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Internuclear Distances in Carbaboranes

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Structural data for different carbaboranes, investigated in the solid and gas phases, have been compiled and arranged systematically. The subdivision of bonds into polyhedral and exopolyhedral, proposed previously, is illustrated by additional examples. It is shown that the concept of the coordination number helps to discover the rules governing the variation of the polyhedral C - C and B - C distances. Since this approach proved to be relatively ineffective in relation to B - B bonds, an attempt was made to estimate the influence of electronic factors on these distances on the basis of a modified inductive rule. This has shown that the polyhedral and exopolyhedral C - X and B - X distances in carbaboranes obey different rules.
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I. INTRODUCTION

Vigorous studies in the field of boron hydrides led at the end of the 1950s and the beginning of 1960 to the discovery of a new class of organic derivatives of boron—carbaboranes. The structural basis of carbaboranes consists of fragments of polyhedral boranes incorporating carbon atoms as an intrinsic component of the skeleton, in contrast, for example, to alkylboranes, in which carbon is a substituent. After a short time, this field of chemistry developed so actively that the possibilities for the synthesis of new compounds now appear almost unlimited. Interest in carbaboranes is to a large extent due to the fact that, both experimentally and theoretically, they occupy a strategically important position at the junction of many fields of chemistry: those of boron hydrides, organoelemental compounds, transition metal complexes, and metallic clusters. These common features were manifested particularly strikingly in the middle of the 1960s when metallocarbaboranes were discovered.

closo-Carbaboranes, forming closed polyhedral structures, were initially investigated in greatest detail. The inclusion of carbon atoms in the boron hydride skeleton is accompanied by the disappearance of hydrogen bridge atoms and greatly increases the thermal and chemical stabilities of the initial systems. The majority of studies were carried out on $C_2B_{10}H_{12}$ and $C_2B_5H_7$ and were designed to synthesise thermostable polymers. However, other ways of using carbaboranes were also found. Even before the polyhedral structure of carbaboranes was demonstrated by direct structural methods, their structure had been correctly predicted on the basis of indirect considerations. Both certain experimental methods (infrared spectroscopy, NMR, and mass spectrometry) and theoretical ideas, to a large extent developed by the American investigator Lipscomb†, played an important role here. In particular, one of the simple fundamental ideas was the observed analogy between the structures of *closo*-carbaboranes $C_2B_{n-2}H_n$ and the isoelectronic $B_nH_n^{2-}$ ions, for example, $C_2B_4H_6$ and $B_6H_6^{2-}$, etc. The vigorous development of the chemistry of carbaboranes would have been impossible without the exact knowledge of their structure. The majority of structural results for substituted carbaboranes were obtained by single crystal X-ray diffraction. The structure of volatile lower carbaboranes was established mainly by gas electron diffraction and microwave spectroscopy.

Data on the structure of carbaboranes are usually included in reviews on their chemical properties. As a result, extensive structural data have accumulated, the compilation and systematic arrangement of which are both urgently required and desirable. Furthermore, there is a possibility of surveying these experimental data and examining them from a single standpoint, for example in terms of coordination numbers (C.N.).

The stereochemistry of carbon with C.N. = 2, 3, and 4 has been studied in detail in relation to organic compounds. An expansion of the coordinating capacity of carbon has been observed in carbaboranes, where C.N. = 4, 5, and 6 are encountered. In the present review we attempted to compare these two ranges of C.N. on the basis of carbaborane data obtained in the gas and crystalline phases. The polyhedral and exopolyhedral bonds formed by carbon are considered separately; next, bonds involving boron atoms are analysed by analogy. The classification of exopolyhedral distances as an independent group, which we proposed on the basis of geometrical considerations[1], has been confirmed independently in the study of the photoelectron spectra of carbaboranes[2].

