Supplementary information

Synthesis of new ω-amino- and ω-azidoalkyl carboranes

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Experimental

Materials, instruments and general procedures

The triethylammonium salt of 1-mercapto-*ortho*-carborane was prepared according to our previous work procedure[1]. All reactions were carried out in air. Thin-layer chromatograms (Merck F254 silica gel on aluminium plates) were visualized using 0.1% $PdCl_2$ in 3 M HCl(aq). Acros organics silica gel (0.060–0.200 mm) was used for column chromatography. The ^{1}H, ^{11}B, and $^{11}B\{^{1}H\}$, ^{13}C NMR spectra were collected using Bruker Avance-400 spectrometer. The residual signal of the NMR solvent relative to tetramethylsilane was taken as the internal reference for ^{1}H NMR and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced using a $BF_3 \cdot Et_2O$ external standard. Infrared spectra were recorded on Specord IR 75 and Infralum FT-801 spectrophotometers. Mass spectra were obtained using Kratos MS 890 mass spectrometer. Elemental analyses were performed at the Laboratory of Microanalysis of the Institute of Organoelement Compounds.

Synthesis of 1-$C_6H_4(CO)_2NCH_2S$-1,2-$C_2B_{10}H_{11}$ (1).

To solution of triethylammonium salt of 1-mercapto-*ortho*-carborane (0.40 g, 1.5 mmol) in ethanol (50 ml), *N*-(bromomethyl)phthalimide (0.35 g, 1.5 mmol) was added, stirred at room temperature for 15 min and heated under reflux for 20 h. The reaction mixture was cooled and evaporated to dryness *in vacuo*. The residue was treated with diethyl ether (50 ml) and water (50 ml). The organic layer was separated, washed with water (2 x 30 ml) and evaporated *in vacuo*. The crude product was purified using column chromatography on silica with $CHCl_3$ as eluent. The solvent was evaporated under vacuum to yield a white residue (0.31 g, 64% yield). ^{1}H NMR ($CDCl_3$): δ 7.91 (2H, m, C*H*$_{ar}$), 7.81 (2H, m, C*H*$_{ar}$), 5.1 (2H, s, CH_2), 3.92 (1H, s, C*H*$_{carb}$), 3.0–1.3 (10H, br s, B*H*). ^{13}C NMR ($CDCl_3$): δ 166.5, 134.8, 131.6, 124.0, 72.8, 67.6, 42.4. ^{11}B NMR ($CDCl_3$): δ -1.3 (1B, d, J = 154 Hz), -4.5 (1B, d, J = 140 Hz), -8.6 (2B, d, J =142 Hz), -9.6 (2B, d, J =147 Hz), -12.4 (4B, d, J = 167 Hz). IR (Nujol, cm^{-1}): 2639, 2611, 2588,

2558 (ν_{B-H}), 1738, 1726 ($\nu_{C=O}$). MS *m/z* for $C_{11}H_{17}B_{10}NO_2S$: calcd 335.4, obsd 334.4 $[M-H]^+$.

Synthesis of 1-$C_6H_4(CO)_2NCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (2).

The procedure was analogous to that described for synthesis of **1** using triethylammonium salt of 1-mercapto-*ortho*-carborane (0.30 g, 1.1 mmol) in ethanol (30 ml) and N-(2-bromoethyl)phthalimide (0.28 g, 1.1 mmol) to yield a white residue (0.25 g, 68% yield). ^{1}H NMR ($CDCl_3$): δ 7.92 (2H, m, C*H*$_{ar}$), 7.78 (2H, m, C*H*$_{ar}$), 4.02 (1H, s, C*H*$_{carb}$), 3.96 (2H, t, *J* = 7.1 Hz, C*H*$_2$N), 3.25 (2H, t, *J* = 7.1 Hz, SC*H*$_2$), 3.0–1.2 (10H, br s, B*H*). ^{13}C NMR ($CDCl_3$): δ 168.0, 134.4, 131.7, 123.6, 74.1, 67.2, 36.7, 35.3. ^{11}B NMR ($CDCl_3$): δ -1.4 (1B, d, *J* = 155 Hz), -4.8 (1B, d, *J* = 159 Hz), -8.9 (4B, d, *J* =147 Hz), -12.4 (4B, d, *J* = 163 Hz). IR (Nujol, cm^{-1}): 2656, 2605, 2566 (ν_{B-H}), 1770, 1721, 1708 ($\nu_{C=O}$). MS *m/z* for $C_{12}H_{19}B_{10}NO_2S$: calcd 349.4, obsd 349.3 $[M]^+$.

Synthesis of 1-$C_6H_4(CO)_2NCH_2CH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (3).

