UNIQUE DIALKYLSULFONIO-METHYLATION OF THE 7,8-$C_2B_9H_{12}^{(-)}$ ION TO THE 9-R_2S-CH_2-7,8-$C_2B_9H_{11}$ ZWITTERIONS BY FORMALDEHYDE AND DIALKYL SULFIDES. GENERAL SYNTHESIS OF THE COMPOUNDS 10-R_2E-7,8-$C_2B_9H_{11}$ (E = O, S)

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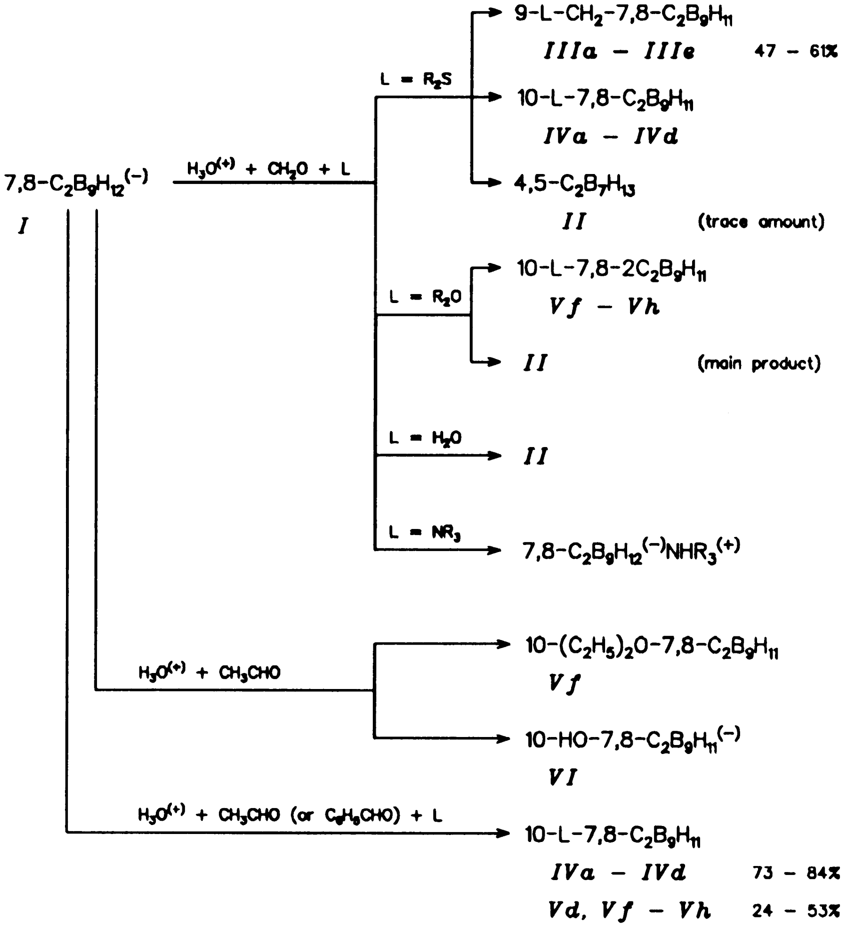
Dialkylsulfonio-methylation has been observed on the treatment of the 7,8-$C_2B_9H_{12}^{(-)}$ ion with formaldehyde and dialkyl sulfides in aqueous acidic medium. Four zwitterions of the type 9-R_2S-CH_2-7,8-$C_2B_9H_{11}$ were formed with dimethyl and diethyl sulfide, tetrahydrothiophene and thioxane. In contrast, dialkyl ethers (diethyl ether, tetrahydrofuran, dioxane) afforded low amounts of the 10-R_2O-7,8-$C_2B_9H_{11}$ zwitterions, with the carborane 4,5-$C_2B_7H_{13}$ being the principal product. Using acetaldehyde instead of formaldehyde, moderate yields of the 10-R_2O- and high yields of the 10-R_2S-7,8-$C_2B_9H_{11}$ derivatives were obtained. With tertiary amines, only corresponding ammonium salts precipitated. Possible reaction pathways for these transformations are discussed and compared with the specific degradation of the 7,8-$C_2B_9H_{12}^{(-)}$ ion to the *arachno*-4,5-$C_2B_7H_{13}$ carborane.

Treatment of the 7,8-$C_2B_9H_{12}^{(-)}$ ion (*I*) with formaldehyde in aqueous acidic medium results in a selective high-yield two-boron degradation to give the *arachno*-4,5-$C_2B_7H_{13}$ carborane *II* (refs[1 – 3]). No other carbonyl compound can replace formaldehyde in this respect. For example, as will be shown in this paper, acetaldehyde gives rise to entirely different species. The same applies for benzaldehyde, but acetone behaves as a nearly inert compound in this regard.

When investigating the possible pathways of this specific degradation, we added some weak Lewis bases to the acidic aqueous reaction mixture in order to trap potential intermediates in the form of relevant zwitterions. Scheme 1 demonstrates that the results with formaldehyde and dialkyl sulfides R_2S were surprising, showing an incorporation of the -CH_2SR_2 group into boron clusters under the formation of the type *III* that is, as far we are aware, unprecedented. Besides, low amount of 10-R_2S derivatives *IV* and a trace amount of *II* were obtained. In the case of thioxane, a small quantity of the O–B species *Vd* accompanied the S–B congener *IVd*.

No compounds of the type *III* were obtained when dialkyl ethers were used instead of dialkyl sulfides, but the relevant species *Vf* – *Vh* were isolated in small yields with diethyl ether, tetrahydrofuran, and dioxane, respectively. Most of the starting anion became solvolyzed to the carborane *II* in this case (Scheme 1).



