THE SYNTHESIS AND STRUCTURE
OF THE HETEROBORANES $6,8\text{-}S_2B_7H_9$ AND $6,8\text{-}CSB_7H_{11}$

J.PLEŠEK, S.HEŘMÁNEK and Z.JANOUŠEK

Institute of Inorganic Chemistry,
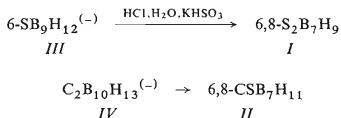*Czechoslovak Academy of Sciences, 250 68 Prague - Řež*

The $SB_9H_{12}^{(-)}$ anion reacts in acid medium with $KHSO_3$ to give dithiaborane, $6,8\text{-}S_2B_7H_9$. Under similar conditions the reactive isomer $C_2B_{10}H_{13}^{(-)}$ is degraded to give $6,8\text{-}CSB_7H_{11}$. The structures of the two new compounds are proposed on the basis of ^1H and ^{11}B NMR spectra and topological rules. The possibility of the presence of one or two lone electron pairs on the sulphur atom is discussed. On the basis of the ^{11}B NMR isospectrality with the C-analogues, the presence of two lone electron pairs on the heteroatom of the *arachno* compounds and of one pair on *nido*-boranes seems most likely.

Recently, Stanko and coworkers described the reaction of the $7,8\text{-}C_2B_9H_{12}^{(-)}$ anion with potassium hydrogen sulphite, in which 7,8-dicarba-10-thia-*nido*-undecaborane (10) is produced[1]. The reaction conditions are not specified in the short communication. In an attempt to reproduce this degradative insertion[2], we found that the reaction is very sensitive to the acidity of the medium. It does not occur at all in hydrochloric acid medium and the initial anion remains unchanged.

On the other hand, these "unfavourable conditions" proved to be particularly suitable for the degradative insertion of a sulphur atom into other anions. This finding led to the synthesis of two interesting nine-vertex heteroboranes, 6,8-dithia-*nido*-nonaborane(9) (*I*) and 6-carba-8-thia-*nido*-nonaborane(11) (*II*) according to the scheme:

$$6\text{-}SB_9H_{12}^{(-)} \xrightarrow{\text{HCl, H}_2\text{O, KHSO}_3} 6,8\text{-}S_2B_7H_9$$
$$\qquad III \qquad\qquad\qquad\qquad\qquad\quad I$$

$$C_2B_{10}H_{13}^{(-)} \rightarrow 6,8\text{-}CSB_7H_{11}$$
$$\quad IV \qquad\qquad\qquad II$$

The anion *III* is easily accessible[3]; anion *IV* was described by Hawthorne and coworkers[4] as the so called "reactive isomer" whose exact constitution is unknown. On the basis of the ^{11}B-NMR spectra and some reactions, these authors first suggested the structure $(13)\text{-}7,8\text{-}C_2B_{10}H_{13}^{(-)}$ in which the carbon atoms remain neigh-

bouring; they, however, soon reinterpreted the structure as $(13)\text{-}9,11\text{-}C_2B_{10}H_{13}^{(-)}$ in which the two carbon atoms also lie on the edge of the *nido*-skeleton but are separated by one B atom[4]. The results of the degradative insertion described here strongly support the alternative with separated carbon atoms, as in all known cases the C—C bond was very resistent to hydrolytic splitting.

Compounds *I* and *II* are crystalline substances with very low dipole moments. They sublime easily and are soluble in all organic solvents including paraffinic hydrocarbons. They have long elution paths in TLC even when hexane is used for the elution. Some of their properties are given in Table I.

The general formulae of compounds *I* and *II* were found by high resolution mass spectrometry. Their constitution followed from topological rules derived for hetero-boranes and from interpretation of ^{1}H and ^{11}B-NMR spectra. All known nine-vertex *nido*-heteroboranes have skeletons arranged as depicted in Fig. 1. The Williams rule[5] predicts that sulphur and carbon atoms will preferentially occupy positions with the lowest possible coordination with respect to the surrounding atoms, *i.e.* positions 4, 6 and 8. After occupation by the two heteroatoms, only one position remains, which is occupied by a boron atom bearing both hydrogen bridges, as this arrangement is most stable (decaborane-like).

