

**ELECTRONIC STRUCTURE AND ^{11}B -NMR SPECTRA
OF NINE-VERTEX HETEROBORANES:
4- CB_8H_{14} , 4- NB_8H_{13} , 4- SB_8H_{12} AND 4,6- $\text{C}_2\text{B}_7\text{H}_{13}$**

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^{11}B -NMR Spectra of 4- CB_8H_{14} , 4- NB_8H_{13} , 4- SB_8H_{12} and 4,6- $\text{C}_2\text{B}_7\text{H}_{13}$ are presented, together with a detailed assignment of individual signals. Correlations of ^{11}B -NMR chemical shifts with some STO-3G and CNDO/2 density matrix properties are evaluated. Similarities in the electronic structure and the nature of heteroatom bonding are discussed.

Boranes and carbaboranes have attracted the attention of both experimental and theoretical chemists for a relatively long time¹. Recent syntheses and ^{11}B -NMR spectra²⁻⁴ as well as X-ray structure determination^{3,5} have enabled us to study a series of structurally analogous nine-vertex monoheteroboranes. These belong to the same class as the dicarbaborane, 4,6- $\text{C}_2\text{B}_7\text{H}_{13}$. This study seems to be the first published quantum-chemical investigation of aza- and thia-boranes (see Note).

It is well established that, similarly to the substitution of hydrogen⁶⁻⁸, the presence of a heteroatom in a boron skeleton causes distinct ^{11}B -NMR chemical shifts of the boron atom placed in an antipodal position to the substituted boron or a heteroatom^{6,7,9-11}. In view of our long-term research program on the correlation of ^{11}B -NMR spectra with molecular and electronic structure, in addition to some relatively good results from other authors in interpreting ^{11}B -NMR chemical shifts on the basis of density matrix changes^{12,13}, we have started a systematic study of correlations between chemical shifts and density matrix properties.

^{11}B - and ^1H -NMR Results

The structure of 4- NB_8H_{13} (II) was unambiguously determined by the X-ray structural analysis^{3,5}. The ^1H -NMR spectrum of this compound is in full agreement with the solid state structure showing two types of H-bridges of intensity two each at $\delta -1.18$ and -2.94 ppm, the (N)H signal at 1.38 ppm, and an integral intensity of eight further protons in the molecule. The symmetrical structure of 4- NB_8H_{13} follows also

from the ^{11}B -NMR spectrum³ (Fig. 1*b*) which is composed of 5 signals of relative intensities 1 : 2 : 1 : 2 : 2 centered at 7.8, -7.1, -25.4, -46.0 and -47.7 ppm (signals in the lower magnetic field from $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ are taken for positive ones) The line-narrowed spectrum (Fig. 2) revealed a splitting of the signal at -47.7 ppm to give a distinct doublet of triplets with J_{BH_a} 150 Hz and J_{BH_b} 54 Hz, which has allowed us to assign this signal to the B(6,8) atoms. A fair implication of splitting to a triplet has also been observed in both arms of the doublet centered at 7.8 ppm. The fact that this weak coupling is evoked by an interaction with two H-atoms was confirmed by the ^1H decoupled ^{11}B spectrum, in which the ^{11}B signal at 7.8 ppm has shown perceptible narrowing in contrast to the second signal of intensity 1, (centered at -25.4 ppm) the width of which did not change. A distinct narrowing has also been observed with the signal of intensity 2, centered at -7.1 which belongs therefore to the B(5,9) atoms. Following the above elimination, the remaining signal