To solution of triethylammonium salt of 1-mercapto-*ortho*-carborane (1.00 g, 3.6 mmol) in ethanol (50 ml), *N*-(3-bromopropylphthalimide) (0.97 g, 3.6 mmol) was added, stirred at room temperature for 15 min and heated under reflux for 4 h. The reaction mixture was cooled and evaporated to dryness *in vacuo*. The residue was treated with diethyl ether (50 ml) and water (50 ml). The organic layer was separated, washed with water (2 x 30 ml) and evaporated *in vacuo*. The residue was purified by recrystallization from ethanol to yield white solid (1.19 g, 91%). ^{1}H NMR ($CDCl_3$): δ 7.77 (2H, m, C*H*$_{ar}$), 7.75 (2H, m, C*H*$_{ar}$), 3.98 (1H, s, C*H*$_{carb}$), 3.78 (2H, t, *J* = 7.0 Hz, C*H*$_2$N), 3.0–1.3 (10H, br s, B*H*), 2.97 (2H, t, *J* = 7.1 Hz, SC*H*$_2$), 1.99 (2H, m, SCH$_2$C*H*$_2$). ^{13}C NMR ($CDCl_3$): δ 168.3, 134.2, 131.9, 123.4, 74.5, 68.1, 36.5, 34.4, 27.5. ^{11}B NMR ($CDCl_3$): δ -1.5 (1B, d, *J* = 165 Hz), -5.1 (1B, d, *J* = 153 Hz), -8.8 (2B, d, *J* =144 Hz), -9.8 (2B, d, *J* =152 Hz), -12.6 (4B, d, *J* = 165 Hz). IR (Nujol, cm^{-1}): 2603, 2574 (ν_{B-H}), 1708 ($\nu_{C=O}$). MS *m/z* for $C_{13}H_{21}B_{10}NO_2S$: calcd 363.5, obsd 363.1 $[M]^+$.

Synthesis of 7-$NH_3CH_2CH_2S$-7,8-$C_2B_9H_{11}$*1.4N_2H_4 (4a).

To solution of **2** (0.10 g, 0.3 mmol) in ethanol (20 ml) hydrazine monohydrate (0.30 g, 6.0 mmol) was added. The reaction mixture was heated under reflux for 30 min, cooled to room temperature and filtered. The solvent was evaporated *in vacuo* to give a white residue (0.06 g, 97%). ^{1}H NMR (acetone-d_6): δ 3.25 (1H, m, $SCH_2CH_2NH_3$), 3.21 (1H, m, $SCH_2CH_2NH_3$), 3.09 (1H, m, $SCH_2CH_2NH_3$), 2.75 (1H, m, $SCH_2CH_2NH_3$), 2.4-(-0.3) (9H, br s, B*H*), 1.99 (1H, s, CH_{carb}), -2.75 (1H, br s, B*H*B). ^{13}C NMR (acetone-d_6): δ 55.4, 52.9, 41.6, 38.2. ^{11}B NMR (acetone-d_6): δ -9.6 (1B, d, J = 137 Hz), 11.0 (1B, d, J = 139 Hz), -14.8 (1B, d, J = 157 Hz), -16.4 (1B, d, J = 141 Hz), -18.0 (2B, d, J = 151 Hz), -21.6 (1B, d, J = 156 Hz), -32.7 (1B, dd, J = 146, 57 Hz), -36.5 (1B, d, J =137 Hz). IR (Nujol, cm^{-1}): 3393, 3389, 3387, 3277, 3153 (ν_{N-H}), 2523 (ν_{B-H}). MS *m*/*z* for: calcd 209.5, obsd 208.2 $[M-H]^+$. Anal. Calc. for $C_4H_{23.6}B_9N_{3.8}S$: C, 18.88; H, 9.37; N, 20.33; B, 38.24. Found: C, 18.72; H, 9.33; N, 20.43; B, 38.25%.

Synthesis of (Me_3NH)[7-$NH_2CH_2CH_2S$-7,8-$C_2B_9H_{11}$] (4).

To solution of **4a** (0.05 g, 0.20 mmol) in water (10 ml) solution of trimethylamine hydrochloride (0.10 g, 1.00 mmol) in water (5 ml) was added. The white precipitate was filtered, washed with water (5 ml), and dried overnight over P_2O_5 to give the product **4** (0.05 g, 95%). ^{1}H NMR (CD_3OD): δ 3.21 (1H, m, $SCH_2CH_2NH_2$), 3.13 (1H, m, $SCH_2CH_2NH_2$), 3.06 (1H, m, $SCH_2CH_2NH_2$), 2.72 (1H, m, $SCH_2CH_2NH_2$), 2.40 (9H, s, $N(CH_3)_3$), 2.2-(-0.4) (9H, br s, B*H*), 2.00 (1H, s, CH_{carb}), -2.85 (1H, br s, B*H*B). ^{11}B NMR (CD_3OD): δ -9.9 (1B, d, J = 142 Hz), 11.5 (1B, d, J = 149 Hz), -14.8 (1B, d, J = 157 Hz), -16.3 (1B, d, J = 151 Hz), -17.5 (1B, d, J = 138 Hz), -18.4 (1B, d, J = 151 Hz), -21.2 (1B, d, J = 154 Hz), -32.6 (1B, d, J = 136 Hz), -36.7 (1B, d, J =142 Hz).

