicarba-*closo*-carboranyl)naphthyl selenide (**1**) dissolved in a 0.1 M LiClO₄ acetonitrile solution; and (b) 10 mM 1-(2-Me-1,2-dicarba-*closo*-carboranyl)naphthyl sulfide dissolved in a 0.1 M LiClO₄ acetonitrile solution.

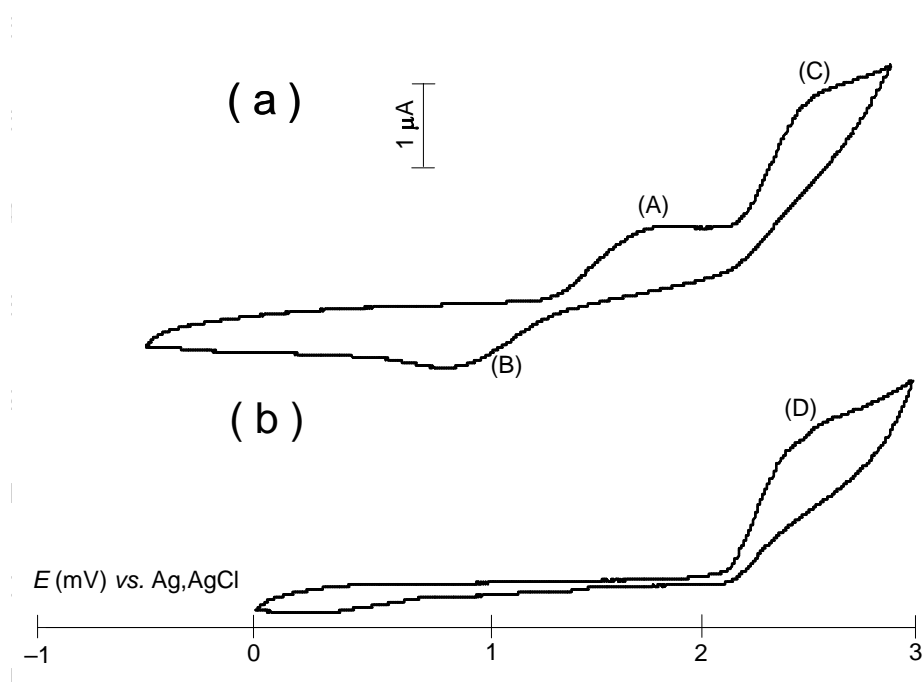
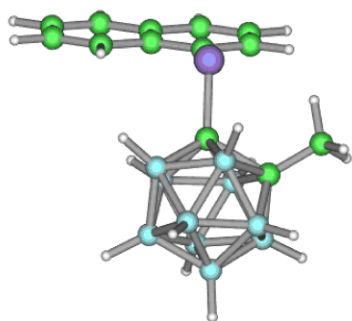
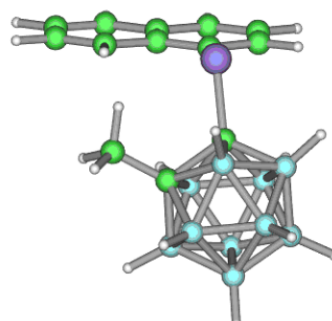


Figure 8. Predicted structures of **1** and **4**, together with their energies.

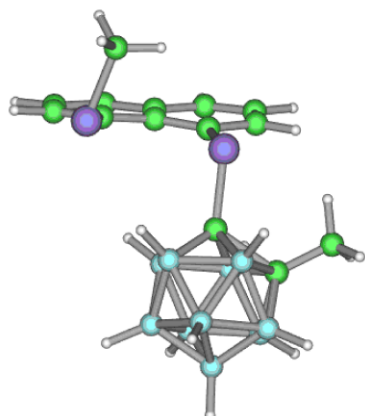


1 (A₁): -3157.4383 au

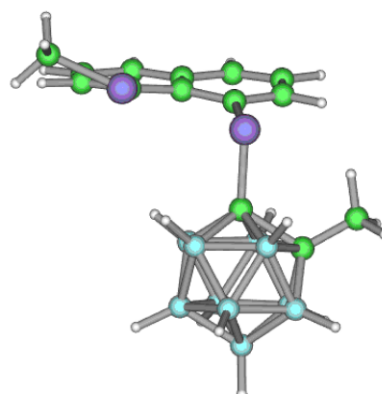


1 (A₂): -3157.4378 au

$$\Delta E = E(1(A_1)) - E(1(A_2)) = -1.3 \text{ kJ mol}^{-1}$$



4 (A₁A): -5598.2690 au



4 (A₁B): -5598.2738 au

$$\Delta E = E(4(A_1A)) - E(4(A_1B)) = 12.6 \text{ kJ mol}^{-1}$$

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