In formulae *III* – *V*: ***a***, L = $(CH_3)_2S$; ***b***, L = $(C_2H_5)_2S$; ***c***, L = $(CH_2)_4S$; ***d***, L = $O(CH_2CH_2)_2S$; ***e***, L = $(C_6H_5CH_2)_2S$; ***f***, L = $(C_2H_5)_2O$; ***g***, L = $(CH_2)_4O$; ***h***, L = $O(CH_2CH_2)_2O$

SCHEME 1

Trialkylamines afforded neither the species *III* nor *IV* as the reaction was prevented by the formation of the water insoluble $C_2B_9H_{12}^{(-)}$ $NHR_3^{(+)}$ salts.

The above reactions are acid catalyzed. The first signs of a reaction are observed at the autogeneous acidity of the conjugated acid $C_2B_9H_{12}^{(-)} . H_3O^{(+)}$ (pK_a 2.25), and the rate becomes optimum if the concentration of hydrochloric acid is kept in the range 2 – 4 mol l^{-1}. Exceeding this acidity limit sharply decreases the yields of both types of zwitterions. The acidity of acetic acid is insufficient to induce any reaction.

Addition of a water-immiscible cosolvent facilitates the reaction. No difference has been observed in this respect between benzene and ethyl acetate, except that the reaction rate decreased distinctly with the latter. However, in homogeneous solution, with ethanol as homogenizing solvent, no reaction took place at all.

These qualitative observations indicate that protonation of the formaldehyde present plays an essential role. If it is suppressed either by a low acidity of the medium or by the addition of competing solvents like ethanol, no reaction is observed. Additionally, the ion *I* needs to be present in a sufficient concentration. With a large excess of concentrated hydrochloric acid, the dicarbollide anion becomes protonated to the carborane $7,8\text{-}C_2B_9H_{13}$, which may then be the cause of the strongly diminished yields.

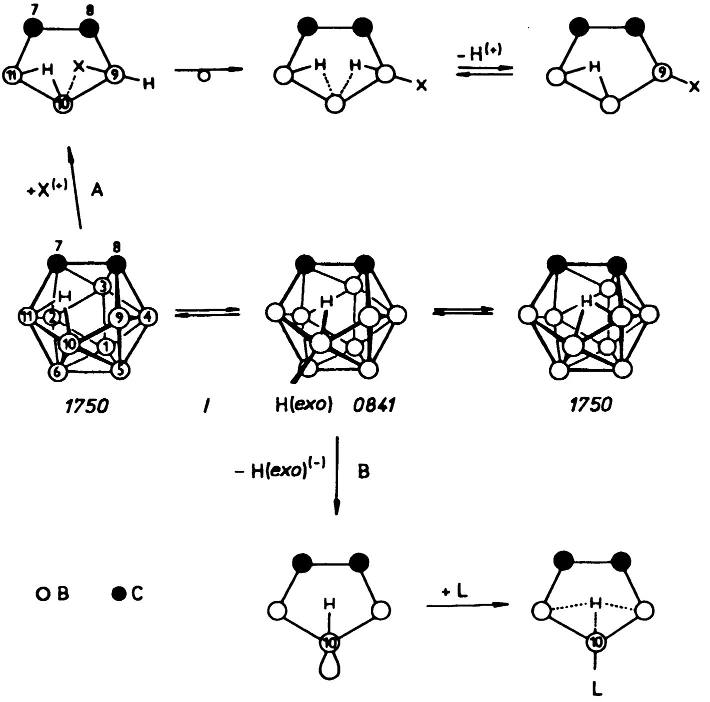
The substitution of CH_2O by CH_3CHO affords a different pattern. Acetaldehyde alone reacts with *I* in acidified water to give $10\text{-}(C_2H_5)_2O\text{-}7,8\text{-}C_2B_9H_{11}$ (*Vf*) and $10\text{-}HO\text{-}7,8\text{-}C_2B_9H_{11}^{(-)}$ (*VI*). In the presence of suitable bases (ethers, sulfides), however, their introduction dominated and compounds $10\text{-}R_2O\text{-}7,8\text{-}C_2B_9H_{11}$ (*V*) in moderate (24 – 53%) and $10\text{-}R_2S\text{-}7,8\text{-}C_2B_9H_{11}$ (*IV*) in high yields (73 – 84%) are obtained. The uniformity of the products renders this reaction the method of choice in the synthesis of these zwitterionic species which were generally not previously accessible[4,5].

Benzaldehyde can substitute acetaldehyde in respect of syntheses of the species *IVa* – *IVd* and *Vd* – *Vh*, but its high boiling point and solvating power complicate the isolation of pure products. Acetone reacts in the same sense, but extremely slowly, so its use is impractical.

Proposal of the Reaction Courses in the Discussed Substitutions of $7,8\text{-}C_2B_9H_{12}^{(-)}$ (I)

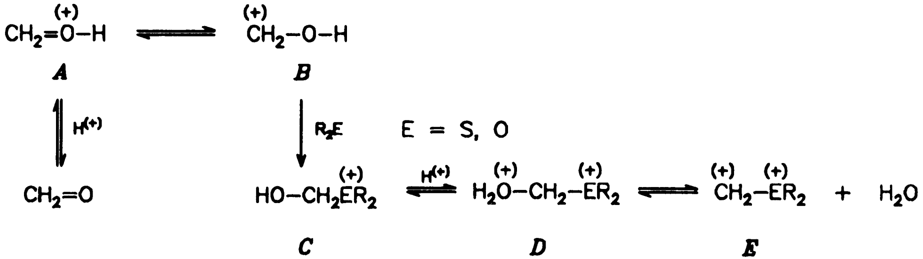
As stated above, the non-charged carborane $7,8\text{-}C_2B_9H_{13}$ is not a key compound in the substitution reactions mentioned. In substitutions at both B(9) and B(10) vertices, the most probable precursor is, therefore, the anion $7,8\text{-}C_2B_9H_{12}^{(-)}$. This anion can be considered as a species in which the *endo*-hydrogen oscillates in a fast tautomerism among three distinct positions which can be described by the *styx* formulae *1750* (μH-tautomer) and *0841* (BH_2-tautomer) (see the middle part in Scheme 2).