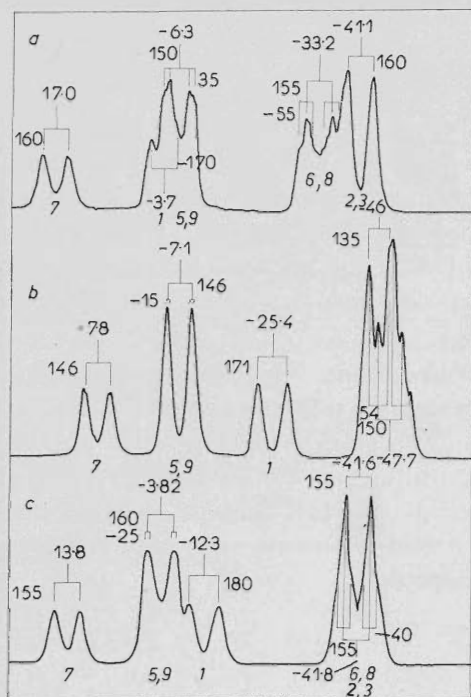


FIG. 1

32.1 MHz ^{11}B -NMR spectra in benzene. *a* 4- CB_8H_{14} (I), *b* 4- NB_8H_{13} (II), *c* 4- SB_8H_{12} (III)

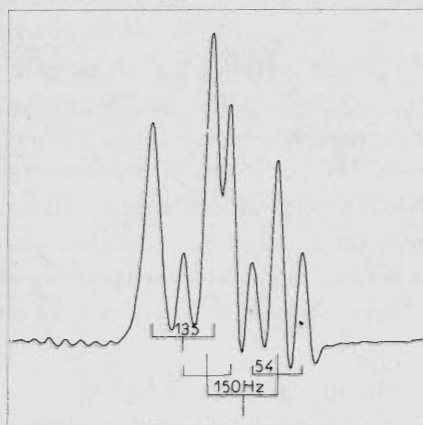


FIG. 2

70.6 MHz line-narrowed ^{11}B -NMR spectrum (neat, region 40 to 50 ppm) of 4- NB_8H_{13} (II)

of intensity 1 at -25.4 ppm corresponds to the B(1) atom and that of intensity 2 at -46.0 ppm fits with the B(2,3) atoms. The assignment of the last signal is also in agreement with the empirical rule which says that the signal of an atom which is opposite to the hydrogen bridge lies in the high field region of the given ^{11}B -NMR spectrum¹⁴.

The structure of $4\text{-CB}_8\text{H}_{14}$ (I) was deduced from the ^1H - and ^{11}B -NMR spectra². When comparing these spectra with those of $4\text{-NB}_8\text{H}_{13}$ we can contemplate similar features with almost all signals what permits us to include both compounds into the same structural class of the $4\text{-XB}_8\text{H}_{12}$ compounds ($\text{X} = \text{CH}_2$, NH , S). The ^1H -NMR spectrum in C_6D_6 exhibits, besides eight B—H_t proton signals (deduced from integral intensities), four outstanding singlets of intensity two each belonging to the C—H_{equat.} ($\delta = 0.10$ ppm), C—H_{axial} (-1.75 ppm) and two hydrogen bridges (-0.45 and -3.52 ppm). The ^{11}B -NMR spectrum of $4\text{-CB}_8\text{H}_{14}$ (Fig. 1a) has shown the same characteristics of particular signals as observed with $4\text{-NB}_8\text{H}_{13}$ (Fig. 1b). The presence of CH_2 instead of NH in position 4 has not invalidated the general character of the $4\text{-XB}_8\text{H}_{12}$ ^{11}B -NMR spectrum. It has only brought some changes in the chemical shifts of the B(7), B(1) and B(6,8) signals which all are shifted to the lower field (in comparison with II), and in the magnitude of the B—H_t interaction which is, for example, more evident with B(5,9) at I than at II. The as-

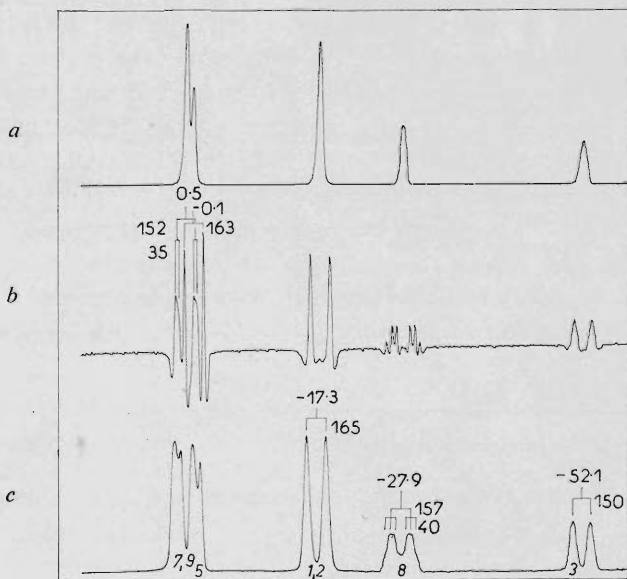


FIG. 3

64.2 MHz ^{11}B -NMR spectra of $4,6\text{-C}_2\text{B}_7\text{H}_{13}$ (IV) in cyclohexane. a ^1H -decoupled, b line-narrowed undecoupled, c undecoupled

signment of particular signals with *I* has been performed analogously as with *II* (Fig. 1b).

A special story is the structure of 4-SB₈H₁₂ (*III*) which was not long ago described¹⁵ as 4-SB₈H₁₀ on the ground of the mass and ¹¹B-NMR spectra. The interpretation of the ¹¹B-NMR spectrum was immediately criticized from the standpoint of ¹¹B-NMR empirical rules^{16,14} which rather supported the 4-SB₈H₁₂ structure with two more H atoms. This structure has been now confirmed by the ¹H-NMR spectrum which has shown two different hydrogen bridges of intensity two each at δ -1.35 and -2.40 ppm (C₆D₆) and an integrated intensity of eight B—H_i signals⁴. The ¹¹B-NMR spectrum exhibits the same features as those of *I* and *II*, which documents the relevance of *III* to the 4-XB₈H₁₂ class. The character of the ¹¹B-NMR spectrum of *III* and the assignment of all of the observed signals is shown in Fig. 1c.