One cannot assume *a priori* that a fairly formal characteristic of the atom such as its coordination number will exert a unique or even a decisive influence on the lengths of all the bonds involving the given atom. In particular, this applies to systems with a considerable delocalisation of electrons, to which carbaboranes belong. Such cases may require an additional allowance for electronic factors.

II. C–C BONDS

Stoichev's rule, expressing the dependence of the C–C bond length on the number of bonds or atoms attached to

†Lipscomb also played an important role in the experimental determination of the structures of numerous boron hydrides and carbaboranes by X-ray diffraction. His work in this field was recognised by the award of the Nobel prize in 1976.

it, is well known in the stereochemistry of organic compounds:

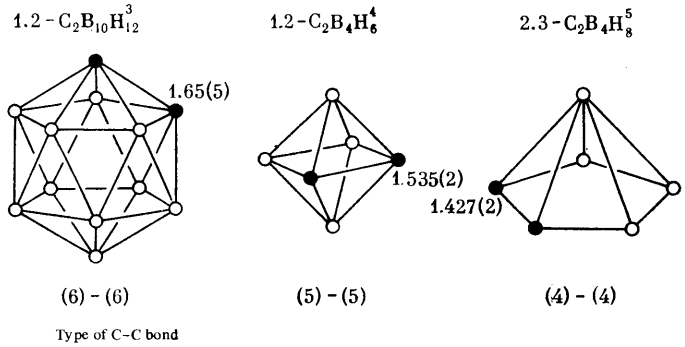
$$r(C-C) = 1.299 + 0.040\,n(\text{Å});\ n = 2-6, \qquad (1)$$

where n is equal to the sum of the C.N. of the atoms forming the bond minus two.

This equation reproduces satisfactorily the C–C bond lengths in diacetylene ($n = 2$), vinylacetylene ($n = 3$), butadiene ($n = 4$), propene ($n = 5$), and ethane ($n = 6$), constituting a convincing illustration of the usefulness of the concept of the coordination number. Numerous attempts have been made at a theoretical justification of Stoichev's rule (these include the theory of orbital hybridisation, allowance for the influence of the delocalisation of electrons, steric effects, electronegativity, amount of ionic character of the bond, etc), but as yet there is no unanimous view on this subject.

The problem arises of the possibility of extrapolating Stoichev's equation to higher C.N. for carbon atoms, characteristic of carbaboranes. We have shown[1] that, for the C–C bond of the type (6)–(6) (the C.N. of the carbon atoms are indicated in brackets), Eqn.(1) leads to 1.699 Å, which agrees, within the limits of the errors of the individual measurements, with the value 1.655 Å found for 1,2-$C_2B_{10}H_{12}$ (Bohn and Bohn[3]) and its derivatives.

Analogous treatment yields 1.619 and 1.539 Å for bonds of the type (5)–(5) and (4)–(4) respectively, which differ appreciably from the experimental data quoted below:



Such a marked discrepancy led us to compile additional literature data for the structures of carbaboranes, which are listed in the Table. The coordination numbers for all the bonds, with the exception of those of the (6)–(6) type, are indicated here as superscripts; for C–B bonds, the C.N. of the carbon atoms is given first. Additional alphabetic subscripts are used only for B–B bonds and correspond to their classification in relation to carbon atoms (see below).

The majority of the compounds investigated are *closo*-carbaboranes; the letters (n) and (a) denote *nido*- and *arachno*-carbaboranes respectively. Carbaboranes with heteroatoms (1-$CH_3GaC_2B_4H_6$, 1,12-$CHPB_{10}H_{10}$, etc.) are not included in the Table.

The results for C–C bonds are presented in a graphical form in Fig.1. Inspection of this figure permits the following observations.