In the proton-promoted reactions, the positively charged particle $X^{(+)}$ can either: (i) enter the open face of the "μH-tautomer" *1750* (similarly as does $H^{(+)}$) forming the intermediate $7,8\text{-}C_2B_9H_{12}X$ which changes, after the inversion of the B(9)X,H couple and the H(*endo*)$^{(+)}$ elimination, to the B(9)X(*exo*) substituted compound (pathway A, Scheme 2, open faces only), or (ii) remove the *exo*-hydrogen $H^{(-)}$ from the BH_2-vertex, thus generating a vacant orbital in the B(10) position which can be immediately occupied by some of the nucleophile particles or molecules from the reaction mixture (pathway B, Scheme 2).



SCHEME 2

The introduction of the CH_2–L substituent into the anion *I* presumes its reaction with a $\text{-}CH_2^{(+)}$ species. Possible $C^{(+)}$ cations expected in the system $CH_2O/H_3O^{(+)}/L$ are shown in Scheme 3 (ref.[6]).

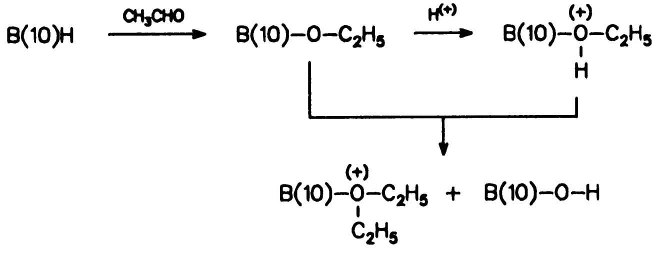


SCHEME 3

Of these, only the species $^{(+)}CH_2$–OH (*B*) and $^{(+)}CH_2$–$^{(+)}ER_2$ (*E*) represent the $C^{(+)}$ cations. The particle (*B*) (Scheme 3) should generate the intermediate 9-(CH_2OH)-7,8-$C_2B_9H_{11}^{(-)}$ which, after the protonization to the 9-($CH_2^{(+)}OH_2$)-7,8-$C_2B_9H_{11}^{(-)}$ zwitterion, should alkylate both dialkyl sulfides and dialkyl ethers to the appropriate zwitterions 9-($CH_2^{(+)}SR_2$)- and 9-($CH_2^{(+)}OR_2$)-, respectively. The absence of the latter type in the reaction mixture implies, however, that the intermediate (*B*) is not operating here.

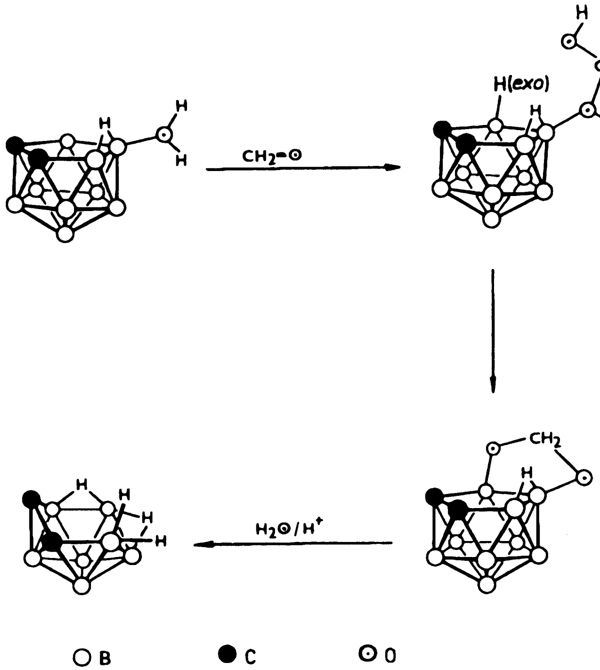
We prefer, therefore, the incorporation of the second candidate, the $^{(+)}CH_2$–$L^{(+)}$ species (*E*), with two positively charged atoms in the close neighborhood, which is unlikely with ethers (L = OR_2) but possible with dialkyl sulfides (L = SR_2) due to the stabilization of the dication $^{(+)}CH_2$–$^{(+)}SR_2$ by an interaction with *d*-orbitals on sulfur atom[6]. This is, in our opinion, the main reason for the distinct difference between S and O nucleophiles in this unique B(9) "alkylation". Using CH_3CHO and higher aldehydes, the 9-substituted derivatives were not observed even with dialkyl sulfides, thus indicating that the appropriately substituted bulky analogues $^{(+)}CHR$–$^{(+)}SR_2$ of (*E*) were not operating if present. In the absence of the reactive component $^{(+)}CH_2$–$^{(+)}SR_2$, competitive reactions shown in the pathway B (Scheme 2) can take place.

The formation of the compounds 10-$(C_2H_5)_2O$-7,8-$C_2B_9H_{11}$ (*Vf*) and 10-HO-7,8-$C_2B_9H_{11}^{(-)}$ (*VI*) in the reaction with acetaldehyde can be explained as resulting from a disproportionation, i. e. of an intermolecular transfer of the $C_2H_5^{(+)}$ group under acidic conditions (Scheme 4):



SCHEME 4

That, in the two-boron degradation of the anion *I* to the *arachno*-carborane *II* (refs[1–3]) (Scheme 1), formaldehyde cannot be replaced by higher aldehydes, which indicates that an explanation of this behavior lies in some characteristic significantly different from that of other aldehydes. This distinction we see in the stability of $CH_2(OH)_2$ in comparison with $RCH(OH)_2$. As a probable pathway we therefore suggest the following sequence (Scheme 5): *1*) the formation of the zwitterion 10-H_2O-7,8-$C_2B_9H_{11}$; *2*) its addition to formaldehyde; *3*) intramolecular elimination of a molecule of hydrogen from the terminal -$^{(+)}OH_2$ group and the hydridic H–B(9) vertex; and O-activated hydrolytic attack on both B(9) and B(10) vertices, resulting in the removal of both of them.