Further compounds belonging to the B₉H₁₄⁻ class are the 4,6-C₂B₇H₁₃ and 4,6(CH₃)₂-4,6-C₂B₇H₁₁ carboranes; the structure of the second one was determined by X-ray analysis²⁰. Of these compounds, only the dimethyl derivative was characterized by the ¹¹B-NMR spectrum³⁴ but the signals have not yet been assigned. The ¹¹B-NMR spectrum of 4,6-C₂B₇H₁₃ is shown in Fig. 3 which documents the presence of five signals of relative intensities 2 : 1 : 2 : 1 : 1 to increasing magnetic field. The doublet at -27.9 ppm is split into a triplet by two hydrogen bridges (and each branch to a quartet by ¹¹B—¹¹B coupling) as emerged from the ¹¹B-NMR spectrum²⁸ at 32.1 MHz and belongs therefore to the B(8) atom. The highest field doublet, at -52.1 ppm, may be assigned to the B(3) atom which is opposite to the H-bridges¹⁴. The last signal of intensity one, at -0.1 ppm, is due to the B(5) atom, which is supported by the fact that this signal is distinctly sharp. This is a characteristic feature of signals of B-atoms located between two C-atoms in the open mouth of a *nido*-molecule²⁸. A detailed inspection of the undecoupled line-narrowed and ¹H-decoupled spectra in Fig. 3a,b reveals that the signal at 0.5 ppm is a doublet of doublets with H-bridge coupling of about 35 Hz, which allows us to attribute it to the B(7,9) atoms, and the last doublet of intensity 2 at -17.3 ppm, explicitly, to the B(1,2) atoms.

Methods of Calculation and Results

In order to compromise both demands of accuracy and reasonable cost we have chosen minimum basis set STO-3G *ab initio*^{17,18} and standard CNDO/2 semi-empirical calculations.

The molecular geometry for NB₈H₁₃ has been obtained from an X-ray diffraction study^{3,5} and symmetrized to the C_s symmetry (available on request). The structural parameters of CB₈H₁₄ and SB₈H₁₂ are not yet known. These structures are analogous to NB₈H₁₃ as shown by the ¹¹B-NMR investigation (see preceding paragraph).

We have adopted the following models for the CB_8H_{14} and SB_8H_{12} molecules. The B—S bond lengths have been set equal to 0.189 nm, using the average B—S distance found in the X-ray structure of the dodecahydro-6-thia-*nido*-decaborate(1-) anion¹⁹. The B—C bond lengths of 0.169 nm have been inferred from an X-ray diffraction study of $\text{C}_2\text{B}_7\text{H}_{11}(\text{CH}_3)_2$ (ref.²⁰), the C—H distance of 0.11 nm and dihedral angles of the CH_2 group were set the same as in $\text{C}_2\text{B}_7\text{H}_{13}$ (ref.²⁰). The geometry of the rest of the boron skeleton of both SB_8H_{12} and CB_8H_{14} has been taken to be the same as in 4- NB_8H_{13} . The geometry of $\text{C}_2\text{B}_7\text{H}_{13}$ has been taken from ref.²⁰.

STO-3G total energies, the frontier orbital eigenvalues and the calculated dipole moments are presented in Table I. Table II summarizes the calculated static reactivity indices and Tables III and IV give the STO-3G overlap populations and CNDO/2 Wiberg indices. In order to give a better sterical image, the STO-3G atomic charges and overlap populations are presented in Figs 4–7.

DISCUSSION

There are very few experimental data published on the reactivity of the heteroboranes under study and therefore our results are mainly of predictive value.

The negative of the HOMO eigenvalue corresponds to the first ionization potential, according to the Koopmans' theorem. The calculated static reactivity indices have been commonly used for predicting reactivity sites for nucleophilic and electrophilic attacks. Besides the STO-3G Mulliken atomic charges and CNDO/2 charges, it has been proposed²¹ to use *ab initio* inner shell eigenvalues (*ISE*) as a measure of the charge distribution on atoms. Differences in inner shell orbital energies for like atoms directly reflect differences in the valence charge distribution — the higher the 1s orbital energy the more negative the environment about its corresponding nucleus. Electrophilic attack should occur at negatively charged centres (lowest absolute value of *ISE*) while nucleophilic attack should occur at positive centres (highest absolute value of *ISE*). Needless to say this is valid only if the reaction

TABLE I
STO-3G Total energy, frontier orbital eigenvalues (all in eV) and dipole moments (Cm)

Compound	Total energy	HOMO	LUMO	Dipole moment
CB_8H_{14}	— 6 540.49	—8.53	5.83	$1.39 \cdot 10^{-29}$
NB_8H_{13}	— 6 971.09	—8.92	6.85	$1.28 \cdot 10^{-29}$
SB_8H_{12}	—16 192.05	—8.87	5.95	$1.24 \cdot 10^{-29}$
$\text{C}_2\text{B}_7\text{H}_{13}$	— 6 882.10	—8.50	5.09	—

