EXPERIMENTAL EVALUATION OF CHARGE DISTRIBUTION ON PARTICULAR SKELETAL ATOMS IN ICOSAHEDRAL CARBORANES BY MEANS OF HS-DERIVATIVES

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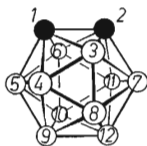
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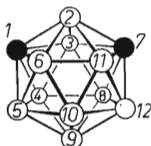*Dedicated to Professor F. Čůta on the occasion of his 80th birthday.*

From the analysis of pK_a values of eight mercaptodicarba-*closo*-dodecaboranes (1-*o*, 8-*o*, 9-*o*-1-*m*, 4-*m*, 9-*m*, 1-*p*, 2-*p*) and pK_a' values of five of their —SCH$_2$COOH derivatives was stated: 1) icosahedral skeleton is capable of conjugative interactions with HS- and generally with all groups of +M character, 2) the measure of M interaction with HS is practically the same in all positions and is very similar to that in benzenethiol, 3) pK_a value of HS-isomer reflects the magnitude of the group charge ε on BH or CH according to equation p$K_a = 7·43 - 26·5\varepsilon$; ε values lie between $-0·10$ (9-*o*) and $+0·156$ (1-*o*) and correlate well with dipole moment and chemical reactivity.

The group of dicarba-*closo*-dodecaboranes consists of three isomers, *ortho*-carborane 1,2-C$_2$B$_{10}$H$_{12}$ (*I*), *meta*-carborane 1,7-C$_2$B$_{10}$H$_{12}$ (*II*) and *para*-carborane 1,12--C$_2$B$_{10}$H$_{12}$ (*III*) differing in the location of two C-atoms in vertices of an icosahedron. If we take these three isomers as a common group, we can find here twelve different vertices, which allows the existence of twelve monosubstituted dicarba-*closo*-dodeca-boranes. Five different positions are in *I*, five more in *II* and further two are in *III*.
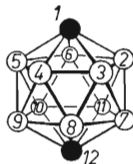

I	*II*	*III*
1 = 2	1 = 7	1 = 12
3 = 6	2 = 3	2—11 identical
4 = 5 = 7 = 11	4 = 6 = 8 = 11	
8 = 10	5 = 12	
9 = 12	9 = 10	

In this paper, these twelve particular vertices as well as the corresponding substituted isomers are designated by a position number together with a letter index, showing the parent skeleton; $1\text{-}HS\text{-}1,2\text{-}C_2B_{10}H_{11}$ is thus denoted as $1\text{-}o$, $9\text{-}HS\text{-}1,7\text{-}C_2B_{10}H_{11}$ as $9\text{-}m$ mercaptane, *etc.*

Icosahedral dicarba-*closo*-dodecaboranes are charge-compensated analogues of $B_{12}H_{12}^{2-}$ with which they are isoelectronic and isostructural. The charge-compensation is caused by a formal substitution of two $\overset{..}{\cdot}BH^-$ units in the $B_{12}H_{12}^{2-}$ anion by two uncharged $\overset{..}{\cdot}CH$ fragments in a carborane skeleton. Due to the fact that both $\overset{..}{\cdot}CH$ units give a part of their electron density to the common fund of 26 skeletal electrons, the CH vertices are holders of the $\delta+$ charges which are compensated by a sum of $\delta-$ charges on particular BH vertices. We may therefore expect distinct differences in electron densities in particular positions. Electron density should increase with an increasing distance of the given vertex from both CH vertices[1,2] and — in the second approximation — it should increase with the decreasing magnitude of $\delta+$ charge in the present CH vertices ($o\text{-} > m\text{-} > p\text{-}$). According to these considerations the electron density has to increase in the following order:

$$1\text{-}o < 1\text{-}m < 1\text{-}p < 3\text{-}o \leqq 2\text{-}m < 4\text{-}o \leqq 4\text{-}m \leqq 2\text{-}p < 5\text{-}m < 8\text{-}o \leqq 9\text{-}m < 9\text{-}o \,.$$

Most reactions are in a good agreement with this qualitative order; for instance a metallation on C-atoms decreases in order $1\text{-}o > 1\text{-}m > 1\text{-}p$ (ref.[3,4]), alkaline