SCHEME 5

The structure of the representative compound *IIIa* has been established on the basis of: (i) multinuclear and 2D [^{11}B–^{11}B]-COSY NMR spectroscopy (Table I, Fig. 1), and (ii) some conclusive chemical reactions.

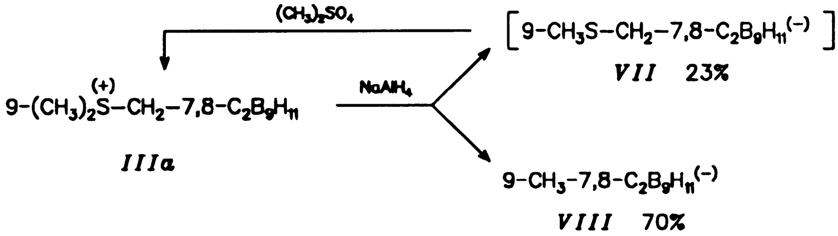
The ^{1}H NMR spectrum (Table I) implies two nonequivalent H–C(carb) vertices, one B–CH_2–S group, one B–H–B bridge (μH) and two nearly equivalent methyl groups in the moiety -$S(CH_3)_2$. The ^{13}C spectrum (CD_3COCD_3) reveals two broad doublets from the H–C(carb) vertices at δ (*J*, Hz) 48.74 (164) and 37.00 (153), a broad triplet of the B–CH_2–S methylene group at δ 35.5 that overlaps the latter H–C doublet, and two quartets from the almost equivalent methyl groups in the $(CH_3)_2S$- unit at 27.47 (144) and 28.10 (144).

A verification of the existence of the B–CH_2–S arrangement was obtained from a ^{13}C APT experiment in CD_3CN that showed three signals split by ^{11}B neighbors into broad quartets; these were the H–C(carb) signals at δ 49.81 and 36.05, and the signal from the B–CH_2–S group at δ 35.00. Two sharp singlets from the $(CH_3)_2S$- methyl groups were found at δ 27.23 and 26.67, respectively. The nonequivalency of both these methyl groups indicates a restricted rotation of the $(CH_3)_2S$- group about the S-methylene bond axis.

The 2D ^{11}B–^{11}B NMR spectrum of *IIIa* (Fig. 1) is compatible with the 9-substituted 7,8-$C_2B_9H_{11}$ framework, and all signals have been assigned to the pertinent boron vertices.

Reduction of *IIIa* with $NaAlH_4$ in tetrahydrofuran confirmed the presence of a B–CH_2-arrangement in the vicinity of the C–H vertex (Scheme 6).

The methylthiomethyl ionic species *VII* was not isolated, but was reconverted to the starting compound by methylation of the clear aqueous reduction mixture. After removal of the insoluble *IIIa*, the tetramethylammonium salt of the ion 9-CH_3-7,8-$C_2B_9H_{11}^{(-)}$ (*VIII*) was precipitated from the aqueous filtrate. The same results were obtained on reduction of *IIIa* with Na/naphthalene in tetrahydrofuran. Here, however, the methylthiomethyl ionic species *VII* was obtained in 36% yield, and the ion *VIII* in 45% yield only.



SCHEME 6

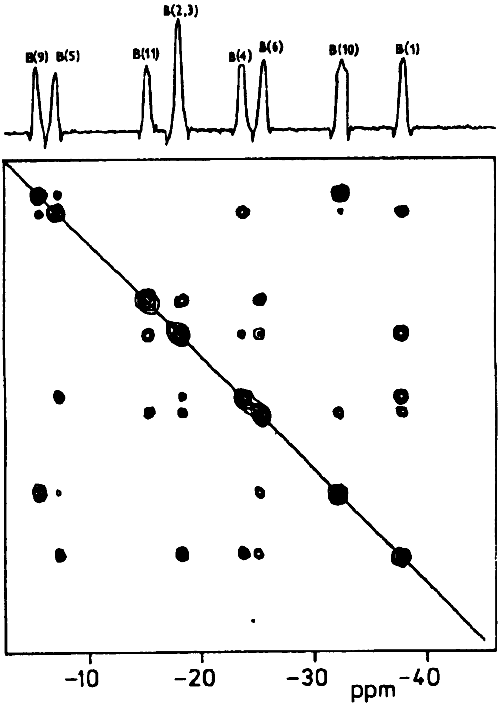


FIG. 1

2D [^{11}B–^{11}B] {^1H} NMR COSY spectrum of 9-$(CH_3)_2S$-CH_2-7,8-$C_2B_9H_{11}$ (*IIIa*) in CD_3COCD_3

The constitution of *VIII* has been revealed by the usual combination of NMR results. In ^1H NMR spectrum, the following signals were found (δ): 3.44 for methyl groups in $[(CH_3)_4N^{(+)}]$, 1.74 and 1.65 for two H–C(carb) signals, and a broad singlet at δ 0.26 for the CH_3–B methyl. Eight of the nine ^{11}B signals were well separated in the ^{11}B NMR spectrum. The 2D $[^{11}B-^{11}B]$-COSY NMR spectrum (Fig. 2) fitted with the suggested structure of the ion *VIII*, with all signals being assigned to the pertinent boron vertices.

A very interesting displacement of dimethyl sulfide occurred on treatment of *IIIa* with excess pyridine. This latter ligand attacked the remote B(11) position, shifting some hydrogen atoms and replacing the distant $(CH_3)_2S$ group by hydrogen under the formation of 9-CH_3-11-NC_5H_5-(9,10-μH)-7,8-$C_2B_9H_{10}$ (*IX*) (Scheme 7).