TABLE II
Static reactivity indices, valences and coordination numbers

Compound	Atom, position	Atomic charge ^a		Group charge ^b		ISE ^c STO-3G	Valence ^d CNDO/2	Coordination number ^e
		STO-3G	CNDO/2	STO-3G	CNDO/2			
4-CB ₈ H ₁₄	C4	-0.32	-0.07	-0.07	-0.03		3.90	5 (3 + 2)
	B1	+0.11	+0.07	+0.09	+0.00	-202.67	3.63	6 (5 + 1)
	B2,3	-0.07	-0.05	-0.10	-0.12	-200.93	3.71	6 (5 + 1)
	B5,9	+0.14	+0.10	+0.11	+0.01	-203.30	3.63	6 (4 + 2)
	B6,8	-0.10	-0.11	-0.10	-0.16	-202.20	3.73	6 (3 + 3)
	B7	+0.15	+0.17	+0.15	+0.09	-204.13	3.58	7 (4 + 3)
	N4	-0.56	-0.13	-0.26	+0.01		3.41	4 (3 + 1)
4-NB ₈ H ₁₃	B1	+0.13	+0.08	+0.10	+0.01	-202.57	3.62	6 (5 + 1)
	B2,3	-0.07	-0.05	-0.11	-0.12	-200.83	3.71	6 (5 + 1)
	B5,9	+0.23	+0.15	+0.21	+0.05	-203.84	3.60	6 (4 + 2)
	B6,8	-0.11	-0.12	-0.12	-0.17	-201.95	3.74	6 (3 + 3)
	B7	+0.15	+0.17	+0.14	+0.09	-203.99	3.58	7 (4 + 3)
	S4	+0.20	-0.02 (-0.06)				2.12 (2.74)	3 (3 + 0)
	B1	-0.02	+0.05 (+0.05)	-0.04	-0.02 (-0.00)	-202.41	3.65 (3.64)	6 (5 + 1)
4-SB ₈ H ₁₂	B2,3	-0.05	-0.04 (-0.02)	-0.07	-0.11 (-0.09)	-201.25	3.70 (3.69)	6 (5 + 1)
	B5,9	+0.03	+0.13 (+0.09)	+0.01	+0.09 (+0.05)	-203.37	3.61 (3.65)	6 (4 + 2)
	B6,8	-0.10	-0.12 (-0.12)	-0.11	-0.20 (-0.20)	-202.24	3.73 (3.73)	6 (3 + 3)
	B7	+0.15	+0.17 (+0.16)	+0.15	+0.13 (+0.12)	-204.28	3.58 (3.58)	7 (4 + 3)
	C4,6	-0.31	-0.03	-0.10	-0.11		3.92	5 (3 + 2)
	B1,2	+0.05	+0.06	+0.03	+0.02	-202.25	3.65	6 (5 + 1)
	B3	-0.06	-0.05	-0.10	-0.13	-200.76	3.71	6 (5 + 1)
4,6-C ₂ B ₇ H ₁₃	B5	+0.15	+0.02	+0.10	-0.07	-202.28	3.68	5 (4 + 1)
	B7,9	+0.13	+0.09	+0.10	-0.11	-203.11	3.64	6 (4 + 2)
	B8	-0.03	-0.06	-0.05	-0.11	-202.48	3.70	6 (3 + 3)

^a Mulliken gross atomic population in the STO-3G case; $n - \sum P_{\alpha\alpha}$ (where n is the number of the valence electrons, $P_{\alpha\alpha}$ are the diagonal elements of density matrix) in the CNDO/2 case. All values are in e⁻. Results of CNDO/2 calculations with inclusion of the sulphur 3d-orbitals are presented in brackets; ^b Group charge is the sum of the previously defined atomic charge and the attached hydrogen atom charge. All values are in e⁻. Results of CNDO/2 calculations with inclusion of the sulphur 3d-orbitals are presented in brackets; ^c Inner-shell eigenvalue in eV; ^d For definition of valence see text; ^e Overall coordination number, in parentheses divided into coordination number with heavy atoms plus coordination number with hydrogens.

under study is charge-controlled. Moreover, complications may be expected if a complex mechanism occurs, especially skeletal rearrangements during this course of seemingly simple reactions.

It is evident from both the STO-3G and CNDO/2 charge distributions (Table II and Figs 4–7) that nitrogen and carbon behave as acceptors of electron density from the borane framework and attached hydrogens. Sulphur behaves as an electron donor according to the STO-3G charge (sulphur atomic charge is distinctly positive, $+0.20 e^-$). The CNDO/2 charge on sulphur is slightly negative. The overall agreement between the STO-3G and CNDO/2 charge distributions is good, the differences in absolute values stemming from the different population analyses used. Each heteroatom influences mainly the charge of the neighbouring atoms. The charge differences

TABLE III

Overlap populations (STO-3G) and Wiberg indices (CNDO/2) of 4-CB₈H₁₄, 4-NB₈H₁₃ and 4-SB₈H₁₂