TABLE I

Group Charge Densities in BH and CH Vertices Estimated from HS- pK_a Values (Column 1) as Compared with Charge Densities Obtained from EHMO (column 2) and NEMO (columns 3—7) Calculations

Position	1 this paper	2 ref.[15]	3 ref.[16]	4 ref.[17,19]	5 ref.[18]	6 ref.[19]	7 ref.[20]
$1\text{-}o$	+0·156	+0·29	+0·22	+0·38	+0·29	—	+0·07
$1\text{-}m$	0·080	0·15	0·04	—	—	+0·24	0·03
$1\text{-}p$	0·059	0·15	0·02	—	—	—	0·04
$3\text{-}o$	—	0·08	0·07	0·22	0·26	—	0·03
$2\text{-}m$	—	0·10	0·09	—	—	0·13	0·04
$4\text{-}o$	—	−0·03	0·02	−0·02	−0·02	—	0·00
$4\text{-}m$	+0·002	−0·03	0·02	—	—	−0·03	−0·01
$2\text{-}p$	−0·012	−0·03	0·00	—	—	—	−0·01
$5\text{-}m$	—	−0·03	+0·01	—	—	−0·06	0·00
$8\text{-}o$	−0·071	−0·16	−0·16	−0·29	−0·28	—	−0·05
$9\text{-}m$	−0·076	−0·16	−0·19	—	—	−0·25	−0·05
$9\text{-}o$	−0·100	−0·16	−0·17	−0·27	−0·24	—	−0·05

solvolysis attacks preferentially B-atoms which are neighbours of C-atoms with decreasing rate $3\text{-}o > 2\text{-}m \gg 2\text{-}p$ (ref.[5,6]), pseudoelectrophilic[7] substitution proceeds preferentially in positions $9\text{-}o > 8\text{-}o$, $9\text{-}m > 4\text{-}m$ and $2\text{-}p$ (ref.[8]) and the attack of BH vertices in oxidation decreases in order[9] $9\text{-}o > 8\text{-}o > 4\text{-}o > 3\text{-}o$ and $9\text{-}m > 5\text{-}m > 4\text{-}m > 2\text{-}m$. Similarly the trend of pK_a values of particular carboxylic acids[4,10–14] as well as of hydroxy derivatives[9] is in a satisfactory accord with the above order. In a relatively good agreement is also the order of electron density values calculated by the semiempirical EHMO method[15] (Table I, column 2), while the values calculated by *ab initio* methods[16–19] do not correspond to this order in all points (Table I, columns 3–6). An acceptable accord with the above order show the quite recent calculations of group charges[20] (*i.e.* charge of C—H or B—H unit, Table I, column 7) but also here some values or orders (*cf.* for instance $1\text{-}o > 1\text{-}p > 1\text{-}m$; $2\text{-}m > 3\text{-}o$) are disputable.

Experimental estimation of electron densities was only partially successful up to present. In Table II there are collected the published pK_a values of known carboxy and hydroxyderivatives of the dicarba-*closo*-dodecaboranes. Isomeric carboxy acids show an expected decrease in acidity in the order $1\text{-}o > 1\text{-}m > 1\text{-}p$ and a distinct decrease in acidity from C- to B-substituted isomers, but differences among particular B—COOH isomers are unexpectedly small and in some cases do not reflect the reality (*cf.* pK_a of $3\text{-}o$ *vs* $9\text{-}o$). A better situation is with HO-derivatives where ten isomers

TABLE II

pK_a Values of Isomeric Icosahedral Carboxylic Acids and Hydroxy Derivatives

$X\text{—}C_2B_{10}H_{11}$	X				
	COOH[a] ref.[14]	COOH[b]	OH[a] ref.[12]	OH[c] ref.[9]	OH[d] ref.[9]
$1\text{-}o$	$2\cdot61^{11}$	$5\cdot5$	$5\cdot25$	—	—
$1\text{-}m$	$3\cdot34^{11}$	$6\cdot6$	—	—	—
$1\text{-}p$	$3\cdot64^{4}$	$7\cdot15$	—	—	—
$3\text{-}o$	$5\cdot38^{11}$	—	$8\cdot70$	$22\cdot6$	$21\cdot0$
$2\text{-}m$	$5\cdot11^{12}$	—	$9\cdot63$	$24\cdot3$	$23\cdot5$
$4\text{-}o$	—	—	$11\cdot51$	$25\cdot6$	$26\cdot7$
$4\text{-}m$	$6\cdot28^{12}$	—	$11\cdot67$	$28\cdot4$	$28\cdot0$
$2\text{-}p$	—	—	—	$27\cdot3$	$27\cdot3$
$5\text{-}m$	—	—	—	$27\cdot8$	$27\cdot3$
$8\text{-}o$	—	—	$11\cdot50$	$24\cdot7$	$31\cdot8$
$9\text{-}m$	$5\cdot26^{13}$	—	12	$29\cdot6$	$30\cdot4$
$9\text{-}o$	$5\cdot30^{13}$	—	untitr.	$30\cdot5$	$32\cdot3$