The mass spectrum, and the ^1H and ^{11}B NMR spectra (see Experimental) agree with the suggested structure of the species *IX*. Characteristic features of *IX* are the signal at δ 0.25 from the B–CH_3 group in the ^1H NMR and two singlets at δ +2.41 and −6.5,

TABLE I

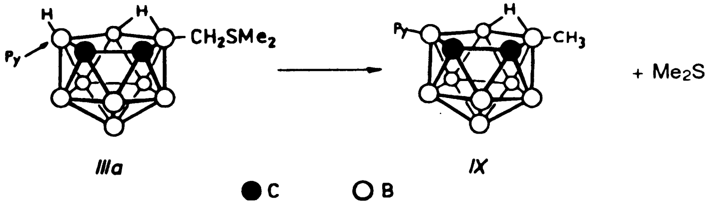
NMR Characteristics, R_F values and yields of the 9-R_2S-CH_2-7,8-$C_2B_9H_{11}$ zwitterions *IIIa* – *IIIe*

Parameter	*IIIa*	*IIIb*	*IIIc*	*IIId*	*IIIe*
Yield, %	61.2	50.7	47.0	70.0	43.2
R_F	0.23	0.32	0.32	0.35	0.42
Atom			^{11}B NMR		
B(9)	-5.82	-5.80	-5.39	-6.26	-5.96
B(5)	-6.86	-7.01	-7.11	-6.75	-6.30
B(11)	-15.12	-15.11	-14.90	-15.17	-15.23
B(2,3)	-17.82	-17.85	-17.87	-17.80	-17.82
B(4)	-23.62	-23.49	-23.69	-23.61	-23.46
B(6)	-24.91	-24.90	-24.83	-24.99	-24.97
B(10)	-31.82	-31.81	-31.85	-31.79	-31.59
			^1H NMR		
H-C(carb)	2.16	2.17	2.16		2.11
H-C(carb)	1.81	1.81	1.79		1.81
S-CH_2-B	2.99	2.90	2.95		2.85
μH	-3.15	-3.07	-3.07		-3.23
CH_3	3.06	1.52	–		7.48[a]
CH_2	–	3.45	3.56		4.70
CH_2	–	–	2.46		4.77

[a] Phenyl protons.

respectively, in the ^{11}B NMR spectra. In the crystalline state, the compound shows a characteristic greenish fluorescence in UV light.

Relevant NMR spectra of the species *IIIa* – *IIId* are very similar (Table I), as the compounds differ apparently only in the nature of the dialkyl sulfide, other features being essentially the same.



According to the low R_F values on TLC (Table I), the species *IIIa* – *IIId* are very polar, as may be expected. They are insoluble in water, sparingly soluble in benzene and cold ethanol, somewhat more in chloroform, well in methylene chloride and very well in acetone, tetrahydrofuran and acetonitrile. However, no suitable crystals for

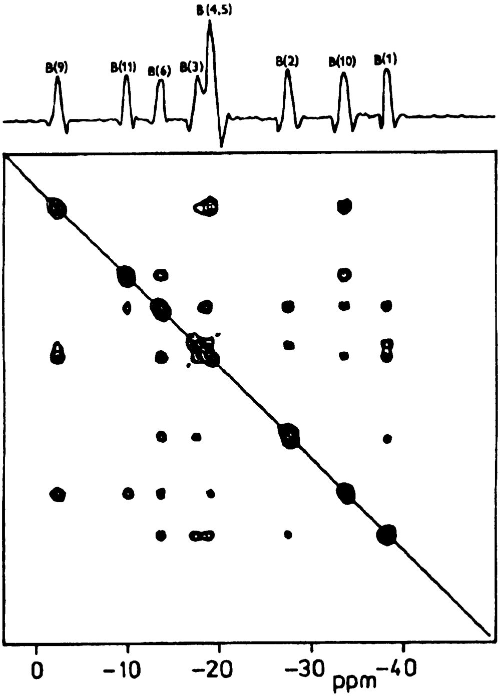


FIG. 2

2D [^{11}B–^{11}B] {^{1}H} NMR COSY spectrum of 9-CH$_3$-7,8-C$_2$B$_9$H$_{11}^{(-)}$ N(CH$_3$)$_4^{(+)}$ (*VIII*) in CD$_3$COCD$_3$

X-ray diffraction could be grown. The TLC and NMR pure samples gave only shining aggregates of smaller glassy particles.

No defined melting points were observed with *IIIa* – *IIId*. For example, the species *IIIa* began to melt around 130 °C with decomposition; upon TLC analysis of the melted sample, two components were revealed. One of these did belong to 9-$(CH_3)_2S$-7,8-$C_2B_9H_{11}$, the other seemingly to *IVa*. The ^1H NMR spectra confirmed the identity of the former species, but the last compound was in fact the B-methylated derivative of *IVa* (broad singlet from a B-methyl group at δ 0.28). This easy decomposition is apparently the explanation of why no unequivocal mass spectra could be obtained corresponding to the molecular edges of *IIIa* – *IIId*.

Generally, the zwitterions of the type *IVa* – *IVc* are less polar by far than their remote relatives *IIIa* – *IIIc*. This is apparent on comparison of the respective R_F values on TLC; whereas *IIIa* does not move on silica gel thin layer with toluene as eluent, its counterpart *IVa* shows an R_F value of 0.36. This difference is apparently due to the special characters of the zwitterionic species *IIIa* – *IIId* and *IVa* – *IVd*, *Vd* – *Vh*, respectively. The former class behaves almost as inner salts with separated positive and negative charges, whereas the latter compounds behave as if they are polar covalent species, evidently due to a conjugative charge compensation within the molecules (*IVa* – *IVd*, *Vd* – *Vh*). It is noteworthy, however, that the relevant O–B species *V* are somewhat more polar than the respective S–B analogs *IV* (cf. the R_F values of the

TABLE II
Yields and some properties of the 10-L-7,8-$C_2B_9H_{11}$ compounds *IVa* – *IVd* and *Vd* – *Vh*