Bond	4-CB ₈ H ₁₄		4-NB ₈ H ₁₃		4-SB ₈ H ₁₂		
	STO-3G	CNDO/2	STO-3G	CNDO/2	STO-3G	CNDO/2 ^a	CNDO/2 ^b
1–2	0.470	0.577	0.475	0.580	0.451	0.577	0.556
1–4	0.381	0.558	0.381	0.613	0.310	0.508	0.631
1–5	0.297	0.439	0.208	0.403	0.301	0.477	0.467
2–3	0.332	0.483	0.339	0.489	0.340	0.487	0.491
2–5	0.420	0.533	0.427	0.527	0.412	0.531	0.508
2–6	0.452	0.600	0.450	0.601	0.454	0.602	0.603
2–7	0.415	0.518	0.413	0.518	0.415	0.513	0.512
4–5	0.533	0.738	0.627	0.845	0.486	0.709	0.842
5–6	0.297	0.464	0.293	0.458	0.287	0.474	0.469
6–7	0.295	0.456	0.293	0.452	0.295	0.455	0.456
B1–H _t	0.854	0.947	0.846	0.957	0.846	0.955	0.918
B2–H _t	0.848	0.937	0.848	0.938	0.848	0.933	0.933
B5–H _t	0.837	0.952	0.847	0.955	0.835	0.955	0.922
B5–H _b 56	0.273	0.365	0.244	0.342	0.261	0.369	0.356
B5–H _b 56	0.521	0.563	0.542	0.580	0.526	0.559	0.557
B5–H _t	0.837	0.960	0.837	0.961	0.837	0.958	0.958
B5–H _t 67	0.559	0.621	0.556	0.618	0.557	0.616	0.613
B7–H _t	0.847	0.957	0.847	0.956	0.847	0.957	0.958
B7–H _b 67	0.221	0.293	0.225	0.297	0.223	0.297	0.298
N–H			0.748	0.951			
C–H eq.	0.785	0.966					
C–H ax.	0.675	0.802					

^a Without *d*-orbitals on sulphur; ^b sulphur *d*-orbitals included.

between heteroatom and neighbour borons are larger from the STO-3G data than from the CNDO/2 calculation, what manifests itself in the different order of the most positive atoms. Atoms in the *meta* positions (2,3,6,8 in XB_8H_{12} and 3,8 in $\text{C}_2\text{B}_7\text{H}_{13}$) are always negative, antipodal atoms (7 in XB_8H_{12} and 7,9 in $\text{C}_2\text{B}_7\text{H}_{13}$) are always positive. *ISE* values do not strictly parallel STO-3G or CNDO/2 atomic charges, but they do indicate the group of more negative atoms (2,3,6,8 in XB_8H_{12} and 3,8 in $\text{C}_2\text{B}_7\text{H}_{13}$) and the group of more positive atoms (1,5,7,9 in XB_8H_{12} and 1,2,5,7,9 in $\text{C}_2\text{B}_7\text{H}_{13}$). It has been found useful^{23,24} to discuss bonding in boron hydrides and carboranes in terms of valencies and degrees of bonding, introduced by Armstrong and coworkers²⁴. The valency of atom *a*, V_a , is defined as a sum of the degrees of bonding, B_{ab} , between atom *a* and all other atoms, *b*,

$$V_a = \sum_{a \neq b} B_{ab} = \sum_{a \neq b} \sum_{i_a} \sum_{j_b} P_{i_a j_b}^2$$

The quantity B_{ab} is the sum of the squares of the elements of the density matrix, P_{ij} , (Wiberg bond index). It is well known that boron atoms in boranes tend to ex-

TABLE IV
Overlap populations (STO-3G) and Wiberg indices (CNDO/2) of 4,6- $\text{C}_2\text{B}_7\text{H}_{13}$

Bond	STO-3G	CNDO/2
1-2	0.489	0.564
1-3	0.394	0.518
1-4	0.376	0.541
1-5	0.380	0.551
1-9	0.345	0.474
3-7	0.395	0.521
3-8	0.502	0.643
4-5	0.514	0.732
4-9	0.527	0.721
7-8	0.292	0.469
B1-H _t	0.811	0.931
B3-H _t	0.810	0.938
B5-H _t	0.805	0.954
B7-H _t	0.811	0.953
B7-H _b 78	0.306	0.390
B8-H _t	0.809	0.962
B8-H _b 78	0.487	0.539
C-H eq.	0.779	0.969
C-H ax.	0.736	0.872

pand their valency to four²²⁻²⁴. Whilst the valency of boron in BH_3 is 2.9 (CNDO/2 ref.²⁴), values of the valencies with polyhedral boranes and carboranes vary between 3.55 and 3.88 (PRDDO) (ref.²²). An interesting correlation of valencies, or atomic charges, with coordination number of boron atoms can be deduced from