Synthesis of 7-$NH_3CH_2CH_2CH_2S$-7,8-$C_2B_9H_{11}$*1.2N_2H_4 (5a).

The procedure was analogous to that described for synthesis of **4a** using **3** (0.68 g, 1.9 mmol) and hydrazine monohydrate (1.88 g, 38.0 mmol) in ethanol (50 ml) to yield a

white residue (0.46 g, 96% yield). ^{1}H NMR (acetone-d_6): δ 3.03 (2H, t, J = 7.1 Hz, $SCH_2CH_2CH_2NH_3$), 2.96 (1H, m, $SCH_2CH_2CH_2NH_3$), 2.61 (1H, m, $SCH_2CH_2CH_2NH_3$), 2.5-(-0.5) (9H, br s, B*H*), 2.06 (1H, m, $SCH_2CH_2CH_2NH_2$), 2.01 (1H, s, CH_{carb}), 1.91 (1H, m, $SCH_2CH_2CH_2NH_2$), -2.75 (1H, br s, B*H*B). ^{13}C NMR (acetone-d_6): δ 55.5, 52.6, 40.8, 33.0, 27.7. ^{11}B NMR (acetone-d_6): δ -9.7 (1B, d, J = 136 Hz), 10.6 (1B, d, J = 136 Hz), -14.8 (1B, d, J = 161 Hz), -17.2 (3B, d, J = 139 Hz), -21.9 (1B, d, J = 146 Hz), -32.8 (1B, dd, J = 133, 46 Hz), -36.5 (1B, d, J =140 Hz). IR (Nujol, cm^{-1}): 3359, 3349, 3330, 3329 (ν_{N-H}), 2577, 2550, 2537, 2497, 2475 (ν_{B-H}). MS *m*/*z* for $C_5H_{24}B_9N_3S$: calcd 255.6, obsd 222.2 $[M-N_2H_5]^+$. Calc. for $C_5H_{24.8}B_9N_{3.4}S$: C, 22.92; H, 9.56; N, 18.18; B, 37.13. Found: C, 22.78; H, 9.64; N, 18.24; B, 37.18%.

Synthesis of $(Me_3NH)[7\text{-}NH_2CH_2CH_2CH_2S\text{-}7,8\text{-}C_2B_9H_{11}]$ (5).

To solution of **5a** (0.38 g, 1.5 mmol) in water (30 ml) solution of trimethylamine hydrochloride (0.50 g, 5.00 mmol) in water (10 ml) was added. The white precipitate was filtered, washed with water (10 ml), and dried overnight over P_2O_5 to give the product **3a** (0.38 g, 97%). ^{1}H NMR (CD_3OD): δ 3.03 (2H, t, J = 7.1 Hz, $SCH_2CH_2CH_2NH_2$), 2.98 (1H, m, $SCH_2CH_2CH_2NH_2$), 2.61 (1H, m, $SCH_2CH_2CH_2NH_2$), 2.5-(-0.5) (9H, br s, B*H*), 2.33 (9H, s, $N(CH_3)_3$), 2.02 (1H, m, $SCH_2CH_2CH_2NH_2$), 1.98 (1H, s, CH_{carb}), 1.92 (1H, m, $SCH_2CH_2CH_2NH_2$), -2.85 (1H, br s, B*H*B). ^{11}B NMR (CD_3OD): δ -10.2 (1B, d, J = 135 Hz), -11.2 (1B, d, J = 134 Hz), -14.8 (1B, d, J = 158 Hz), -17.1 (2B, d, J = 151 Hz), -17.7 (1B, d, J = 138 Hz), -21.7 (1B, d, J = 151 Hz), -32.8 (1B, d, J = 130 Hz), -36.7 (1B, d, J =142 Hz).

Synthesis of $1\text{-}(C_6H_4(2\text{-}CH_2OH)(CO)NHCH_2CH_2CH_2S)\text{-}1,2\text{-}C_2B_{10}H_{11}$ (6).

To solution of **3** (0.29 g, 0.8 mmol) in 2-propanol (25 ml) and water (5 ml) sodium borohydride (0.15 g, 3.9 mmol) was added. The suspension was stirred for 20 h. The solvent was evaporated and the residue was extracted with hot water and Et_2O. The organic layer was evaporated to dryness *in vacuo* to give white precipitate (0.07 g, 24% yield). ^{1}H NMR (DMSO-d_6): δ 9.96 (1H, s, N*H*), 7.53 (1H, m, CH_{ar}), 7.43 (2H, m,

CH_{ar}), 7.32 (1H, m, CH_{ar}), 5.42 (1H, s, O*H*), (2 H, s, CH_2OH), 3.88 (1H, s, CH_{carb}), 3.29 (2H, t, *J* = 7.0 Hz, CH_2N), 3.04 (2H, t, *J* = 7.0 Hz, SCH_2), 3.0–1.0 (10H, br s, B*H*), 1.80 (2H, m, SCH$_2$CH_2). ^{11}B NMR (DMSO-d$_6$): δ -2.3 (1B, d, *J* = 168 Hz), -5.8 (1B, d, *J* = 149 Hz), -9.6 (4B, d, *J* =151 Hz), -12.4 (4B, d, *J* =150 Hz).