TABLE I

Some Characteristics of 6,8-$S_2B_7H_9$ (*I*), 6,8-CSB_7H_{11} (*II*) and 6,8-$C_2B_7H_{13}$ (*V*) Heteroboranes

Characteristic	*I*	*II*	*V*
M/e found	150·0797	132·1234	114
(calc.)	(150·0795)	(132·1234)	(114)
M.p., °C	103—104	108—110	61
R_F (relat.[a])	201	100	11
λ/nm (ε)[b]	233	240	245
	(3 430)	(3 660)	(3 806)
^{1}H-NMR δ[c] [intens.]			
C—H (equator.)	—	−0·47[d] [1]	−0·27[d] [2]
C—H (axial)	—	−1·25 [1]	−1·67 [2]
B—H—B bridge	−1·1[e] [2]	c. −1·2 [1]	−2·62 [2]
		−3·0 [1]	

[a] TLC on Silufol, eluted by hexane; 5,6-$C_2B_8H_{12}$ R_F 0·27 (100%); [b] measured in CH_2Cl_2; [c] relative to tetramethylsilane; [d] in C_6D_6; [e] in $CDCl_3$.

The constitution derived in this way agrees very well with the results of ^{1}H NMR spectroscopy (Table I). The presence of two equivalent hydrogen bridges was demonstrated for compound *I*, which has one plane of symmetry. This fact practically decides the constitution as two equivalent hydrogen bridges would not fit into a different position than that corresponding to the proposed structure. In compound *II*, which has no symmetry element, two different hydrogen bridges were found and the presence of a CH₂ group was demonstrated. The ^{11}B-NMR spectra (Fig. 2a, b) also agree with the proposed structure of the two compounds. The signal in the highest field corresponds to the B₍₁₎ atom in both cases, as only this atom is bound to B-atoms connected by hydrogen bridges[6]. The doublet of intensity 1, with indications of an additional triplet splitting of both shoulders at 37·3 ppm for *I* and 33·3 ppm for *II*, produced by simultaneous interaction with two hydrogen bridges can be unambiguously attributed to atom B₍₄₎. The doublet with the lowest band half-width (at 4·0 ppm for *I* and 0·7 ppm for *II*) can be attributed to atom B₍₇₎, which has a low field symmetry gradient around the B-H axis (compare ref.[7]), bears no hydrogen bridge, is next to only two B-atoms and consequently is relatively little broadened by ^{11}B–^{11}B (or ^{10}B–^{11}B) interaction.* Attribution of the remaining signals with an
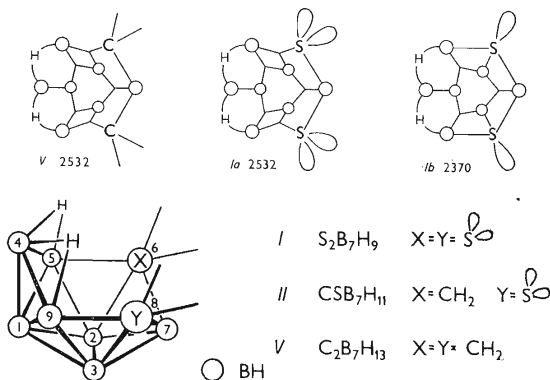

FIG. 1
Skeleton and Numbering of 6,8-X,YB₇ Nine-Vertex Heteroboranes

---

* Similarly narrow signals are shown generally by B-atoms located between two hetero-atoms on the 'edge of a molecule. This finding can be used in interpretation of similar ^{11}B signals, *e.g.* for 7,9-C₂B₉H₁₂⁽⁻⁾ (at 6·2 ppm[7], B₍₈₎); 7,8,10-C₂NB₈H₁₀ (14·6 ppm², B₍₉,₁₁₎); 6,8(CH₃)₂-6,8-C₂B₇H₁₁ (−7·7 ppm⁸, B₍₇₎), *etc.*

overall intensity of $4(-3\cdot2[2]$ and $22\cdot7[2]$ ppm I; $-1\cdot2[2]$, $15\cdot2[1]$ and $26\cdot9[1]$ for II) is difficult as $^1H_{bridge}-^{11}B$ interaction is not sufficiently apparent with any of them.