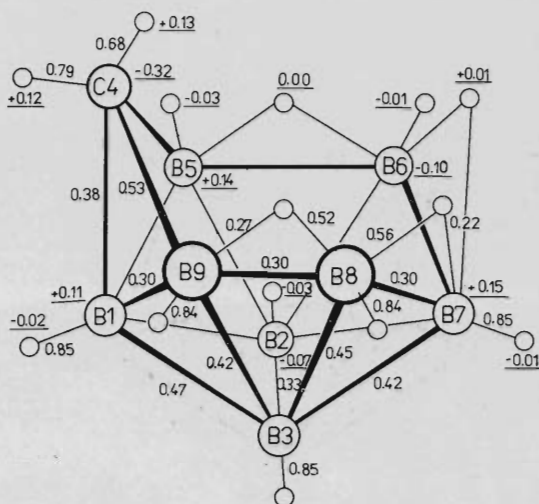


FIG. 4

STO-3G Mulliken atomic charges (underlined) and overlap populations of 4-CB₈H₁₄ (I)

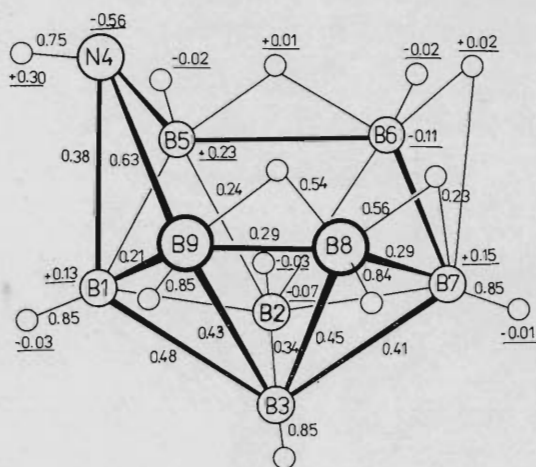


FIG. 5

STO-3G Mulliken atomic charges (underlined) and overlap populations of 4-NB₈H₁₃ (II)

the Lipscomb²⁴ PRDDO results (Table V). The higher the coordination number, the lower the valency (and the lower the electron density around the boron nucleus) in the polyhedral anions. This dependence is less straightforward in icosahedral dicarbaboranes. The compounds under study exhibit a larger variety of boron atom environments (3 to 5 heavy atoms plus 3 to 1 hydrogen atoms, see Table II and Figs 4–7). The total coordination number is 6, except for atom 7 in XB_8H_{12}

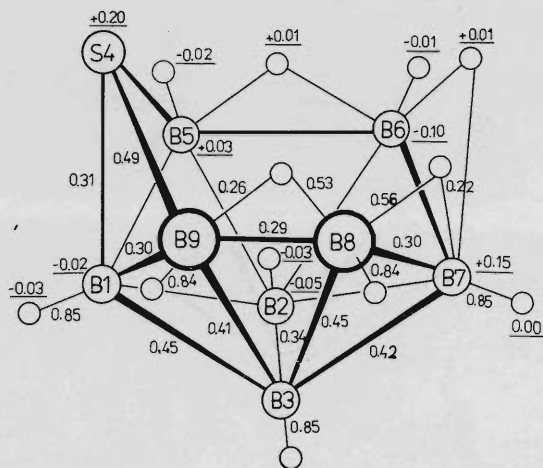


FIG. 6

STO-3G Mulliken atomic charges (underlined) and overlap populations of 4-SB₈H₁₂ (III)

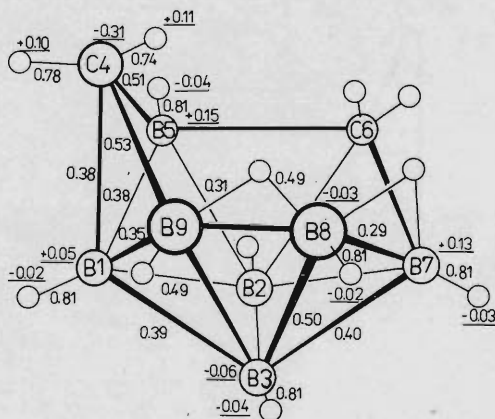


FIG. 7

STO-3G Mulliken atomic charges (underlined) and overlap populations of 4,6-C₂B₇H₁₃ (IV)

TABLE V
Valencies of boron atoms (summarized from ref.²²)

Coordination number	Valency of boron atom in polyhedral anion	Valency of boron atom in icosahedral carborane
4	3.88	—
5	3.77—3.82	3.65—3.70
6	3.72—3.76	3.64—3.71
7	3.55	3.61

TABLE VI
The linear least-squares regression coefficients^a for ¹¹B-NMR chemical shift correlations:
 $\delta = mx + b$