1. The length of polyhedral C–C bonds in *closo*- and *nido*-carbaboranes varies linearly with the C.N. of the carbon atoms, which is described by the empirical equation

$$r(C-C) = 1.074 + 0.058\,n(\text{Å});\ n = 6, 8, 9, 10. \qquad (2)$$

Evidently the observed relation for carbaboranes lies below that for hydrocarbons and the straight lines corresponding to Eqns.(1) and (2) diverge appreciably in the region of low C.N., which also accounts for the unsatisfactory estimates of the lengths of bonds of the type (4)–(4) and (5)–(5) in carbaboranes by Eqn.(1).

2. Extrapolation of Eqn.(2) to the region of small C.N., shown by a dashed line, yields satisfactory estimates of the lengths of the C=C and C≡C multiple bonds. This phenomenon is especially interesting in the light of the fact that a considerable amount of double-bond character has been postulated for the (4)–(4) bond in $C_2B_4H_8$ and $C_4B_2H_6$.[7,8,50]

3. The exopolyhedral C–C_e bonds form a special group of distances, depending little on the immediate environment, which is described by the empirical equation

$$r(C-C_e) = 1.510 + 0.002\,n(\text{Å});\ n = 6, 7, 8, 10. \qquad (3)$$

These distances vary on average from 1.52 to 1.53 Å with increase of n from 6 to 10, i.e. they are almost constant and intersect the bond corresponding to Eqn.(2) in the region of bonds of the type (6)–(4).

Overall, the data for the exopolyhedral C–X distances in carbaboranes are few and are in essence limited to C–C distances. However, for X = I or Si, the substituent is seen to exert a considerable influence, since the C–I bonds in 1,7-$C_2I_2B_{10}H_{10}$ [51] and 1,12-$C_2I_2B_{10}H_{10}$ [28] are much shorter and the C–Si bond in 1,2-$C_2(CH_3)[Si(CH_3)_3]B_{10}H_{10}$ [37] is much longer than might have been expected on the basis of stereochemical analogies. The structural data for C–H bonds are not very accurate and are therefore not discussed here. One should only note that the high vibration frequencies of the C–H bonds, characteristic of ethylenic and aromatic compounds, are also characteristic of carbaboranes: with increase of the C.N. of the carbon atom, the frequencies diminish[52].

III. POLYHEDRAL C–B BONDS

In the most symmetrical *closo*-carbaboranes the polyhedral C–B bonds depend only on the C.N. of the carbon atom n_C (Mastryukov et al.[1]):

$$r(C-B) = 1.249 + 0.077\,n_C(\text{Å});\ n_C = 4, 5, 6. \qquad (4)$$

When data for 1,10-$C_2B_8H_{10}$ were published[23], it became possible to estimate the influence of the C.N. of the boron atom for a constant C.N. of the carbon atom. The C–B bond lengths are indicated below for symmetrical *closo*-carbaboranes having C_2B_4, C_2B_8, and C_2B_{10} skeletons with an indication of the C.N. of the atoms forming the bond:

C(5)–B(5)	C(5)–B(6)	C(6)–B(6)
1.634 (4)[12]	1.602 (2)[23]	1.710 (11)[3]

This comparison shows that, when the C.N. of the boron atom is altered, there is a smaller change in the C–B bond lengths than after the alteration of the C.N. of the carbon atom. This justifies the choice of n_C as the variable quantity in Eqn.(4). On the other hand, when one employs the atomic radii of boron proposed by Brown and Lipscomb[53], then the C–B(6) bond should be longer by 0.070 Å than the C–B(5) bond.

A more complex picture arises for the C–B bonds when account is taken of less symmetrical *closo*-carbaboranes and data for *nido*-carbaboranes are included (see Table). It then becomes clear that Eqn.(4) is applicable only to the most symmetrical *closo*-carbaboranes. It can be assumed that the wide variety of C–B bonds is best characterised by the simplest relation in the form of Eqn.(4), taking into account

The bond lengths in carbaboranes (in Å).