The ^{11}B NMR spectra of substances I and II are similar to the spectrum of carborane $6,8$-$C_2B_7H_{13}$ (V, Fig. 2c) whose constitution is known with certainty[8], but the individual signals in this spectrum have not been assigned. In V, the high field doublet (at $52\cdot0$ ppm) can also be assigned to atom $B_{(1)}$ and the doublet with the indication of additional triplet splitting (at $27\cdot4$ ppm) can be assigned to atom $B_{(4)}$. The third doublet of intensity 1, *i.e.* corresponding to atom $B_{(7)}$, is overlapped by a doublet of intensity 2 at $-0\cdot8$ ppm.
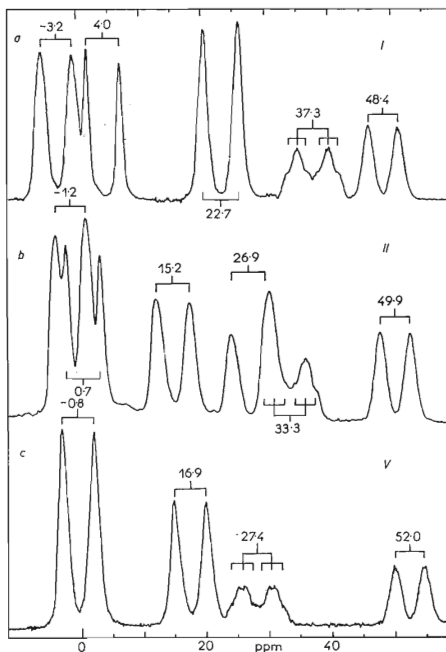

Fig. 2

$32\cdot1$ MHz ^{11}B NMR Spectra a $6,8$-$S_2B_7H_9$ (I), b $6,8$-CSB_7H_{11} (II), c $6,8$-$C_2B_7H_{13}$ (V)

Substances I, II and V form a group of structurally very similar *nido*-compounds with nine skeletal atoms. The existence of compounds I and II pointed out a serious problem in the structural theory of heteroboranes, in which the heteroatom can exhibit dual behaviour bearing either one or two lone electron pairs[9]. Such an electron pair can be considered as completely equivalent to other ligands, *e.g.* to a terminal Y-H group or its equivalent Y-R, Y-Hlg groups, *etc.* While the number of classic ligands on a particular heteroatom can be determined directly, this is not yet possible for the lone electron pairs. This fact has serious consequences for all structural considerations for compounds containing heteroatoms with dual behaviour. The problem can be explained most easily using compound I. A sulphur atom with one lone electron pair contributes four electrons and three orbitals to the skeleton and is formally equivalent to a $\ddot{\,}BH^{2-}$ or $\ddot{\,}CH^-$ group. A sulphur atom with two lone electron pairs, however, contributes only two electrons and two orbitals and is consequently equivalent to a $:BH_2^-$ or $:CH_2$ group. In the first alternative, compound I would have a topological formula of the type 2370 (Ib) and would be isoelectronic with the $B_9H_{11}^{4-}$ anion. In the second alternative it would have topological formula 2532 (Ia) and would be isoelectronic with anion $B_9H_{13}^{2-}$. As long as the conditions under which one or the other alternative predominates are unknown, the probable topological formula of heteroboranes, whose heteroatoms can exhibit dual behaviour, *i.e.* $\overline{Y}$ or $\overline{\overline{Y}}$ ($Y = O, S, etc.$), $\overline{Y}$—H or Y—H ($Y = N, P, etc.$), cannot be determined.

Knowledge of the topological formula is of key importance for calculation or estimation of the electron density distribution in the molecule, for determining the dipole moment and its direction, for the interpretation of NMR spectra[10] and for understanding the behaviour and reactivity of the given substance. Determination of the electron density in the neighbourhood of the heteroatom by the ESCA method or mathematical methods, based on knowledge of the exact positions of the individual atoms in the molecular framework, should provide information on which alternative is more important. Comparison of the ^{11}B NMR spectra with those of structurally similar carboranes and heteroboranes with dual atoms can indirectly support one of the alternatives. We found that the chemical shifts of the [11]B signals are affected by the character and positions of bonds in the neighbourhood of the atom studied[10]. This finding led to the hypothesis that compounds which are isostructural, isoelectronic and isobonded are also ^{11}B NMR isospectral. The similarity of the spectrum character for compounds I and II with that for compound V (Fig. 2) indicates that these apparently different substances are actually similar as far as electron distribution in the skeleton is concerned. As the presence of two CH_2 groups in 6,8-$-C_2B_7H_{13}$ carborane (Va) has been demonstrated with certainty[4], *i.e.* topology 2532, the same topology (represented by formula Ia) is suggested for both sulphur derivatives; this structure has two lone electron pairs on the S atom. This topology seems more lifely than topology 2370 (Ib), and the S atom also has more favourable electron density distribution than the alternative with one electron pair on the S atom.