[a] In 50% C_2H_5OH; [b] in CH_3OH; [c] in CH_3CN; [d] in $(C_2H_5)_2O$.

are known. The pK_a values obtained in 50% ethanol are in a good agreement with the expected order but the generally low acidity allows to compare only a part of isomers. Attempts to infer electron densities from the acidities of HO-isomers measured in acetonitrile or diethyl ether were, however, less successful due to unexplained changes in the order and in the magnitude of pK_a values evoked by the change of measuring conditions (*cf*. Table II, columns 4,5).

Unresolved remains the possibility of a mesomeric interaction between a substituent and the carborane skeleton. Up to now, it has been uncertain whether such an effect exists and, in the positive case, to what extent it takes place in particular positions, and what sign it has. While some attempts showed only an insignificant $+M$ effect with icosahedral carboranes[8,21], our study concerned with the influence of a substituent on the chemical shift of the antipodal skeletal atom has indicated that a distinct „antipodal effect" of the substituent is an analogy of the mesomeric effect[22].

The above survey together with further information gathered in review books[8,23] document that a direct estimation of electron densities in particular positions of dicarba-*closo*-dodecaboranes as well as the question of an existence of the mesomeric effect within these skeletons are still pending.

Very recently we have described a method for introducing the HS-group into the most electronegative positions in icosahedral carboranes[24,25], which has allowed to prepare five isomeric B-mercaptocarboranes. All of the three C—SH isomers are accessible by metallation of the appropriate carborane and by subsequent reaction with sulfur. The comparison of these eight (of twelve possible) isomers has shown that this class of compounds has several advantageous properties which could help in solving both the problem of charge densities and the existence of the mesomeric effect in dicarba-*closo*-dodecaborane series.

With mercaptans it is known that the acidity of the mercapto group is influenced by three factors[26,27]:

1) induction effect I of the R group, *2*) mesomeric acidification (Ma): $R \overset{\frown}{-} \underset{\delta+}{\underline{S}}$—H →
→ $R = S$—H, *3*) mesomeric stabilization (Ms): $R — \underline{\overline{S}}|^{(-)} → {}^{(-)}R = \underline{S}|$.

While with aliphatic mercaptans only the I effect can apply, all of the three effects are to operate with aromatic mercaptans. The sum of Ma + Ms-effects is of a great importance, being the reason why aromatic mercaptans are by three orders more acidic than those of aliphatic series. The Ma contribution can be taken as a relatively small because it results in undesirable "charge separation". The main part of the mesomeric effect is therefore represented by the Ms-effect which leads to the advantageous "charge delocalization"[27]. It is possible to expect that the Ms-effect can be excluded by a transformation of HS-group to the appropriate —S—CH$_2$COOH thioglycollic acid, the pK_a' value of which is thus influenced largely by the I-effect and in a small extent by the Ma-effect.

We have applied the latter idea in mercaptocarboranes and the appropriate thio-glycollic acids. The obtained pK_a values of mercaptans and pK_a' values of thioglycollic acids are gathered in Table III together with pK_a values of some analogous organic mercaptans.

From the comparison of the pK_a values of 4-m and 2-p HS-isomers (in which the mentioned vertex bears a negligible charge when non substituted) it follows that the acidity of these mercaptocarboranes ($C_2B_{10}H_{11}SH$) is by three orders as high as that of aliphatic mercaptans. Higher acidities than the latter show even the 9-m and 9-o derivatives in which the HS-group is bound to the strongly electronegative B-atom. The very high acidity of $C_2B_{10}H_{11}SH$ mercaptans can be therefore explained only as a result of the existence of a mesomeric relation between the carborane skeleton and the sulfur atom.