No.	Molecule	C–C (polyhedral)	C–C (exopolyhedral)	C–B (polyhedral)	B–B (polyhedral)	Method	Refs
1	1,5-$C_2B_3H_5$	—	—	1.556(4)–(5)	1.853(5)–(5), i	E	6
2	2,3-$C_2B_4H_8$ (*n*)	1.419(4)–(4)	—	1.500(4)–(5), 1.750(4)–(6)	1.714c, 1.772(5)–(6), g, 1.790(5)–(6), b	X	7
	»	1.427(4)–(4)	—	1.538(4)–(5), 1.764(4)–(6)	1.695c, 1.816(5)–(6), b, 1.821(5)–(6), g	E	5
3	2,3-$C_2(CH_3)_2B_4H_6$ (*n*)	1.431(4)–(4)	1.516(4)–(4)	1.520(4)–(5), 1.763(4)–(6)	1.705c, 1.768(5)–(6), g, 1.778(5)–(6), b	X	7
4	$C_4B_2H_6$ (*n*) *	1.424(4)–(4), 1.436(4)–(4)	—	1.541(4)–(4), 1.697(4)–(6), 1.709(4)–(6)	1.886(4)–(6), i	M	8
5	CB_5H_9 (*n*)	—	—	position of C atom not determined	1.759(5)–(6), b, 1.781b, 1.782(5)–(6), d, 1.830a	M	10
6	1,2-$C_2B_4H_6$	1.535(5)–(5)	—	1.618(5)–(5), 1.621(5)–(5)	1.723(5)–(5), g, 1.745(5)–(5), e	E	4
	»	1.540(5)–(5)	—	1.605(5)–(5), 1.627(5)–(5)	1.721(5)–(5), g, 1.752(5)–(5), e	M	11
7	1,6-$C_2B_4H_6$ **	—	—	1.633(5)–(5)	1.720(5)–(5), i	E	6
	»	—	—	1.634(5)–(5)	1.724(5)–(5), i	E	12
8	CB_5H_7	—	—	1.60(5)–(6), 1.63(5)–(5)	1.70(5)–(6), b,d 1.72(5)–(5),d, 1.87d 1.89b	M	14
	»	—	—	1.602(5)–(6), 1.660(5)–(5)	1.686(5)–(6),d, 1.690(5)–(6),b, 1.756(5)–(5),d, 1.910b, 1.921d	E	4
9	2,4-$C_2B_5H_7$	—	—	1.546(5)–(5), 1.563(5)–(5), 1.708(5)–(6)	1.651(5)–(5),f, 1.815(5)–(6),h, 1.818(5)–(6), i	M	15
	»	—	—	1.537(5)–(5), 1.558(5)–(5), 1.717(5)–(6)	1.659(5)–(5),f, 1.772(5)–(6),h, 1.852(5)–(6), i	E	16
10	1,7-$C_2(CH_3)_2B_6H_6$	—	1.521(5)–(4)	1.500(5)–(5), 1.595(5)–(6), 1.695(5)–(6), 1.697(5)–(6)	1.696(5)–(6),f, 1.772(5)–(6),f, 1.806(5)–(6),d, 1.842h 1.894i, 1.902f	X	17
11	1,6-$C_2B_7H_9$	—	—	position of C atoms not determined	1.712(5)–(6), b, 1.784(d),1.805i, 1.976h, 1.995f	M	18
12	1,6-$C_2(CH_3)_2B_7H_7$	—	1.529(5)–(4)	1.595(5)–(6), 1.615(5)–(6)	1.698(5)–(6), b, 1.764i, 1.772d, 1.969h, 1.984f	X	19
13	5,9-$C_2(CH_3)_2B_7H_{11}$ (*a*)	—	1.559(5)–(4)	1.672(5)–(6), 1.704(5)–(5), 1.706(5)–(6)	1.714f, 1.725a, 1.730(5)–(6),h, 1.777b, 1.779d, 1.819b, 1.823b	X	20