δ	x	STO-3G			CNDO/2		
		Mulliken atomic charge	2p orbital density	inner shell eigenvalue	atomic charge	2p orbital density	valence
CB ₈ H ₁₄	m	180.3	161.6	— 18.4	195.1	206.6	—367.8
	b	—21.8	—327.3	—3 746.0	—20.5	—455.4	1 331.2
	r	0.92	0.94	— 0.94	0.94	0.97	0.97
NB ₈ H ₁₃	m	142.4	140.9	— 16.9	182.4	182.3	—324.9
	b	—32.6	—271.7	—3 461.9	—31.6	—388.8	1 159.4
	r	0.87	0.91	— 0.93	0.95	0.96	— 0.95
SB ₈ H ₁₂	m	238.0	199.8	— 19.3	214.5	223.5	—407.4
	b	—17.6	—410.1	—3 933.6	—24.0	—489.3	1 473.0
	r	0.93	0.96	— 0.92	0.94	0.98	— 0.94
C ₂ B ₇ H ₁₃	m	223.6	190.8	— 21.6	254.4	298.6	—540.2
	b	—30.1	—390.8	—4 384.2	—22.4	—663.1	1 966.5
	r	0.95	0.87	— 0.85	0.77	0.95	— 0.75
Overall	m	169.5	158.6	— 18.0	197.2	209.4	—359.0
	b	—20.2	—318.3	—3 661.9	—24.5	—457.1	1 295.6
correlation	r	0.85	0.88	— 0.89	0.88	0.93	— 0.87

^a $\delta, m, b,$ and r are chemical shift(ppm), slope, intercept, and correlation coefficient, respectively; x is the characteristic correlated with the chemical shift: atomic charge, orbital densities (both in e^-), ISE in eV. For definition of valence, see text. Number of points with the individual systems amounts to five; for the overall correlation to twenty.

(coordination number 7) and atom 5 in $C_2B_7H_{13}$ (coordination number 5). Hexacoordinate negative atoms possess higher valencies (3.70–3.74), while positive atoms have lower valencies (3.60–3.65). The unique heptacoordinate atom, B(7) in XB_8H_{12} , has an extremely low valency (3.58) and positive charge, in accord with general trends. Pentacoordinate B(5) in $C_2B_7H_{13}$ has a relatively low valency (3.68) and positive charge due to the two carbon atoms in its neighbourhood.

The valencies of heteroatoms (Table II) reflect (together with the other quantities given in Tables II–IV) the way of heteroatom incorporation into the borane skeleton. Carbon tends to have its valency close to four (*cf.* PRDDO valencies of carboranes 3.96–3.99 (ref.²³), CNDO/2 valency for carbon in CH_4 is 3.95 (ref.²⁴). Nitrogen exceeds significantly the values of three (3.41, *cf.* CNDO/2 value for N in NH_3 is 2.94 (ref.²⁴). The sulphur valency value of 2.12 significantly rises when the sulphur *d*-orbitals (2.74) are included.

Some limited success has been achieved in correlating ^{11}B -NMR chemical shifts with density matrix properties. Kroner and coworkers^{13,33} have published linear correlations of chemical shift *vs* CNDO/S and *ab initio* boron 2*p* orbital densities and atomic charges for diverse boron compounds. In Table VI there are linear regression coefficients for some correlations of XB_8H_{12} and $C_2B_7H_{13}$ ^{11}B -NMR chemical shifts. The correlations for individual compounds are better than the overall correlation. The best one seems to be the chemical shift *vs* CNDO/2 2*p* orbital density correlation.

Bonding in boranes is most instructively described (for chemical purposes) by localized molecular orbitals (LMO's) which are now being derived from objective calculational procedures²⁵. Most of the boron–boron bonds derived in this way have centres

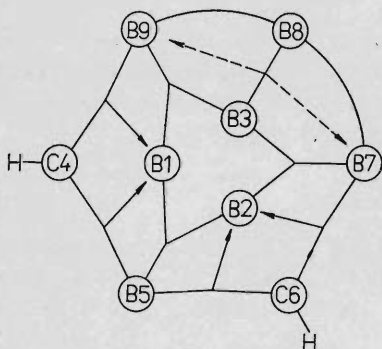


FIG. 8
Localized molecular orbitals of 4,6- $C_2B_7H_{13}$ (IV) (from ref.²⁷)

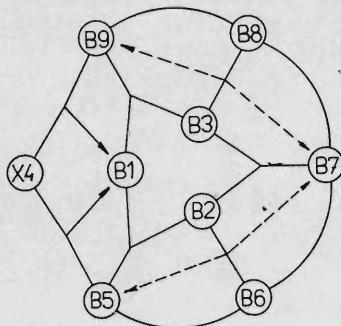


FIG. 9
Probable localized molecular orbitals of 4- XB_8H_{12} (I, II, III) molecules

of electron density in the triangular faces of a borane polyhedron. This closely corresponds to the older three-center bond theory²⁶. The LCAO-MO approach does not give a bonding description directly comparable with the localized bond or three-centre bond theories. From the Mulliken overlap populations, or Wiberg indices, we are able to infer only qualitatively whether particular bonding between two atoms is close to a "two-centre two-electron bond" or to some type of (more less unsymmetrical) "three-centre two-electron bond". Overlap populations and Wiberg indices (Tables III, IV, Figs 4–7) between all three heteroatoms and neighbouring atoms reflect a stronger bonding of the heteroatom to the boron atoms in open faces (5 and 9 in XB_8H_{12} , 5, 7 and 9 in $\text{C}_2\text{B}_7\text{H}_{13}$) and weaker bonding between the heteroatom and boron atoms in base (1 in XB_8H_{12} , 1 and 2 in $\text{C}_2\text{B}_7\text{H}_{13}$). This is consistent with fractional three-centre bonds being localized in the 1-4-5 and 1-4-9 triangles of XB_8H_{12} (or in the 1-4-5, 1-4-9, 2-5-6, 2-6-7 triangles of $\text{C}_2\text{B}_7\text{H}_{13}$). Localized orbitals derived²⁷ from PRDDO wave functions of $\text{C}_2\text{B}_7\text{H}_{13}$ are presented in Fig. 8.

