

# SYNTHESES AND PROPERTIES OF SUBSTITUTED ICOSAHEDRAL CARBORANE THIOLS

Jaromír PLEŠEK and Stanislav HEŘMÁNEK

*Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 150 68 Řež*

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Syntheses of twelve C—SH and eight B—SH carborane thiols of the formula  $\text{HS}, \text{X}-\text{C}_2\text{B}_{10}\text{H}_{10}$  ( $\text{X} = \text{H}, \text{Hlg}, \text{CH}_3$ ) and some of their properties ( $\text{p}K_a$ ,  $R_F$ ,  $^1\text{H}$ -,  $^{11}\text{B}$ -NMR) are described. All compounds are crystalline. For C—SH compounds a new convenient route was elaborated. B—SH compounds were prepared directly from substituted carborane, sulfur and  $\text{AlCl}_3$ .

In this contribution, syntheses and some properties of following icosahedral carborane thiols are described:

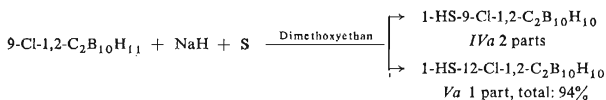
$\text{HS}, \text{X}-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}$	$\text{HS}, \text{X}-1,7-\text{C}_2\text{B}_{10}\text{H}_{10}$	$1-\text{HS}-1,12-\text{C}_2\text{B}_{10}\text{H}_{11}$
<i>I</i> , 1-HS; X = H	<i>II</i> , 1-HS; X = H	<i>III</i>
<i>IV</i> , 1-HS; X = 9-Hlg	<i>X</i> , 1-HS; X = 9-Hlg	
<i>V</i> , 1-HS; X = 12-Hlg	<i>XI</i> , 9-HS; X = 10-Hlg	
<i>VI</i> , 9-HS; X = 12-Hlg		
<i>VII</i> , 1-HS; X = 2- $\text{CH}_3$		
<i>VIII</i> , 9-HS; X = 1- $\text{CH}_3$		
<i>IX</i> , 12-HS; X = 1- $\text{CH}_3$		

These compounds were prepared for a study of the distribution of electron densities on skeletal atoms and for following a transfer of electrons evoked by substituents in icosahedral carboranes as representatives of superaromatic *closo*-heteroboranes. Electron density transmissions come distinctly evident in the acidities of HS-group<sup>1,2</sup>, in chemical shifts of  $^{11}\text{B}$ -NMR signals of vicinal and antipodal atoms<sup>3,4</sup>, and in electron spectra, as well as in chemical behaviour of the HS-group and of the carborane skeleton. At present, all these topics are a subject of an extensive study.

Up to now, only three of the presented compounds, namely *I* (ref.<sup>5</sup>), *II* (ref.<sup>6</sup>) and *VII* (ref.<sup>5,7</sup>) have been prepared by reacting the starting carborane with sodium amide and sulfur in liquid ammonia.

## Preparation of the C—SH Derivatives

For the preparation of C—SH derivatives a new convenient modification of the known metallation procedures has been elaborated.



The ratio of 2 : 1 clearly shows that the halogen atom has a distinct influence on the CH reactivity which is higher in the *meta*- than in the *para*-position with respect to the halogen atom. Similar results were found with 9-Br- and 9-I-*o*-carboranes. In all cases the 1-HS-12-Hlg-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> isomers (V, a = Cl, b = Br, c = I) were separated by crystallization as the less soluble compounds. The mother liquors were separated by silica gel-column chromatography, in which isomers IVa–IVc were eluted as the first ones. Melting points of the Va–Vc isomers are higher than these of IVa–IVc. The ratio of both isomers was estimated from the intensity ratios of particular SH and CH signals in the <sup>1</sup>H-NMR spectra of crude reaction products obtained after the first sublimation. The constitution of single isomers resulted from the <sup>11</sup>B-NMR spectra. The same procedure was successful also with the parent *o*-carborane and its 1-methyl derivative, yielding practically pure I and VII, respectively.