Compound	Ligand	Yield[a] %		M. p. °C	R_F[b]	R_F[c]	^1H NMR[d]			
							H–C(carb)	ligand signals		
								CH_3	CH_2	CH_2
IVa	$(CH_3)_2S$	16.5	(84.0)	97 – 98	0.36	0.60	2.22	2.56	–	–
IVb	$(C_2H_5)_2S$	9.0	(73.7)	51 – 52	0.36	0.64	2.21	1.48	2.97	–
IVc	$(CH_2)_4S$	12.1	(78.4)	149 – 150	0.40	0.75	2.12	–	3.31	2.28
IVd	$O(C_2H_4)_2S$	11.8	(32.9)	140	0.15	0.28	2.32	–	4.08	3.11
Vd	$S(C_2H_4)_2O$	2.2	(6.3)	144	0.22	0.35	2.02	–	4.77	3.01
Vf	$(C_2H_5)_2O$	26.1	(24.0)	69 – 70	0.22	0.46	1.96	1.55	4.66	–
Vg	$(CH_2)_4O$	18.9	(53.2)	130 – 132	0.22	0.46	1.95	–	4.49	2.27
Vh	$O(C_2H_4)_2O$	8.9	(44.2)	164 – 165	0.17	0.34	2.07	–	4.57	3.99

[a] With CH_2O (or CH_3CHO, in parentheses). [b] In toluene. [c] In chloroform. [d] 200 MHz, $CDCl_3$.

couples *IVb*/*Vf* and *IVc*/*Vg* in Table II). In contrast to the compounds of the type *III*, all the type-*IV* species show defined melting points (Table II).

The ^{1}H NMR spectra of the species *IVa* – *IVd* and *Vd* – *Vh* are informative primarily about the respective ligands. In the skeletal region, two equivalent C–H carborane signals are visible near δ 2.0 and no sign of a B–H–B bridge signal has been found for any of these compounds.

The ^{11}B NMR spectra of the compounds *IVa* – *IVd* and *Vd*, *Vf* – *Vh* are recorded in Table III. Due to a quite low effect of the R_2S ligand on the chemical shift of the B(10) vertex, along with low long-range effects of the R_2S- groups, the overall patterns of the spectra *IVa* – *IVd* are the same as that for the parent ion *I*, showing relative intensities 2 : 2 : 1 : 2 : 1 : 1 reading upfield (Table III).

On the other hand, these effects are very pronounced with R_2O ligands. Thus, the general pattern of the ^{11}B NMR spectra changes to 1 : 2 : 2 : 2 : 1 : 1 for *Vd* – *Vh*. Here the lowest field (i.e. highest frequency) signal belongs to the B(10) vertex directly bound to the respective ligand, and it is shifted downfield from the original position by some 20 ppm. The "antipodal effect" (ref.[9]) shifts the signal of the B(3) vertex to the higher field by some 6 – 8 ppm. Vicinal and meta effects are not too strong here (Table III).

A very interesting feature is the shape of the signal from the B(10) vertex, which looks like a broad singlet. But with the compounds *IVa* and *IVd* it shows a distinct doublet with a coupling constant *J*(B–H(*endo*)) = 80 Hz. This unusual value clearly reflects the dual character of the respective L–B(10)–H hydrogen atom, which behaves partially as a delocalized B–H–B bridge and partially as an *endo*-hydrogen of a true BH_2 group. In contrast, the isomeric 9-L-7,8-$C_2B_9H_{11}$ species do not show these

TABLE III

^{11}B NMR spectra of the 10-L-7,8-$C_2B_9H_{11}$ species *IVa* – *IVd* and *Vd* – *Vh* in $CDCl_3$

Compound	Ligand	B(9,11)	B(5,6)	B(3)	B(2,4)	B(10)	B(1)
I [a]	$H^{(-)}$	-12.56	-18.48	-18.48	-22.85	-34.51	-39.11
IVa	$(CH_3)_2S$	-12.51	-17.00	-18.23	-21.60	-27.06	-38.33
IVb	$(C_2H_5)_2S$	-12.56	-18.86	-18.03	-21.49	-28.22	-38.30
IVc	$(CH_2)_4S$	-12.26	-16.60	-18.24	-21.59	-26.56	-38.10
IVd	$O(C_2H_4)_2S$	-12.48	-16.81	-17.80	-21.23	-28.60	-38.18
Vf	$(C_2H_5)_2O$	-13.61	-17.72	-22.90	-22.90	-11.61	-40.54
Vg [a]	$(CH_2)_4O$	-12.51	-16.99	-22.43	-22.43	-11.29	-39.78
Vh	$O(C_2H_4)_2O$	-13.51	-17.88	-22.74	-22.74	-10.19	-40.39
Vd	$S(C_2H_4)_2O$	-13.31	-17.46	-22.51	-22.51	-10.52	-40.28

[a] In CD_3COCD_3.

features. Instead, the hydrogen bridge is located between the B(10) and B(11) vertices[10], the L–B(9) signal is a true singlet, and the molecule shows a distinct μH signal at δ ca −3 (ref.[6]) in the ^1H NMR spectrum.

EXPERIMENTAL

^{11}B NMR spectra were recorded at 64.184 MHz with a Varian XL-200 spectrometer and were externally referenced to $BF_3 \cdot O(C_2H_5)_2$ sealed in a capillary in the solvents given in Tables I – III. The two-dimensional [^{11}B–^{11}B] {^1H} NMR spectra were measured using standard Varian XL-200 software HOMCOR and COSY pulse sequence (matrix 512 × 512). Acquisition parameters: acquisition time (AT) 0.1 and 0.05 s, relaxation delay (D_1) 0.1 s, sweep width (SW) 2 500 Hz and 5 100 Hz, number of transitions 100 and 500 for *IIIa* and *VIII*, respectively. The resulting spectra were line-narrowed using resolution enhancement (RE) 0.003 and the apodization function (AF) 0.01, and symmetrized and recorded using a Nicol Zeta 1553 plotter. ^1H NMR spectra were obtained at 60 MHz on a Tesla BS-467 and at 200 MHz on a Varian XL-200 equipment and were internally referenced to tetramethylsilane. Chemical shifts (^{11}B and ^1H) are given in δ values, positive values downfield. Purity of individual products was monitored by TLC on Silufol (silica gel on aluminium foil, starch as binder, producer Kavalier, The Czech Republic; detection by I_2 vapours followed by $AgNO_3$ spray) using eluents given in Tables I and II. Melting points were determined in sealed capillaries and are uncorrected. Solvents for spectral measurements were of spectral grade and chemicals were of reagent grade.