The fact that the plot of the pK_a values of $C_2B_{10}H_{11}SH$ against the pK_a' values of the corresponding $C_2B_{10}H_{11}$—S—CH_2—COOH derivatives is strictly linear (Fig. 1) has indicated that a measure of the mesomeric effect is practically the same in all positions within the $C_2B_{10}H_{11}SH$ isomer. This fact allows to state that the great difference in acidities of the particular mercaptocarboranes are evoked by the diffe-rences in the I-effects; *i.e.* by the differences in the magnitude of the group charges on particular icosahedral vertices* to which the HS-group is bound.

The relation between the acidity (pK_a) and the charge of the substituted vertex with $C_2B_{10}H_{11}SH$ derivatives is an example of the "linear free energy relationship" and can be expressed by equation (1),

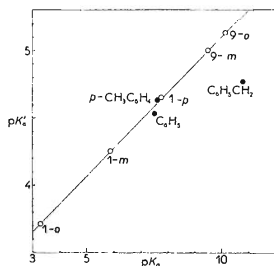$$pK_a = pK_{a0} - \varrho\varepsilon , \qquad (1)$$

Fig. 1

Correlation of pK_a Values of R—SH with pK_a' Values of the Corresponding R—SCH$_2$. .COOH Derivatives

* When speaking about the charge of a vertex we mean the group-charge in the centre of electricity (*i.e.* somewhere between E and H) of the E—H group (E = B or C) before the transformation to the E—S—H acid.

where pK_{a0} is the hypothetic value of the acidity of the HS-group bound to the icosahedral vertex of $\varepsilon = 0{\cdot}00$; ε corresponds to the charge magnitude in electron units, and ϱ is a proportionality constant.

The zero point on the straight line, *i.e.* the pK_{a0} value, was deduced from the pK_a values of both mercapto-p-carboranes. In p-carborane, there are only two types of vertices, C and B, the former being a centre of a positive charge $+\delta$ which must be compensated with altogether five equal negative charges, of $-\delta/5$ each, localized on the neighbour BH vertices. Presuming that the difference between the charges of these two positions are proportional to the difference of pK_a values of 1-p and 2-p HS-derivatives (Table III) then it holds:

$$pK_{a0} - pK_{a1\text{-}p} = 5\left(pK_{a2\text{-}p} - pK_{a0}\right)$$

$$i.e.\ pK_{a0} = 7{\cdot}43$$

With known pK_{a0}, equation (*1*) makes it possible to establish the magnitude of particular vertex-charges if also a charge of one of vertices is known. No such a value has been, however, available. Due to this fact we have tried to estimate a probable charge in the position 9-o by the method of "best guess". The estimation was based on following considerations:

1) In the icosahedron the limit ε value of a B—H vertex may be expected to be found at $B_{12}H_{12}^{2-}$ where 2e are distributed among 12 BH vertices, *i.e.* $\varepsilon = -0{\cdot}166$ e.u.

TABLE III

pK_a Values of $C_2B_{10}H_{11}SH$ and pK_a' Values of $C_2B_{10}H_{11}SCH_2COOH$ Derivatives, Ordered according to the Increasing Electron Density (qualitatively), and of Analogous Organic Compounds (measured in 50% C_2H_5OH)

Radical	pK_a	pK_a'
1-o	3·30	3·71
1-m	5·30	—
1-p	5·85	4·25
4-m	7·38	—
2-p	7·75	4·65
8-o	9·32	—
9-m	9·45	5·00
9-o	10·08	5·13
C_6H_5	7·50	4·53
p-$CH_3C_6H_4$	7·60	4·63
$C_6H_5CH_2$	10·74	4·77

(cf.[20]). 2) In dicarba-*closo*-dodecaboranes the most electronegative B—H vertex exists in 9-*o* but also in this position the ε value is reduced by the presence of two remoted $C^{\delta+}$ skeletal atoms, i.e. ε9-*o* < −0·166 e.u. 3) The charges of all E—H vertices are in a relation with the pK_a values of the appropriate HS-isomers. 4) The sign, location and magnitude of particular charges must correspond to the dipole moment of *o*-carborane ($\mu = 4\cdot53$ D (ref.[28])).