14	1,2-$C_2(CH_3)_2B_7H_9$ (*n*)	1.55(5)–(5)	1.50(5)–(4)	1.60(5)–(5), (5)–(6), 1.65(5)–(6), 1.67(5)–(6), 1.75(5)–(5)	1.69a, 1.75(5)–(6), b, 1.78—1.81	X	21
15	1,6-$C_2(CH_3)_2B_8H_8$	—	1.505(5)–(4), 1.527(6)–(4)	1.597(5)–(6), 1,600(5)–(6), 1,632(6)–(5) 1.751, 1.776	1.681(5)–(6), b, 1.694(5)–(6), d, 1.783h 1.797f, 1.812h, 1.828b, 1.831d, 1.861i	X	22
16	1,10-$C_2B_8H_{10}$	—	—	1.602(5)–(6)	1.829f, 1.850d	E	23
17	6,9-$C_2(CH_3)_2B_9H_9$	—	1.52(5)–(4)	1.60(5)–(6), 1.67(5)–(7), 1.70(5)–(6)	1.78b 1.80b, 1.82d, 1.85a, 1.87f, 2.06(5)–(7), h	X	24
18	11-CH_3-2,7-$C_2B_9H_{12}$ (*n*)	1.606(5)–(6)	—	1.621(5)–(6), 1.657(5)–(6), 1.660, 1.677, 1.682, 1.707(5)–(6), 1.791	1.734b, 1.746a, 1.752a, 1.755c, 1.774b, 1.776g, 1.784a, 1.786b, 1.792b, 1.796b, 1.800g, 1.836g, 1.849b, 1.856c, 1.920a	X	25
19	$C_4(CH_3)_4B_8H_8$ (i)	1.49(5)–(5)	1.52(5)–(4)	1.62—2.15 (cf. 1.78(5)–(6))	1.68—1.86 (cf. 1.78)	X	26
20	1,12-$C_2B_{10}H_{12}$	—	—	1.710	1.772f, 1.792d	E	3
21	(1,12-$C_2B_{10}H_{11})_2$	—	—	1.709	1.756f, 1.777d	X	27
22	1,12-$C_2I_2B_{10}H_{10}$	—	—	1.708	1.775f, 1.777d	E	28
23	1,2-$C_2B_{10}H_{12}$	1.653	—	1.711 ***	1.798, 1.802 ***	E	3
24	(1,2-$C_2B_{10}H_{11})_2$	—	1.522	1.722	1.768, 1.777	X	29
25	1,2-$C_2H_2B_{10}Cl_8H_2$	1.67	—	1.70, 1.73	1.75c, 1.76b, 1.78b, 1.79d, 1.81a,g, 1.82a	X	30
26	1,2-$C_2(CH_2Br)_2B_{10}H_{10}$	1.64	1.52(6)–(4)	1.71, 1.73	1.75b, 1.76c, 1.77a, 1.78g, 1.79d, 1.81a	X	31
27	1,2-$C_2H_2B_{10}Br_2H_8$	1.63	—	1.71, 1.73	1.73a,c, 7.74b, 1.76b,g, 1.78a, 1.80d	X	32
28	1,2-$C_2(CH_3)_2B_{10}Br_4H_6$	1.65	1.51(6)–(4)	1.71, 1.73	1.76b, 1.77c, 1.78a,d,g, 1.79a,b	X	33
29	1,2-$C_2H_2B_{10}Br_3H_7$	1.65	—	1.70, 1.71	1.74c,g, 1.78b, 1.80a,b,d	X	34
30	(1,2-$C_2B_{10}H_{10}CO)_2$	1.645	1.520(6)–(3)	1.715, 1.745	1.760c, 1.767b, 1.771d, 1.781b, 1.782a, 1.785a, 1.792g	X	35
31	1,2-$C_2B_{10}(CH_3)_4H_8$	1.663	1.504(6)–(4)	1.706, 1.757	1.767d, 1.768b, 1.771b, 1.774a, 1.777c, 1.785g	X	36
32	1,2-$C_2H(C_4H_9)B_{10}H_{10}$	1.670	1.562(6)–(4)	1.714	1.766—1.791 (cf. 1.777)	X	37