Synthesis of 1-(2-OC$_5$H$_9$)OCH$_2$CH$_2$S-1,2-C$_2$B$_{10}$H$_{11}$ (7).

To solution of the triethylammonium salt of 1-mercapto-*ortho*-carborane (1.50 g, 5.4 mmol) in ethanol (50 ml), 2-(2-bromoethoxy)tetrahydropyran (1.13 g, 5.4 mmol) was added, stirred at room temperature for 15 min and heated under reflux for 30 h. The reaction mixture was cooled and evaporated to dryness *in vacuo*. The residue was treated with diethyl ether (50 ml) and water (50 ml). The organic layer was separated, washed with water (2 x 30 ml), dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was purified using column chromatography on silica with $CHCl_3$ as eluent. The solvent was evaporated under vacuum to yield a colorless oil (1.12 g, 68% yield). ^{1}H NMR ($CDCl_3$): δ 4.61 (1H, t, *J* = 6.9 Hz, OC*H*(O)CH$_2$), 3.91 (1H, m, SCH$_2$CH_2O), 3.88 (1H, m, CH_2O), 3.81 (1H, s, CH_{carb}), 3.61 (1H, m, SCH$_2$CH_2O), 3.53 (1H, m, CH_2O), 3.17 (2H, t, *J* = 7.1 Hz, SCH_2), 3.0–1.4 (10H, br s, B*H*), 1.81 (1H, m, CHCH_2CH$_2$), 1.70 (1H, m, CHCH_2CH$_2$), 1.74 (4H, m, CH$_2$CH_2CH_2). ^{13}C NMR ($CDCl_3$): δ 98.5, 68.3, 65.5, 62.3, 60.6, 39.9, 37.3, 30.3, 25.3. ^{11}B NMR ($CDCl_3$): δ -1.6 (1B, d, *J* = 149 Hz), -5.0 (1B, d, *J* = 154 Hz), -8.8 (2B, d, *J* =142 Hz), -9.7 (2B, d, *J* =138 Hz), -12.5 (4B, d, *J* = 163 Hz). IR (neat, cm^{-1}): 2597 (ν_{B-H}). MS *m*/*z* for $C_9H_{24}B_{10}O_2S$: calcd 304.4, obsd 304.3 $[M]^+$.

Synthesis of 1-HOCH$_2$CH$_2$S-1,2-C$_2$B$_{10}$H$_{11}$ (8).

Compound **7** (0.9 g, 2.9 mmol) was dissolved in methanol (30 ml) and *para*-toluenesulfonic acid (1.12 g, 5.9 mmol) was added. The reaction mixture was stirred for 1 h at room temperature and the solvent was evaporated *in vacuo*. The residue was treated with chloroform (50 ml) and water (50 ml). The organic layer was separated and evaporated *in vacuo*. The crude product was purified using column chromatography on

silica with $CHCl_3$ as eluent to give yellow oil (0.56 g, 88% yield). ^{1}H NMR (acetone-d_6): δ 4.81 (1H, s, C*H*$_{carb}$), 3.77 (2H, t, *J* = 7.1 Hz, C*H*$_2$O), 3.18 (2H, t, *J* = 7.1 Hz, SC*H*$_2$), 3.0–1.4 (10H, br s, B*H*). ^{13}C NMR (acetone-d_6): δ 75.7, 68.7, 60.0, 39.9. ^{11}B NMR (aceton-d_6): δ -2.1 (1B, d, *J* = 151 Hz), -5.6 (1B, d, *J* = 147 Hz), -9.4 (4B, d, *J* =156 Hz), -12.0 (2B, d, *J* =161 Hz), -12.5 (2B, d, *J* = 163 Hz). IR (neat, cm^{-1}): 3357 (ν_{O-H}), 2599 (ν_{B-H}). MS *m*/*z* for $C_4H_{16}B_{10}OS$: calcd 220.3, obsd 220.1 $[M]^+$.

Synthesis of 1-$N_3CH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (9).