In accord with these presumptions an arbitrary value ε9-*o* = −0·10 e.u. was chosen. From this value corresponding to $pK_{a9-o} = 10\cdot08$, and from $\varepsilon = 0\cdot00$ corresponding to $pK_{a0} = 7\cdot43$, the proportionality constant $\varrho = 26\cdot5$ was established in equation (1). The calculated values for other vertices are summarized in Table I, column 1.

Using the tabulated ε values for *o*-carborane together with estimated $\varepsilon_{3-o} = 0\cdot015$ (in accord with a decrease of σ_I going from 1-*o* ($\sigma_I = 0\cdot295$) to 3-*o* ($\sigma_I = 0\cdot011$, ref.[21])) and $\varepsilon_{4-o} = 0\cdot00$, and considering that the centre of electricity will be remoted along the E—H bond by 0·15 Å per 0·1 e.u. from E, the dipole moment $\mu = 4\cdot62$ D was calculated. Under the same conditions ($\varepsilon_{5-m} = -0\cdot023$) for *m*-carborane $\mu = 2\cdot28$ D (expt.[28] 2·85 D) was found. Both values are in better agreement with the reality than all other values calculated up to now[16,20].

A relationship similar to (1) was also found for thioglycollic acids derived from icosahedral carboranes where the dependence of pK'_a on E—H vertex charge ε can be expressed by equation (2),

$$pK'_a = pK'_{a0} - \varrho'\varepsilon , \qquad (2)$$

with $pK'_{a0} = 4\cdot58$ and $\varrho' = 5\cdot6$. This equation allows to establish the group charge of strongly negative vertices with pK_a excessively high to be determined by a titration in the ethanol–water mixture.

The found relations could be of a great importance in the chemistry of *closo*-heteroboranes in general. It is highly probable that equations (1) and (2) will be valid (without or with small corrections only) in the series of *closo*-metallocarboranes as well as with other *closo*-heteroboranes and we believe that they will help in studying the transmissions of electron densities evoked by substituents or heteroatoms in the mentioned systems.

EXPERIMENTAL

The ^{1}H- and ^{11}B-NMR spectra were measured on Varian XL-100. TLC was carried out on Silufol (silica gel on Al foil; Kavalier, Votice, Czechoslovakia). Organic mercaptants were distilled (sublimed) *in vacuo* and their purity was checked by the mass and ^{1}H-NMR spectrometry. Preparation of 9-*o*, 9-*m* and 2-*p*-mercaptocarboranes has been described recently[24,25], the 1-*o* and 1-*m* HS-derivatives were prepared according to[29,30].

Dissociation constants of icosahedral mercaptans and their —SCH_2COOH derivatives were determined under identical conditions by potentiometric titration using a glass electrode. In a typical experiment, 0·001 mol of the measured compound was dissolved in 50 g (63·5 ml) of ethanol, diluted with 50 ml of water under stirring and the solution was titrated with 0·1M NaOH in 50% ethanol (w/w) at 20°C. All measured mercaptans exhibit higher acidities in 50% ethanol than in water. This increase in acidity in ethanol can be expresses by equation pK_a (50% C_2H_5OH) = = 0·904 pK_a (H_2O) and holds also for phenylmethanethiol and 4-methylbenzenethiol. In contrast to this, the icosahedral and aryl thioglycollic acids follow an expected relation pK_a' (50% C_2H_5OH) = 1·29 pK_a' (H_2O).

Preparation of 1-HS-1,12-$C_2B_{10}H_{11}$

To the solution of 7·2 g (0·05 mol) of p-carborane in 50 ml of benzene was added 0·02 mo of butyllithium in hexane (20% solution) and the mixture was refluxed for 1 h. Sulfur (0·64 g, 0·02 mol) was added, and when it dissolved under stirring, 50 ml of water were added, benzene layer was separated and extracted with 20 ml of 5% solution of NaOH. By the evaporation of benzene, and by sublimation of the residue, 1·5 g (20·8%) of starting p-carborane was recovered. Water layer was combined with alkaline extract, the mixture was acidified to c. pH 2, and the separated product was extracted three times with 20 ml portions of hexane. The hexane extracts were combined, the solvent was evaporated in vacuo and the residue was sublimed at 80°C (bath) and 1·3 Pa (0·01 Torr). The sublimate (5·5 g) containing according to ^{1}H-NMR c. 10% of 1,12(SH)$_2$-1,12-$C_2B_{10}H_{10}$ was dissolved in 20 ml of diethyl ether and the solution was shaken with the solution of 0·4 g (0·003 mol) of K_2CO_3 in 10 ml of water for 30 min. The ether was removed in vacuo, the solid residue was filtered off, washed with water and dissolved in 30 ml of hexane, the solvent was evaporated in vacuo and the residue was resublimed yielding 4·1 g (59% on recovered p-carborane) of 1-HS-1,12-$C_2B_{10}H_{11}$ (m/e 177, see Table IV).