General Procedure for Synthesis of *IIIa* and *IVa* – *IVd*

Dialkyl sulfide (0.1 mol) in benzene (20 ml), and concentrated HCl (10 ml) were stepwise added to a well stirred aqueous 1 M solution of $7,8\text{-}C_2B_9H_{12}K$ (20 ml) (ref.[11]), placed in a reaction flask cooled externally in a 20 °C water bath. Then, 37% aqueous CH_2O (10 ml, 0.14 mol) was added dropwise within 10 min. The reaction was completed after 4 h of stirring. In the case of *IIIa* and *IIId*, the main products were sucked off, washed with benzene (3 × 10 ml) and water (3 × 10 ml). The two-layer filtrates were collected for chromatographical isolation of the *IVa*, *IVd* and *Vd* by-products, respectively. Insoluble main products were finally washed with three 10 ml portions of diethyl ether and dried on air. Such products were essentially pure. Optimal conditions for their recrystallization were: dissolution in acetone, filtration into excess toluene, evaporation of acetone in vacuo, and sucking of the purified product.

With compounds *IIIb* or *IIIc*, the reaction mixtures exhibit three layers. The lowest one was discarded, and both upper layers were transferred to a flask for evaporation of solvents and of excess dialkyl sulfide in vacuo at 40 °C (bath). The residue was dissolved in a small amount of methylene chloride and chromatographed on a column of silica gel (100 g). The products were eluted with methylene chloride. In the first fractions, species *IVb* or *IVc*, along with some $4,5\text{-}C_2B_7H_{13}$ were eluted. Eluates were concentrated and the residues were triturated with hexane (3 × 5 ml), and the pure species *IVb* or *IVc* were dried in vacuo. The main-product fractions were collected, solvents were stripped off and the residues were triturated with diethyl ether (20 ml) until they completely solidified, and the solid residues were dried in vacuo.

Isolations of *IVa*, *IVd* and *Vd* from the benzene layers after the separations of *IIIa* or *IIId* were done similarly, i.e. the concentrated upper layers were chromatographed on silica gel column (100 g), the products were eluted with benzene and isolated as in the case of the species *IVb* or *IVc*. The yields and properties of compounds *IIIa* – *IIId* and *IVa* – *IVd* are gathered in Tables I – III.

Synthesis of *Vf* – *Vh*

The procedure was the same as above, with dialkyl ethers replacing the dialkyl sulfides (noxious gases evolve due to the formation of 4,5-$C_2B_7H_{13}$). After 4 h of stirring, the layers were separated, solvents were removed using a rotatory evaporator at 30 °C (bath), and the residues were distributed between 10 ml of chloroform and 20 ml of water. The chloroform layers were chromatographed on silica gel columns with chloroform as eluent. The yields and properties of *Vf* – *Vh* are shown in Tables II and III. The compounds *IVa*, *Vf* and *Vg* have already been described in our earlier papers[5,12].

General Procedure for Syntheses of Compounds *IVa* – *IVd* and *Vd* – *Vh* with Acetaldehyde

Lewis base (dialkyl ether or dialkyl sulfide, 0.08 mol) in toluene (20 ml), and conc. HCl (10 ml) were successively added to a well stirred aqueous 1 M solution of 7,8-$C_2B_9H_{12}K$ (20 ml) (ref.[11]), placed in a reaction flask cooled externally in a 20 °C water bath. Within 5 min, 15 ml of 16% aqueous CH_3CHO (15 ml) was added. The orange upper layer turned red. After 4 h of stirring, upper layer was separated and, after addition of water (30 ml), volatile solvents were stripped off at ambient temperature with a rotatory vacuum evaporator. The resulting slurry was vigorously shaken with chloroform (20 ml). The chloroform extract was filtered through a short column of silica gel to remove red by-products, and the compounds *IVa* – *IVd* or *Vd* – *Vh* were eluted by chloroform. After monitoring the eluates by TLC, the chloroform was evaporated in vacuo, and the solid residues were washed with hexane (2 × 10 ml) and dried in vacuo.

Note: Species *Vh* is only sparingly soluble in chloroform. When the evaporation of solvents from the upper layer after the reaction was over, the residual slurry was shaken with diethyl ether (10 ml), the solid was sucked off and washed twice with the same amount of diethyl ether. Majority of the almost pure product *IVa* remained on the filter (despite of pinkish colour). From the filtrates, diethyl ether was stripped off in vacuo and the rest of the procedure was the same as above. By means of chromatography, an additional portion of *Vh* was obtained. The fractions containing the isomers *IVd* or *Vd* were chromatographed using toluene as eluent.