The described sulfhydrylation has an advantage (in comparison with the NaNH<sub>2</sub> : NH<sub>3</sub>(l) metallation) in an easy performance, short time, higher safety and especially in the fact that it affords exclusively monothiols even when the reactivity of both CH-groups is enhanced by a substitution of the carborane nucleus. The enhancement of reactivity is well observable with 9-Hlg-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> which react under evolution of heat during one hour, whereas in the case of 1-CH<sub>3</sub>-1,2-C<sub>2</sub>H<sub>10</sub>H<sub>11</sub>, the reaction mixture has to be heated for 4 h for reaching a satisfactory yield. It is noteworthy that substituted carboranes do not react with NaH in dimethoxyethane. The evolution of hydrogen (together with a trace of hydrogen sulfide) starts, however, immediately after the addition of sulfur, and the reaction mixture turns orange-brown and mostly brings itself to boil.

The great differences in reactivity of CH vertices in the NaH/dimethoxyethane sulfhydrylation, depending on the character and position of the given substituent, indicate that the main factor in this case is the C—H acidity which has to be similar or higher than that of *o*-carborane for achieving a sufficient conversion. A plausible measure of the C—H acidity is the pK<sub>a</sub> value of its C—SH derivative<sup>1</sup>. The values show that the acidity drops in the order: 1-HS-9-Hlg-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (pK 2.55–2.98) > 1-HS-12-Hlg-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (2.75–3.28) > 1-HS-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (3.30) > 1-HS-2-CH<sub>3</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (3.68) ≫ 1-HS-9-Cl-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (4.38) ≫ 1-HS-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (5.30) ≫ 1-HS-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (5.85). In accord with this order, low reactivity was observed with 9-Cl-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (yield 19%) and no reaction was found with *m*- and *p*-carboranes even after a reflux for 6 h, which limits this modification to the sulfhydrylation of carboranes of an elevated C—H acidity. The observed relations allow to presume that a preference of sulfhydrylation of the CH vertex in the *meta*-

-position (affording *IV*) over the CH vertex in the *para*-position (affording *V*) is a result of a greater attraction of electrons from the *meta*- than from the *para*-position evoked by a halogen in the B<sub>(9)</sub> position in the *o*-carborane.

TABLE I  
Carborane Thiols HS,X-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, Yields and Some Properties

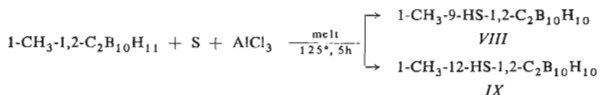
Position		Notation	Yield % <sup>a</sup>	pK <sub>a</sub> <sup>b</sup>	R <sub>F</sub> <sup>c</sup>	<sup>1</sup> H δ ppm <sup>d</sup>		<sup>11</sup> B δ ppm <sup>d,e</sup>	
HS-	X-					(S)H	(C)H	B(SH)	B(H)g
1,2-C <sub>2</sub> B <sub>10</sub>									
1	H	<i>I</i>	75	3.30	0.26 <sup>f</sup>	3.98	3.82	—	—
1	9-Cl	<i>IVa</i>	45	2.68	0.18	4.01	3.68	—	7.9
1	9-Br	<i>IVb</i>	49	2.98	0.38	4.03	3.85	—	0.4
1	9-I	<i>IVc</i>	55	2.55	0.35	4.04	4.13	—	-16.3
1	12-Cl	<i>Va</i>	32	3.15	0.04	3.90	3.82	—	5.0
1	12-Br	<i>Vb</i>	27	3.28	0.32	3.86	3.87	—	-2.4
1	12-I	<i>Vc</i>	22	2.75	0.32	3.81	3.91	—	-19.2
9	12-Cl	<i>VIa</i>	81	9.02	0.09	0.59	3.50	4.0	6.2
9	12-Br	<i>VIb</i>	79	9.00	0.10	0.64	3.65	4.1	-0.5
9	12-I	<i>VIc</i>	83	9.30	0.12	0.70	3.91	4.4	-15.2
						3.57			
1	2-CH <sub>3</sub>	<i>VII</i>	88	3.68	0.30 <sup>f</sup>	3.62	—	—	—
9	1-CH <sub>3</sub>	<i>VIII</i>	29	10.14	0.14 <sup>g</sup>	0.43	3.42	4.4	—
12	1-CH <sub>3</sub>	<i>IX</i>	29	10.54	0.11 <sup>g</sup>	0.29	3.63	0.5	—
1,7-C <sub>2</sub> B <sub>10</sub>									
1	H	<i>II</i>	70	5.30	0.40 <sup>f</sup>	3.38	3.01	—	—
1	9-Cl	<i>Xa</i>	19	4.38	0.57	3.45	3.04	—	0.5
1	9-Br	<i>Xb</i>	73	4.40	0.50	3.48	3.11	—	-7.0
9	10-Cl	<i>XIa</i>	91	9.03	0.40	0.57	2.96	-3.3	-0.1
9	10-Br	<i>XIb</i>	88	9.45	0.35	0.61	3.03	-3.1	-6.3
9	10-I	<i>XIc</i>	85	9.50	0.33	0.67	3.11	-2.7	-21.6
1,12-C <sub>2</sub> B <sub>10</sub>									
1	H	<i>III</i>	48	5.85	0.62 <sup>f</sup>	3.18	2.58	—	—