TABLE IV

^{1}H-NMR and Chromatographic Characteristics of HS-$C_2B_{10}H_{11}$ Isomers

HS—$C_2B_{10}H_{11}$	^{1}H-NMR[a]			R_F[b]	
	CH	CH	SH	H[c]	B—H[d]
1-o	3·80	—	3·95	30	76
1-m	2·98	—	3·36	74	93
1-p	2·54	—	3·16	114	109
4-m	3·15	2·77	0·72	28	68
2-p	3·09	2·90	0·79	61	91
8-o	3·62	3·62	0·46	0	17
9-m	2·97	2·97	0·43	14	51
9-o	3·57	3·45	0·45	0	17

[a] In CDCl$_3$, ppm relative to tetramethylsilane; [b] TLC on Silufol, relative to 1,7-$C_2B_{10}H_{12}$ = = 100; [c] hexane; [d] benzene–hexane 1 : 2.

Isolation of 8-HS-1,2-$C_2B_{10}H_{11}$

The crude product from the preparation of 9-HS-1,2-$C_2B_{10}H_{11}$ contains *c.* 5% of 8-*o* isomer[25]. The latter compound can not be separated by chromatography but it accumulates in mother liquors after the crystallization of 9-*o* from the benzene–hexane 1 : 3 mixture. The combined mother liquors were evaporated and the residue was sublimed *in vacuo* yielding 3·8 g of a mixture which showed the ratio 9-*o* : 8-*o* = 3·16 : 1 (from ^{1}H-NMR). This mixture was dissolved in 50 ml of ethanol, 0·8 g of $KHCO_3$ in 10 ml of water (neutralization of the 8-*o* HS-isomer present) was added and the mixture was boiled for 1 h under bubbling N_2 through it. The solution was diluted with 30 ml of water, ethanol was distilled off *in vacuo* and the solid portion representing practically pure 9-*o* isomer was filtered off. The filtrate was saturated with CO_2 and the separated product was extracted into 20 ml of hexane. After evaporation *in vacuo* the residue was sublimed at 60°C (bath) and 1·3 Pa (0·01 Torr), yielding 1·1 g of 8-HS-1,2-$C_2B_{10}H_{11}$ (*m/e* 177, Table IV).

Isolation of 4-HS-1,7-$C_2B_{10}H_{11}$

The crude product of a direct sulfuration of *m*-carborane[31] contains besides the main component, *i.e.* 9-HS-1,7-$C_2B_{10}H_{11}$, also about 1·5% of the 4-*m* isomer which remains in the mother liquors after the crystallization of 9-*m* isomer from hexane. The hexane mother liquors from 30 g of the crude 9-*m* mercaptan, were concentrated *in vacuo* to approximately 30 ml, the 9-*m* isomer was separated by filtration, the solution was soaked into a column with 200 g of silica gel and the products were eluted with hexane. The fractions containing according to TLC pure 4-*m* isomer were combined, hexane was evaporated *in vacuo* and the residue was sublimed at 60°C and 1·3 Pa yielding 0·4 g of the pure 4-*m* isomer (Table IV).

Preparation of $C_2B_{10}H_{11}SCH_2COOH$ Isomers (1-*o*, 9-*o*, 9-*m*, 1-*p*, 2-*p*)

All thioglycollic acids were prepared by the following procedure: To the solution of a mercaptane (0·01 mol) in 100 ml of 5% solution of potassium hydroxide was added 2·6 g (0·025 mol) of chloroacetic acid. After 1 h standing, the mixture was acidified to pH 2, the separated product was filtered, washed with water and the solid residue was crystallized from hot cyclohexane. All mass spectra were in accord with the expected molecular cut-off *m/e* 204. In a similar way were prepared also the derivatives of phenylmethanethiol, benzenethiol and 4-methylbenzenethiol.