Overlap populations and Wiberg indices (Table V) of $\text{C}_2\text{B}_7\text{H}_{13}$ are consistent with the given LMO picture (high 4-5, 4-9, 3-8 and low 7-8 values). For the XB_8H_{12} ($\text{X} = \text{CH}_2, \text{NH}, \text{S}$) molecules we predict a similar LMO scheme (Fig. 9).

This scheme is in accord with the calculated overlap populations and Wiberg indices (Table III), *i.e.* high values for the 4-5 and 4-9, 2-6 and 3-8 bonds, low values for the 1-5 and 1-9, 5-6 and 8-9, 6-7 and 7-8 bonds.

Molecules XB_8H_{12} ($\text{X} = \text{CH}_2, \text{NH}, \text{S}$) and $\text{C}_2\text{B}_7\text{H}_{13}$ are "isoelectronic" with the known $\text{B}_9\text{H}_{14}^-$ anion in the sense that they possess the same number of valence electrons available for framework bonding. However, this does not imply the same type of electron distribution. Formal substitution of a BH_2 group in $\text{B}_9\text{H}_{14}^-$ (Fig. 10) by $:\text{CH}_2$, $:\text{NH}$ or $:\text{S}$ leads to the formation of "more classical" bonds between heteroatom-neighbouring borons B(5), B(9) and the formation of a fractional centre

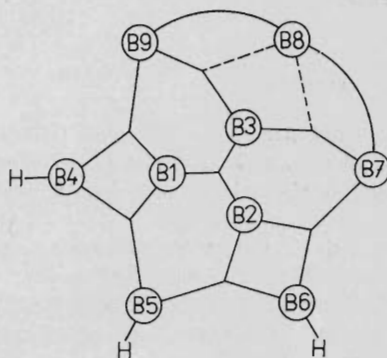


FIG. 10

Localized molecular orbitals of $\text{B}_9\text{H}_{14}^-$ (from ref.²⁷)

B(1). This causes a rearrangement of the "classical" B—H bonds in (another) region of the molecule into more delocalized hydrogen bridges with the formation of a rather unusual heptacoordinate B(7) atom (coordination with four borons and three hydrogens). Both types of hydrogen bridges are strongly asymmetric, the H atoms being closer and strongly bonded to the B(6) and B(8) atoms. This corresponds to an enhanced reactivity of the B(6)-H-B(7) and B(8)-H-B(7) bridges towards hydrogen fission²⁸⁻³².

Some interesting bonding conclusions follow from the shapes of the MO's obtained. The two highest occupied MO's of the compounds under study contain a contribution from the 1s atomic orbitals of the bridge hydrogens. A group consisting of a few of the highest occupied MO's, which in the LCAO description are composed of 2p atomic orbitals from all of the boron atoms and are currently called cage-bonding orbitals, is considered to reflect the bonding of a borane cluster. Even more important than the participation of bridge hydrogens is the strong participation of all of the nitrogen 2p and sulphur 3p atomic orbitals in cage bonding. This participation in delocalized cage orbitals first means that the "lone electron pairs" of nitrogen and sulphur take part in cluster bonding and secondly, provides a possibility for coupling between the heteroatom and all of the boron atoms.

The ¹¹B-NMR studies of substituted boranes and heteroboranes provide us with some experimental indications of a "through cage" interaction. The boron atoms in antipodal positions to the substituted boron, e.g., by a halogen, or the atom which is antipodal to the cage heteroatom often possess unusually large ¹¹B-NMR shifts, both diamagnetic and paramagnetic⁶⁻¹¹. A correlation between ¹³C-NMR chemical shifts of the carbon in the *para* position of mono-substituted benzenes and ¹¹B-NMR chemical shifts of the antipodal boron in substituted carboranes for electron donating substituents has been demonstrated³³.

The interaction of heteroatoms with the *closo*-borane skeleton, resulting in more dramatic chemical shift changes than in the presented *arachno* heteroboranes, is under study.

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Note added in proof: In the time of the editorial processing, a paper on LMO's calculations of some azaboranes appeared (Bicerano J., Lipscomb W. N.: *Inorg. Chem.* **19**, 1825 (1980)), dealing among other with one compound, 4-NB₈H₁₃, studied in our communication. The calculated LMO's of 4-NB₈H₁₃ are in agreement with our proposal, with the exception of the nearest neighbourhood of nitrogen atom. Needless to say LMO's cannot be satisfactorily inferred from density matrix properties, without rigorous transformation of canonical MO's into localized MO's.