A mixture of **8** (0.36 g, 1.6 mmol), sodium azide (0.13 g, 1.9 mmol) and PPh_3 (0.9 g, 3.4 mmol) in 8 ml of CCl_4-DMF (4:1) was heated under reflux for 5 h. After total disappearance of starting materials (monitored by TLC), reaction mixture was cooled to room temperature and 5 ml of H_2O was added. After stirring for 10 min, reaction mixture was diluted with ether (20 ml) and washed with water. The ether fraction was separated and evaporated *in vacuo*. The crude product was purified using column chromatography on silica with ethyl acetate as eluent to give colorless oil (0.23 g, 58% yield). ^{1}H NMR (acetone-d_6): δ 4.86 (1H, s, C*H*$_{carb}$), 3.84 (2H, t, *J* = 7.1 Hz, C*H*$_2$N$_3$), 3.42 (2H, t, *J* = 7.1 Hz, SC*H*$_2$), 3.1–1.3 (10H, br s, B*H*). ^{13}C NMR (acetone-d_6): δ 75.0, 68.4, 50.1, 37.9. ^{11}B NMR (acetone-d_6): δ -1.9 (1B, d, *J* = 151 Hz), -5.3 (1B, d, *J* = 149 Hz), -9.5 (4B, d, *J* =159 Hz), -12.3 (4B, d, *J* =158 Hz). IR (neat, cm^{-1}): 2601 (ν_{B-H}), 2107 (ν_{N_3}). MS *m*/*z* for $C_4H_{15}B_{10}N_3S$: calcd 245.3, obsd 245.2 $[M]^+$.

Synthesis of 1-$ClCH_2CH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (10).

To solution of the triethylammonium salt of 1-mercapto-*ortho*-carborane (2.00 g, 7.2 mmol) in ethanol (50 ml), $BrCH_2CH_2CH_2Cl$ (1.14 g, 7.2 mmol) was added. The reaction mixture was heated under reflux for 30 h, cooled and evaporated to dryness *in vacuo*. The residue was treated with diethyl ether (50 ml) and water (50 ml). The organic layer was separated, dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was purified using column chromatography on silica with CH_2Cl_2 as eluent. The solvent was evaporated under vacuum to yield a colorless oil (1.36 g, 75% yield). ^{1}H NMR ($CDCl_3$):

δ 3.77 (1H, s, C*H*$_{carb}$), 3.62 (2H, t, *J* = 7.0 Hz, C*H*$_2$Cl), 3.11 (2H, t, *J* = 7.1 Hz, SC*H*$_2$), 2.9–1.3 (10H, br s, B*H*), 2.08 (2H, m, *J* = 6.9 Hz, SCH$_2$C*H*$_2$). ^{13}C NMR ($CDCl_3$): δ 74.3, 68.2, 42.7, 34.1, 31.1 ^{11}B NMR ($CDCl_3$): δ -1.5 (1B, d, *J* = 149 Hz), -4.9 (1B, d, *J* = 142 Hz), -8.7 (2B, d, *J* =149 Hz), -9.8 (2B, d, *J* =153 Hz), -12.5 (4B, d, *J* = 165 Hz). IR (neat, cm^{-1}): 2590 ($\nu_{B–H}$). MS *m*/*z* for $C_5H_{17}B_{10}ClS$: calcd 252.8, obsd 252.1 $[M]^+$.

Synthesis of 1-ICH$_2$CH$_2$CH$_2$S-1,2-C$_2$B$_{10}$H$_{11}$ (11).

To a solution of **10** (1.20 g, 4.8 mmol) in acetone (40 ml) sodium iodide (8.92 g, 48.0 mmol) was added. The reaction mixture was heated under reflux for 40 h. The precipitate formed during reaction was filtered out and the solvent was evaporated under vacuum to yield yellow oil (1.58 g, 96% yield). ^{1}H NMR ($CDCl_3$): δ 3.77 (1H, s, C*H*$_{carb}$), 3.23 (2H, t, *J* = 7.1 Hz, C*H*$_2$I), 3.05 (2H, t, *J* = 7.1 Hz, SC*H*$_2$), 2.8–1.3 (10H, br s, B*H*), 2.09 (2H, m, *J* = 7.0 Hz, SCH$_2$C*H*$_2$). ^{13}C NMR ($CDCl_3$): δ 74.3, 68.2, 37.6, 31.5, 23.4 ^{11}B NMR ($CDCl_3$): δ -1.6 (1B, d, *J* = 146 Hz), -4.9 (1B, d, *J* = 153 Hz), -8.7 (2B, d, *J* =164 Hz), -9.8 (2B, d, *J* =168 Hz), -12.6 (4B, d, *J* = 168 Hz). IR (neat, cm^{-1}): 2596 ($\nu_{B–H}$). MS *m*/*z* for $C_5H_{17}B_{10}IS$: calcd 244.3, obsd 244.1 $[M]^+$.

Synthesis of 1-N$_3$CH$_2$CH$_2$CH$_2$S-1,2-C$_2$B$_{10}$H$_{11}$ (12).