The potentiometric titrations were performed by Mr M. Skalický, the ^{1}H-NMR spectra by Dr F. Mareš, both Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řež. The mass spectra were recorded by Dr V. Kubelka and ^{11}B-NMR spectra by Mr P. Pech, Prague Institute of Chemical Technology, Prague. It is a pleasure to thank all these colleagues for their assistance.

REFERENCES

1. Smith H., Knowles T. A., Schroeder H.: Inorg. Chem. *4*, 107 (1965).
2. Boer F. P., Potenza J. A., Lipscomb W. N.: Inorg. Chem. *5*, 1301, (1966).
3. Zakharkin L. I., Kazantsev A. V.: Zh. Obshch. Khim. *37*, 1211 (1967).
4. Zakharkin L. I., Kalinin V. N., Podvisotskaya L. S.: Izv. Akad. Nauk SSSR, Ser. Khim. *1968*, 2661.
5. Hawthorne M. F., Young D. C., Garrett P. M., Owen D. A., Schwerin S. G., Tebbe F. N., Wegner P. A.: J. Amer. Chem. Soc. *90*, 862 (1968).
6. Plešek J., Heřmánek S.: Chem. Ind. (London) *1973*, 381.
7. Plešek J., Heřmánek S.: Unpublished results.

8. Grimes R. N.: *Carboranes*. Academic Press, New York 1970.
9. Stanko V. I., Brattsev V. A., Klimova A. I.: Zh. Obshch. Khim. *44*, 2482 (1974).
10. Stanko V. I., Klimova A. I.: Zh. Obshch. Khim. *36*, 159 (1966).
11. Zakharkin L. I., Kalinin V. N.: Izv. Akad. Nauk SSSR, Ser. Khim. *1968*, 1423.
12. Zakharkin L. I., Kalinin V. N., Kobelkova N. I.: Syn. React. Inorg. Metalorg. Chem. *6*, 91 (1976).
13. Mironov V. F., Pekhurina S. Y., Grigos V. I.: Dokl. Akad. Nauk. SSSR *230*, 865 (1976).
14. Stanko V. I., Ovsyanikov N. N., Klimova A. I., Khranov V. V., Shtyrkov L. G., Garibov R. E.: Zh. Obshch. Khim. *46*, 871 (1976).
15. Hoffmann R., Lipscomb W. N.: J. Chem. Phys. *36*, 2176, 3489 (1962).
16. Koetzle T. F., Lipscomb W. N.: Inorg. Chem. *9*, 2743 (1970).
17. Newton M. D., Boer F. P., Lipscomb W. N.: J. Amer. Chem. Soc. *88*, 2353 (1966).
18. Potenza J. A., Lipscomb W. N.: Inorg. Chem. *5*, 1471 (1966).
19. Newton M. D., Lipscomb W. N., cited according to: Beall H., Lipscomb W. N.: Inorg. Chem. *6*, 874 (1967).
20. Dixon D. A., Kleier D. A., Halgren T. A., Hall J. H., Lipscomb W. N.: J. Amer. Chem. Soc. *99*, 6226 (1977).
21. Adler R. G., Hawthorne M. F.: J. Amer. Chem. Soc. *92*, 6174 (1970).
22. Heřmánek S., Plešek J., Gregor V., Štíbr B.: Chem. Commun. *1977*, 561.
23. Beall H. in the book: *Boron Hydride Chemistry* (E. L. Muatterties, Ed.), p. 302. Academic Press, New York 1975.
24. Plešek J., Heřmánek S.: Chem. Ind. (London) *1977*, 360.
25. Plešek J., Heřmánek S.: This Journal *43*, 1325 (1978).
26. Bordwell F. G., Anderson H. M.: J. Amer. Chem. Soc. *75*, 6019 (1953).
27. Kreevoy M. M., Harper E. T., Duvall R. E., Wilgus III H. S., Ditsch L. T.: J. Amer. Chem. Soc. *82*, 4899 (1960).
28. Laubengayer A. W., Rysz W. R.: Inorg. Chem. *4*, 1513 (1965).
29. Zakharkin L. I., Zhigareva G. G.: Izv. Akad. Nauk SSSR, Ser. Khim. *1967*, 1358.
30. Zakharkin L. I., Zhigareva G. G.: Zh. Obshch. Khim. *45*, 789 (1975).
31. Plešek J., Janoušek Z., Heřmánek S.: This Journal *43*, 1332 (1978).

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