Reaction of 7,8-$C_2B_9H_{12}^{(-)}$ with Acetaldehyde

To a stirred 1 M aqueous solution of 7,8-$C_2B_9H_{12}K$ (20 ml), chloroform (20 ml) and 16% aqueous CH_3CHO (10 ml) were added. Stirring was continued for 4 h at 20 °C. The red chloroform layer was separated from the colourless water layer and, after a partial concentration in vacuo, the chloroform solution was filtered through a short column of silica gel to remove the colour and anionic species. With some additional chloroform, the uncharged product was eluted (R_F 0.25 in toluene). On evaporation of chloroform from the particular fractions, 0.93 g (22%) of *Vf* was obtained and identified by m.p., TLC and ^1H NMR spectrum. Water layer was extracted by diethyl ether (2 × 20 ml), the combined ether extracts were stripped off in vacuo, the residue was diluted with water (20 ml), filtered and precipitated with 20 ml of 1 M $(CH_3)_4NBr$ solution. The precipitate was dissolved by addition of 30% ethanol and heating to 80 °C. After standing overnight, colourless needles of the *VI*-$(CH_3)_4N^{(+)}$ salt separated, 2.21 g (47%): ^1H NMR (deuterioacetonitrile): 4.12 (B(10)-OH), 3.12 [$(CH_3)_4N^{(+)}$] and 1.59 (2 × C-H carborane). ^{11}B NMR in the same solvent: −11.67 (2, B(9,10)), −13.01 (1 s, B(10)), −16.79 (2, B(5,6)), −24.15 (2, B(2,4)), −25.52 (1, B(3)), −40.73 (1, B(1)).

Reduction of *IIIa* with $NaAlH_4$ to 9-CH_3-$C_2B_9H_{11}^{(-)}$ ion (*VIII*)

To a stirred solution of *IIIa* (1.50 g, 7.1 mmol) in tetrahydrofuran (15 ml), a solution of 1.7 g (3.2 mmol) of $NaAlH_4$ was added dropwise during 15 min. A vigorous gas evolution took place. No reduction was observed at ambient temperature during 1 h. On heating the solution to 60 °C for 2 h, a complete reduction has been achieved (TLC). Excessive $NaAlH_4$ has been decomposed by slow addition of dry ethyl acetate

(20 ml), followed by 10% HCl (40 ml). The upper layer was separated and the aqueous layer was extracted with ethyl acetate (20 ml). The combined upper layers were neutralized by 10% K_2CO_3 solution (20 ml), the separated upper layer was stripped off in vacuo; 20 ml of water was added to the residue, the last traces of volatile solvents were removed by short evacuation and the turbid solution was filtered. To the clear filtrate, K_2CO_3 (1.0 g), followed by dimethyl sulfate (1.0 ml) were added. After 15 min stirring, the solid was sucked off, washed with water (2 × 5 ml), ethanol (3 ml) and diethyl ether (2 × 3 ml), and the remaining solid was dried in vacuo, yielding 0.35 g (23%) of the starting species *IIIa*, TLC pure.

The aqueous solution after separation of the regenerate was precipitated by 1 ml of 1 M $(CH_3)_4NCl$, the precipitate was dissolved by heating the solution to 80 °C, and by adding 30% ethanol. After cooling overnight, snow-white needles (0.84 g, 70%) of the tetramethylammonium salt of *VIII* separated. The compound was characterized by ^1H and 2D ^{11}B NMR spectra (vide infra).

Formation of $9\text{-}CH_3\text{-}11\text{-}C_5H_5N\text{-}7,8\text{-}C_2B_9H_{10}$ (*IX*) from *IIIa* and Pyridine

The solution of *IIIa* (1.3 g, 0.0062 mol) in tetrahydrofuran (10 ml) and pyridine (5 ml) was heated for 6 h to 65 °C. The solvents were evaporated in vacuo, the residue was shaken with toluene (30 ml) and 10% hydrochloric acid (30 ml). The upper layer was separated, concentrated to 15 ml in vacuo, and chromatographed on silica gel column with toluene as eluent. The yellow band of the species *VIII* was collected, toluene was stripped off in vacuo, the oily residue was triturated with hexane (5 ml) and, after solidification, the hexane supernatant was discarded. The solid was dissolved in chloroform (10 ml), and the solution was overlayered with 20 ml of hexane. After standing overnight, thin leaflets of *IX* (0.66 g, 47%) separated showing a characteristic yellowish green fluorescence.

M.p. 138 °C, R_F (toluene) 0.15. Mass spectrum (*m/z*) 227. ^1H NMR spectrum: 8.50 (center of the pyridine multiplet – 5 H), 2.97 and 2.02 respectively (2 × C–H carborane), 0.23 (CH_3–B) and –2.57 (one B–H–B bridge); ^{11}B NMR spectrum δ (int., *J*(BH)): 2.38 (1, singlet), –6.58 (1, 119), –6.58 (1, singlet), –14.84 (1, 151), –19.22 (1, 162), –25.21 (2, 146), –29.97 (1, 137), and –37.54 (1, 142).

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REFERENCES

1. Plešek J., Štíbr B., Heřmánek S.: Chem. Ind. (London) *1980*, 626.
2. Štíbr B., Plešek J., Heřmánek S.: Inorg. Synth. *22*, 237 (1983).
3. Heřmánek S., Jelínek T., Plešek J., Štíbr B., Fusek J.: Collect. Czech. Chem. Commun. *53*, 2742 (1988).
4. Young D. C., Howe D. V., Hawthorne M. F.: J. Am. Chem. Soc. *91*, 859 (1969).
5. Janoušek Z., Heřmánek S., Plešek J., Štíbr B.: Collect. Czech. Chem. Commun. *39*, 2363 (1974).
6. Červinka O. (Ed.): *Chemie organických sloučenin*, Vol. I, pp. 760, 777, 796. SNTL, Praha 1985.
7. Stahl I., Metschenko M., Gosselck J.: Tetrahedron Lett. *1971*, 4077.
8. Heydt H., Vilsmeyer E.: *Houben Weyl* E 11/Vol. 1, p. 430. Thieme, Stuttgart 1985.
9. Heřmánek S., Plešek J., Gregor V., Štíbr B.: J. Chem. Soc., Chem. Commun. *1977*, 561.
10. Heřmánek S., Jelínek T., Plešek J., Štíbr B., Fusek J., Mareš F.: *Boron Chemistry*, p. 46. World Scientific, Singapore 1987.
11. Plešek J., Heřmánek S., Štíbr B.: Inorg. Synth. *22*, 231 (1983).
12. Plešek J., Janoušek Z., Heřmánek S.: Collect. Czech. Chem. Commun. *43*, 2862 (1978).

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