To solution of **11** (0.65 g, 1.9 mmol) in acetone (30 ml) NaN_3 (0.73 g, 11.3 mmol) was added. The reaction mixture was heated under reflux for 20 h, cooled to room temperature, filtered and concentrated to dryness *in vacuo*. The residue was treated with diethyl ether (50 ml) and water (50 ml). The organic layer was separated and evaporated *in vacuo* to yield colorless oil (0.42 g, 87% yield). ^{1}H NMR (acetone-d_6): δ 4.83 (1H, s, C*H*$_{carb}$), 3.51 (2H, t, *J* = 6.9 Hz, C*H*$_2$N$_3$), 3.13 (2H, t, *J* = 7.0 Hz, SC*H*$_2$), 2.9–1.4 (10H, br s, B*H*), 1.92 (2H, m, *J* = 6.9 Hz, SCH$_2$C*H*$_2$). ^{13}C NMR (aceton-d_6): δ 74.4, 68.3, 49.7, 34.2, 27.9 ^{11}B NMR (acetone-d_6): δ -2.0 (1B, d, *J* = 149 Hz), -5.4 (1B, d, *J* = 145 Hz), -9.4 (4B, d, *J* =140 Hz), -12.4 (4B, d, *J* = 159 Hz). IR (neat, cm^{-1}): 2597 ($\nu_{B–H}$), 2101 (ν_{N_3}). MS *m*/*z* for $C_5H_{17}B_{10}N_3S$: calcd 259.1, obsd 258.9 $[M]^+$.

Synthesis of NH_4[7-$N_3CH_2CH_2S$-7,8-$C_2B_9H_{11}$] (13).

A mixture of **9** (0.07 g, 0.3 mmol) and sodium formate (0.08 g, 1.3 mmol) in methanol (7 ml) was heated under reflux for 5 h. The reaction was filtered and evaporated *in vacuo*. The residue was treated with CH_2Cl_2 (10 ml) and water (10 ml). The organic layer was evaporated under vacuum to yield yellow oil (0.03 g, 43% yield). ^{1}H NMR (acetone-d_6): δ 3.63 (1H, m, $SCH_2CH_2N_3$), 3.45 (1H, m, $SCH_2CH_2N_3$), 3.11 (1H, m, $SCH_2CH_2N_3$), 2.93 (1H, m, $SCH_2CH_2N_3$), 2.4-(-0.5) (9H, br s, B*H*), 2.00 (1H, s, CH_{carb}), -2.73 (1H, br s, B*H*B). ^{11}B NMR (acetone-d_6): δ -12.4 (2B, d, J = 135 Hz), -14.8 (1B, d, J = 161 Hz), -16.9 (3B, d, J = 149 Hz), -21.7 (1B, d, J = 148 Hz), -32.6 (1B, dd, J = 142, 55 Hz), -36.3 (1B, d, J =140 Hz). IR (neat, cm^{-1}): 2533 (ν_{B-H}), 2102 (ν_{N_3}). Anal. Calc. for $C_4H_{19}B_9N_4S$: C, 19.02; H, 7.58; N, 22.18; B, 38.52. Found: C, 18.94; H, 7.63; N, 22.25; B, 38.57%.

Synthesis of NH_4[7-$N_3CH_2CH_2CH_2S$-7,8-$C_2B_9H_{11}$] (14).

The procedure was analogous to that described for synthesis of **10** using **13** (0.32 g, 1.2 mmol) and sodium formate (0.31 g, 4.9 mmol) methanol (35 ml) to yield a yellow oil (0.15 g, 47% yield). ^{1}H NMR (acetone-d_6): δ 3.48 (2H, t, J = 7.1 Hz, CH_2N_3), 2.98 (1H, m, SCH_2), 2.68 (1H, m, SCH_2), 2.4-(-0.4) (9H, br s, B*H*), 1.98 (1H, s, CH_{carb}), 1.94 (1H, m, $CH_2CH_2CH_2$), 1.83 (1H, m, $CH_2CH_2CH_2$), -2.69 (1H, br s, B*H*B). ^{11}B NMR (acetone-d_6): δ -9.5 (1B, d, J = 135 Hz), -10.7 (1B, d, J = 137 Hz), -14.8 (1B, d, J = 158 Hz), -17.2 (3B, d, J = 151 Hz), -22.0 (1B, d, J = 149 Hz), -32.8 (1B, dd, J = 149, J = 57 Hz), -36.6 (1B, d, J =149 Hz). IR (neat, cm^{-1}): 2535 (ν_{B-H}), 2101 (ν_{N_3}). Anal. Calc. for $C_5H_{21}B_9N_4S$: C, 22.53; H, 7.94; N, 21.02; B, 36.49. Found: C, 22.38; H, 7.99; N, 21.12; B, 36.58%.

Crystal X-ray structure study.