On the basis of similar comparisons, the arrangement with two exohedral ligands on the dual heteroatom ($\underline{Y}$ or $\overline{Y}$—H) is also favoured for heteroboranes $NB_8H_{13}{}^{11}$, $SB_9H_{12}^{-}$ (ref.[3]) and generally substances with skeletal oxidation degree $2n + 6$ (*i.e. arachno*-compounds). On the other hand, the structure with one exohedral ligand on the dual atom ($\underline{Y}$ or $\overline{Y}$—H) is preferred for compounds $SB_9H_{11}{}^3$, $SB_{10}H_{12}{}^3$, $C_2NB_8H_{11}{}^2$, $C_2SB_8H_{10}{}^1$, *i.e.* in general compounds with skeletal oxidation degree $2n + 4$ (*i.e.* the *nido*-series). This problem has already been solved[9] for *closo*-compounds with skeletal oxidation degree $2n + 2$ where the arrangement with one exohedral ligand on the heteroatom ($\underline{Y}$ or $\overline{Y}$—H) is regarded as the only possibility. Details concerning the facts mentioned in this paragraph will be published later.

EXPERIMENTAL

The known anions $C_2B_{10}H_{13}^{(-)}$ (ref.[4]) and $SB_9H_{12}^{(-)}$ (ref.[3]) were prepared by modified procedures which proved to be preferable to those originally described. Reference compound *V* was prepared according to the literature[8]. High resolution mass spectrometry was carried out on an AEI MS 902 instrument, UV spectra were measured on a Beckman DK1 instrument and ^1H (100 MHz) and ^{11}B (32 MHz) NMR spectra were recorded on a Varian XL 100 instrument. TLC was carried out on Silufol (Kavalier, Votice, Czechoslovakia). Melting points were measured in sealed capillaries, and are not corrected.

Preparation of the $C_2SB_8H_{10}$ Compound

An amount of 22·9 g (0·1 mol) of $K_2S_2O_5$ was added to 100 ml of a 1M aqueous solution of 7,8-$C_2B_9H_{12}^{(-)}K^+$ and the mixture was heated on a water bath at 100°C. The yellow solution gradually faded and became cloudy with precipitated product, most of which sublimed into the condenser. After 2 h the product (including the part in the condenser) was extracted into 2 × 30 ml hexane, the aqueous layer was freed of traces of hexane *in vacuo* and a further 22·9 g of $K_2S_2O_5$ were added; the whole operation was repeated twice. After the third operation, the aqueous layer was extracted with 50 ml of ether, the ether phase was separated and the ether evaporated *in vacuo*; the residue was diluted to 100 ml with water and the remaining traces of ether were distilled off *in vacuo*. The remaining solution was then heated to 100°C for 2 hours with a further 22·9 g of $K_2S_2O_5$. The product was extracted with hexane. The combined hexane extracts were rinsed with water, the hexane was evaporated *in vacuo* at room temperature and the residue was sublimed at 50°C (bath) and 1·3 Pa (0·01 Torr). The product is white, camphor-like smelling substance weighing 6·7 g (41·1% yield), m.p. 235—237°C (the literature[1] gives 238—239°C). In hexane R_F 0·52; R_F relat. 191 (R_F for 5,6-$C_2B_8H_{12}$ is 100), The spot is developed with I_2 vapours but does not reduce either Ag^+ or $KMnO_4$. For $^{12}C_2{}^{32}S^{11}B_8{}^1H_{10}$ the value $M/e = 174$ was found. Under the conditions given below for preparation of substances *I* and *II* practically no trace of the above compound was produced from 7,8-$C_2B_9H_{12}^{(-)}$ anions and the initial anion was regenerated as the tetramethylammonium salt with a yield of 93·4%.

Preparation of $S_2B_7H_9$ (I)

An amount of 10 g of sulphur was dissolved in a solution of 15 g KOH in 50 ml water by heating in boiling water for 15 minutes; the orange polysulphide solution was diluted with water to 100 ml and 12·4 g (0·1 mol) of decaborane was gradually added to the solution with stirring at a temperature of 30—60°C. A considerable amount of gas was produced in the reaction and the mixture was heated spontaneously. The reaction ceased in about 1 h when the decaborane dissolved. The raw anion was extracted with 3×50 ml ether, the ether extract was evaporated *in vacuo*, the oily residue was diluted to 100 ml with water, part of the water was distilled off *in vacuo* and the residue was again diluted to 100 ml with water, filtered through activated charcoal and was stored as a 1M solution of the potassium salt of the $SB_9H_{12}^{(-)}$ anion. The yield was practically quantitative (the original procedure[3] employed ammonium polysulphide and the anion was isolated as the Cs salt).