<sup>a</sup> Preparative yields based on starting compounds regardless of a recovery; <sup>b</sup> in 50% C<sub>2</sub>H<sub>5</sub>OH; <sup>c</sup> on Silufol sheets, eluent benzene-hexane 1 : 2 (if no other specification); <sup>d</sup> in CDCl<sub>3</sub>; <sup>e</sup> ppm related to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, minus sign characterizes the signals in the higher magnetic field; <sup>f</sup> hexane; <sup>g</sup> CCl<sub>4</sub>.

The C—SH derivatives derived from *m*-carborane, *i.e.* 1-HS-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (II) and 1-HS-9-Hlg-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (*Xa, Xb*) as well as 1-HS-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (III) were prepared by the known Na/NH<sub>3</sub> (*l*) metallation route<sup>5-7</sup> which allows to substitute even the CH vertices of a relatively low acidity.

#### Preparation of the B—SH Derivatives

All B—SH derivatives were prepared by the general method of direct sulfhydrylation which allows an introduction of the HS-group onto B-atoms in heteroboranes<sup>8,9</sup> or boranes<sup>10</sup>. The scheme of the synthesis is described on the preparation of the couple of the VIII and IX thiols:



The isomers arose in *c.* 1 : 1 ratio with a total yield of 61%. Methyl group did not show any distinct directive effect on the position of the introduced HS-group. Similarly, the 9-HS-12-Hlg-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (VI) and 9-HS-10-Hlg-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (XI) derivatives were prepared (yields *c.* 80%). The result of the syntheses was unambiguous, a presence of isomeric thiols was not observed even by means of TLC, and the products were pure after one sublimation and crystallization from hexane.

The yield and some properties of all of the prepared C—SH and B—SH derivatives are listed in Table I. The <sup>1</sup>H-NMR characteristics are reduced to the  $\delta$  values of S—H and C—H signals; of the <sup>11</sup>B-NMR signals, only  $\delta$  values of B—X and B—SH singlets are shown. The analysis of these complex spectra<sup>11</sup> will be published elsewhere.

#### EXPERIMENTAL

The starting substituted carboranes were prepared according to literature. The <sup>1</sup>H (200 MHz) and <sup>11</sup>B (64.2 MHz) NMR spectra were measured on a Varian XL-200 spectrometer. The informative <sup>1</sup>H-NMR spectra were recorded on Tesla BS 467 spectrometer. Mass spectra were obtained on a LKB 9000 instrument at 70 eV; all described compounds have shown the expected *m/e* molecular cut-off. TLC was carried out on Silufol (Kavalier, Votice, Czechoslovakia); *pK<sub>a</sub>* values were determined in 50% ethanol by potentiometric titration<sup>1</sup> using a glass electrode and 0.1M-NaOH in 50% ethanol (w/w) at 20°C.

#### Preparation of the C—SH Derivatives I, IVa—IVc, Va—Vc, VII, Xa

To the suspension of 0.2 mol of NaH (80% suspension in paraffin oil) in 200 ml of dimethoxyethane was in a nitrogen atmosphere added 0.1 mol of the substituted carborane and 6.4 g (0.2 mol) of sulfur powder. The mixture was shaken without cooling (with 9-Hlg-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>) for 1 h