A colourless plate crystal of **5a** having approximate dimensions of 0.60×0.45×0.20 mm were used for single-crystal X-ray diffraction experiment. Crystal

data: $C_5H_{20}B_9NS \cdot 1.5(N_2H_4)$ (M=4271.65), triclinic, space group *P-1* (No.2), a = 8.437(1), b = 9.536(2), c = 10.671(2) Å, α = 91.896(3), β = 105.717(3), γ = 107.104(3)°, V = 784.0(2) Å^3, Z = 2, D_{calc} = 1.151 g/см^3. All measurements were made on a Bruker APEX2 CCD diffractometer with graphite monochromated Mo-K_α radiation. The data were collected at a temperature of 100 K a maximum 2θ□value of 52.0°. A total of 7041 reflections were measured. Equivalent reflections were averaged to give 3000 unique reflections (R_{int} = 0.0206) that were used for the structure solution and refinement. The minimum and maximum transmission coefficients (μ = 0.190 mm^{-1}), T_{max} = 0.963 and T_{min} = 0.895, were determined using SADABS program. [2-5] The sample studied was triple twinned crystal with approximate components ratio of 6:2:2. An attempt to separate obtained intensity set to individual components using CELL_NOW program was not successful. A HKLF5 file suitable for further structure refinement was created using the PLATON/TwinRotMat option. The structure was solved using direct method and refined over F^2_{hkl} using anisotropic full-matrix least-squares method for all non-hydrogen atoms. The H(N) hydrogen atoms and the carborane H(C) and H(B) hydrogen atoms were found in the difference density Fourier map. The substituent H(C) hydrogen atoms were placed at calculated positions. All the hydrogen atoms were refined using a riding model with U(H) =1.2 U_{eq}(C). The final refinements were converged to R_1 = 0.0447 (from 2688 reflections with $I > 2\sigma(I)$ using F_{hkl}), wR_2 = 0.1241 (from all 3000 reflections using F^2_{hkl}), GOOF = 1.062 (197 parameters). All calculations were performed using SHELXTL program package. [6]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 941869). These data can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request/cif.

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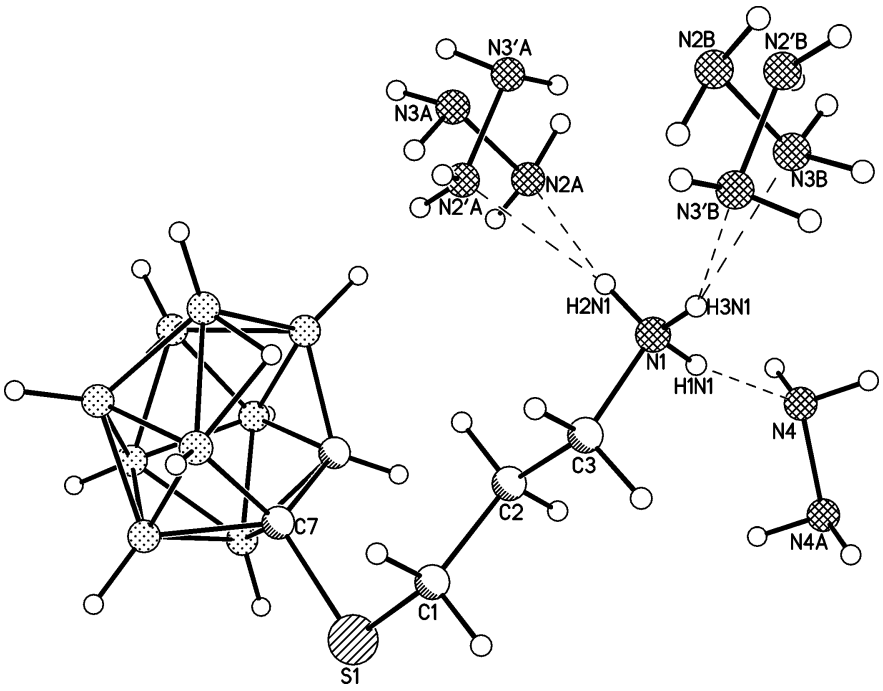

Fig. S1. Hydrogen bonds in the structure of 7-$NH_3CH_2CH_2CH_2$S-7,8-*nido*-$C_2B_9H_{11}$*1.5N_2H_4 (**5a**).