An amount of 50 ml of a 1M-$SB_9H_{12}^{(-)}$ K^+ solution was added to a suspension of 45 g of $K_2S_2O_5$ (0·2 mol) in 50 ml water, the mixture was cooled to $-10°C$ and acidified with 40 ml of 5M-HCl over 5 min with stirring. The temporary orange-brown colour changed gradually to yellow and the product precipitated. The mixture was stirred at $-10°C$ for 1 h between $-10°$ and $+5°C$ for 1 h and at 20°C for 3 h; it was then left to stand overnight. Product *I* was extracted with three 50-ml portions of hexane, the yellow side-products were removed from the combined hexane extracts by washing with 50 ml of 5% aqueous K_2CO_3 and the almost colourless hexane layer was separated. The hexane was evaporated *in vacuo* at room temperature and the residue was sublimed at 50°C (bath) and 1·3 Pa (0·01 Torr). The product was a yellowish crystalline substance with a camphor-like smell, 3·1 (41·9%, calculated with respect to the original decaborane). Its properties are given in Table I.

Preparation of CSB_7H_{11} (II)

An amount of 5·0 g of sodium was added in twenty portions to a suspension of 14·4 g (0·1 mol) of *ortho*-carborane in 300 ml of liquid ammonia. The last addition produced a permanent colouration. Then 7·0 g of dry ammonium chloride were added in ten portions. The solution was left to evaporate overnight through a KOH valve. The residue was dried for 1 h *in vacuo* (water-pump), was dissolved in 100 ml water, the solution was digested for 1 h under the same vacuum, an additional 5·0 g of ammonium chloride was added and the solution was diluted to 200 ml with water. This solution is not stable and gas bubbles are gradually evolved. The actual content of anion *IV* was about 37% (referred to *ortho*-carborane). The tetramethylammonium salt was isolated from an aliquot portion and was compared with a sample prepared according to the original procedure[4] and both substances were identified using TLC and ^{11}B-NMR spectroscopy.

To 100 ml of the above solution 22·9 g $K_2S_2O_5$ were added and the mixture was cooled to $-10°C$ with stirring; 40 ml of 5M-HCl were added to the resulting suspension over 20 minutes with cooling. The further procedure was the same as in the previous experiment except that washing of the hexane extracts with an aqueous K_2CO_3 solution was omitted. The hexane was evaporated *in vacuo* at room temperature and product *II* was sublimed at 50°C (bath) and 1·3 Pa (0·01 Torr); a 1·2 g amount was obtained (18·3%, based on $1,2-C_2B_{10}H_{12}$ consumed). Its properties are given in Table I.

The same product was obtained with a yield of 43·2% from the tetramethylammonium salt, prepared according to the literature[4], which was identical with the salt obtainable from the previous solution. The reaction procedure was the same as described above except that, instead of 100 ml of raw anion solution, a suspension of 4·6 g of the tetramethylammonium salt in 100 ml water was employed.

REFERENCES

1. Brattsev V. A., Knyazev J. P., Danilova G. N., Stanko V. I.: Zh. Obshch. Khim. *45*, 1393 (1975).
2. Plešek J., Štíbr B., Heřmánek S.: Chem. Ind. (London) *1974*, 662.
3. Hertler W. R., Klanberg F., Muetterties E. L.: Inorg. Chem. *6*, 1696 (1967).
4. Dunks G. B., Wiersema R. J., Hawthorne M. F.: Chem. Commun. *1972*, 899; J. Amer. Chem. Soc. *95*, 3174 (1973).
5. Williams R. E.: Inorg. Chem. *10*, 210 (1971).
6. Heřmánek S., Plešek J.: Z. Anorg. Allg. Chem. *409*, 115 (1974).
7. Todd L. J., Siedle A. R., Sato F., Garber A. R., Scholer F. R., Mercer G. D.: Inorg. Chem. *14*, 1249 (1975).
8. Tebbe F. N., Garret P. M., Hawthorne M. F.: J. Amer. Chem. Soc. *90*, 869 (1968).
9. Rudolph R. W., Pretzer W. R.: Inorg. Chem. *11*, 1974 (1972).
10. Heřmánek S., Plešek J., Štíbr B.: III. International Meeting on Boron Chemistry, July 5—9, 1976, Munich, Abstr. No 52.
11. Baše K., Plešek J., Heřmánek S., Huffman J., Ragatz P., Schaeffer R.: Chem. Commun. *1975*, 934.