or stirred under heating to 60°C for 4 h with 1-CH<sub>3</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> and 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, respectively. Originally colorless suspension turned fast red-brown and a great amount of hydrogen together with traces of hydrogen sulfide evolved. After dissolution of all sulfur, the excess of sodium hydride was decomposed by the addition of 20 ml of methanol under cooling in a cold water bath, and the main part of volatile solvents was stripped off *in vacuo* at ambient temperature. The residue was diluted with 100 ml of water, the oily substance was extracted into 50 ml of hexane, the aqueous layer was filtered and acidified with hydrochloric acid. The products were extracted with 100 ml of benzene, the solvent was evaporated *in vacuo* and the residue was sublimed twice at 1.3 Pa/80–100°C (bath). In this way, *I* and *VII* were obtained as practically pure compounds. A mutual ratio of couples *IVa*–*Va*, *IVb*–*Vb* and *IVc*–*Vc* was estimated in this stage from the ratio of <sup>1</sup>H-NMR signals of CH and SH groups, respectively. In all cases, the ratio was close to 2 : 1 in favor of the isomer *IVa*–*IVc*. The separation of *V* from the reaction mixture was achieved by repeated crystallization from hexane, in which *Va*–*Vc* are sparingly soluble. The mother liquors were then chromatographed on silica gel column with benzene–hexane mixture (1 : 2) as an eluent. In all cases, the isomer *IV* was eluted as the first one. The preparative yields and some characteristics of the prepared thiols are shown in Table I.

The same procedure, when applied to 9-Cl-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, gave after a reflux for 6 h only 19% yield of compound *Xa*, whereas 76% of the starting compound was recovered. The parent *m*- and *p*-carboranes were recovered after the same treatment almost quantitatively and even TLC did not prove any trace of the expected *II* and *III* thiols.

#### Preparations of the C–SH Derivatives *II*, *III* and *Xb*

A fresh suspension of NaNH<sub>2</sub> was prepared under the catalytical effect of 0.2 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O by an addition of 2.3 g of sodium (0.1 mol) into 200 ml of liquid ammonia. To this suspension, 0.05 mol of the appropriate carborane and 20 ml of hexane were added. After one hour, 1.6 g (0.05 mol) of sulfur powder was added and the mixture was left aside overnight at ambient temperature. The escaping ammonia was drawn off through a tower filled with KOH pellets. Ethanol (20 ml) and water (100 ml) were added to the solid residue, the remainder of ammonia and hexane were evaporated *in vacuo* at room temperature and the unreacted starting carborane was extracted into 50 ml of hexane (recovery: *m*-carborane 4.5%, *p*-carborane 41%, 9-Br-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> 0%). The blue-black aqueous layer was filtered with charcoal, acidified with hydrochloric acid and products were extracted into three 30 ml portions of hexane. The hexane extracts were combined and extracted with the solution of 0.5 g of KHCO<sub>3</sub> (0.005 mol) in 20 ml of water with the aim of the removal of bis-mercapto derivatives. The hexane solution was evaporated *in vacuo* and the crude thiol was sublimed at 1.3 Pa/80°C (bath). Preparative yields and some characteristics of *II*, *III* and *Xb* are shown in Table I.

#### Preparation of the B–SH Derivatives *VIa*–*VIc*, *VIII*, *IX*, *XIa*–*XIc*

Mixture of 0.1 mol of substituted carborane, 6.4 g (0.2 mol) of sulfur powder and 26.4 g (0.2 mol) of anhydrous aluminum chloride was heated under nitrogen at 125°C for 5 h. In the range of 100–125°C the mixture successively melted and changed during heating into a homogeneous, slightly yellow melt. After cooling by standing overnight the mixture was covered with 200 ml of benzene and decomposed with 200 ml of water under cooling with water and shaking till the glass-like melt disappeared. After the addition of 20 ml of conc. hydrochloric acid, the separated sulfur was filtered, benzene layer separated and washed with two 100 ml portions of water. Thiols were extracted into 3 × 100 ml of 10% aqueous KOH. The remaining benzene layer contained small amount of the starting carborane and the appropriate carboranyl disulfides

which were not worked up despite the easy regeneration and isolation<sup>8</sup>. The alkaline extract was filtered, saturated with gaseous CO<sub>2</sub>, and precipitated thiols were extracted into 2 × 50 ml of benzene. After evaporation of benzene *in vacuo* the residue was sublimed at 1.3 Pa/80–120°C (bath). The sublimate was crystallized from hexane. In the case of the VIII and IX isomers, the mixture was after sublimation separated by silica gel column chromatography with tetrachloromethane as an eluent. The isomer VIII was eluted as the first one. The preparative yields of pure thiols based on the starting carborane, as well as some of their properties are shown in Table I.

*The mass spectra were measured by Dr V. Kubelka, Prague Institute of Chemical Technology, Prague. The <sup>1</sup>H (60 MHz) NMR spectra were recorded by Dr F. Mareš, the pK<sub>a</sub> values were determined by Mr M. Skalický, Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řež. It is our pleasure to thank these colleagues for their assistance.*

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