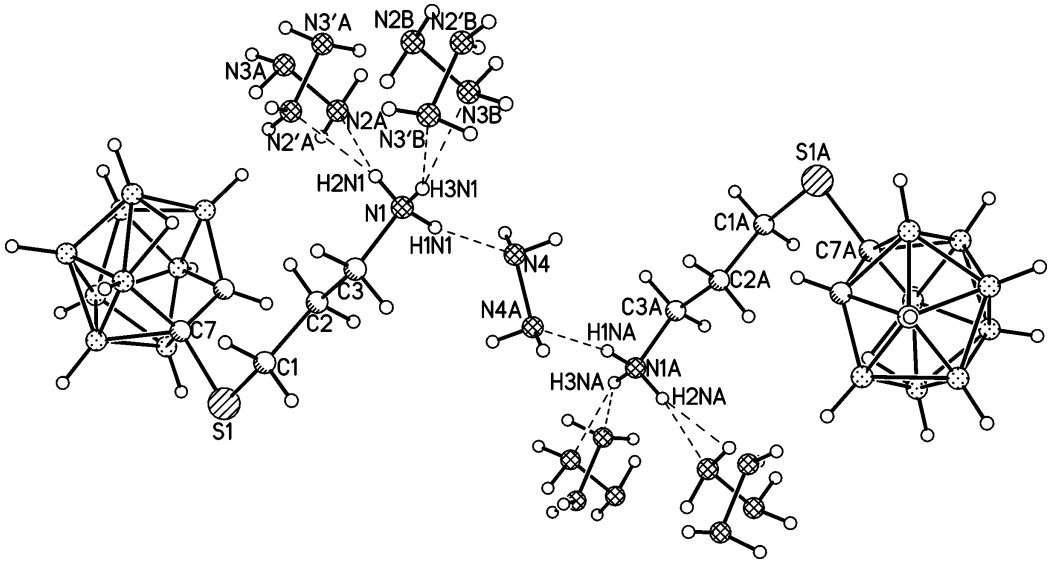

Fig. S2. Association of dimers in the crystal structure of 7-$NH_3CH_2CH_2CH_2$S-7,8-*nido*-$C_2B_9H_{11}$*1.5N_2H_4 (**5a**).

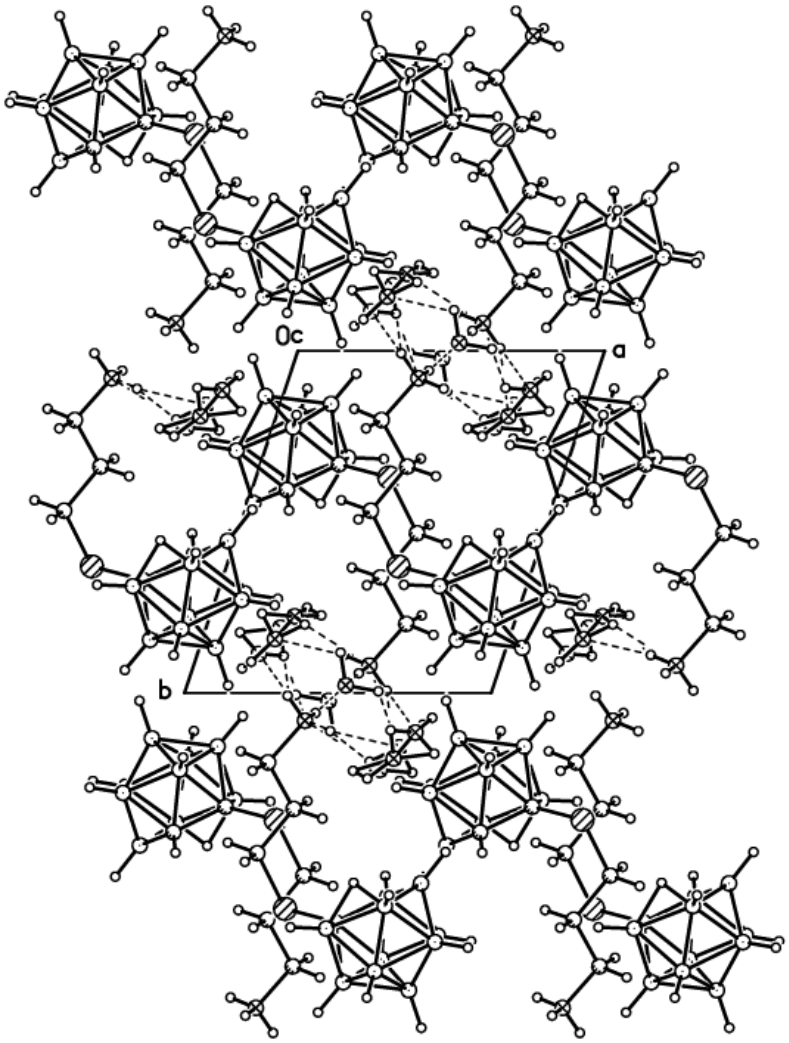

Fig S3. A fragment of crystal structure
of 7-$NH_3CH_2CH_2CH_2S$-7,8-*nido*-$C_2B_9H_{11}$*1.5N_2H_4 (**5a**).

Table S1. Parameters of the N1-H…N hydrogen bonds in the structure
of 7-$NH_3CH_2CH_2CH_2S$-7,8-*nido*-$C_2B_9H_{11}$*1.5N_2H_4 (**5a**).

Bond	N1-H (Å)	H…N (Å)	N1…N (Å)	Angle N1-H…N (°)	Symm.code
N1-H1N1... N4	0.88	2.01	2.883(5)	170	+x, +y, +z
N1-H2N1... N2	0.88	2.01	2.873(6)	165	-x, 1-y, 1-z
N1-H2N1... N2’	0.88	2.17	3.034(5)	166	-x, 1-y, 1-z
N1-H3N1... N3	0.88	2.06	2.887(5)	155	1+x, 1+y, +z

N1-H3N1... N3’	0.88	2.23	3.038(6)	153	1+x, 1+y, +z