33	1,2-$C_2(CH_3)[Si(CH_3)_3]B_{10}H_{10}$	1.669	1.524(6)–(4)	1.718	1.766—1.790 (cf. 1.777)	X	37
34	C_6H_5CO-1,2-$C_2B_{10}H_{11}$	1.62	—	1.71	1.76—1.81 (cf. 1.78)	X	38
35	1,2-$C_2(CH_3)_2B_{10}(C_6H_5)H_9$	1.70	1.52(6)–(4)	1.69	1.71—1.86 (cf. 1.76)	X	39
36	1,2-$C_2H_2B_{10}(CH_3C_6H_4)H_9$	1.62	—	1.69	1.69—1.86 (cf. 1.78)	X	39
37	$(CH_3)_2Ge(1,2\text{-}C_2B_{10}H_{10})_2PC_6H_5$	1.678	—	1.722	1.762—1.794 (cf. 1. 778)	X	40
38	$(CH_3)_2Sn(1,2\text{-}C_2B_{10}H_{10})_2$, $CHOCH_3$	1.71	1.51(6)–(4)	1.73	1.66—1.99 (cf. 1.81)	X	40
39	$CH_2(1,2\text{-}C_2B_{10}H_{10})_2PCH_3$	1.655	1.518(6)–(4)	1.724	1.754—1.798 (cf. 1.770)	X	41
40	$(1,2\text{-}C_2B_{10}H_{10})_2AsCH_3$	1.650	1.529	1.729	1.73—1.81 (cf. 1.772)	X	41
41	1,7-$C_2B_{10}H_{12}$	—	—	1.720****	1.791, 1.817, 1.831i ****	E	3
42	1,7-$C_2H_2B_{10}Br_2H_8$	—	—	1.64, 1.68, 1.74	1.70b, 1.72h, 1.77a, 1.80b, 1.81f, 1.83d, 1.89i	X	42
43	1,7-$C_2H_2B_{10}Cl_{10}$	—	—	1.70	cf. 175	X	43
44	1,7-$C_2H_2B_{10}H_7CH_3Cl$	—	—	1.69, 1.71, 1.74	1.78b,f,h 1.80b, 1.83d, 1.87a, 1.93i	X	44
45	1,7-$C_2H_2B_{10}Br_3H_7$	—	—	1.71, 1.72	1.73b, 1.75a,f 1.76h, 1.79b, 1.80d 1.82i	X	45
46	1,7-$C_2(CH_3)_2B_{10}Cl_2H_8$	—	1.56(6)–(4)	1.72, 1.73	1.74h, 1.76b, 1.79d,f, 1.81b,i, 1.84a	X	46
47	1,7-$C_2H(CH_3)B_{10}Br_3H_7$	—	1.49(6)–(4)	1.73–1.75 (equality of all bond lengths in icosahedron was assumed)		X	47
48	1,7-$C_2H_2B_{10}Cl_3H_7$	—	—	1.680, 1.689, 1.691	1.757f, 1.761h, 1.765i, 1.772b, 1.774d, 1.776b, 1.791a	X	48
49	1,7-$C_2(C_6H_5)B_{10}H_{10}$	—	1.52(6)–(3)	1.70, 1.74	1.75i, 1.78h, 179b,f, 180a,b,d	X	49

Remarks: Research techniques used: E = electron diffraction; X = X-ray diffraction; M = microwave spectroscopy.

*An electron diffraction study of $C_4B_2(CH_3)_6$ has also been carried out[9]. These data are unreliable, since they differ markedly from the results for the unsubstituted molecule.

**The 2-Cl-1,6-$C_2B_4H_5$ molecule has been investigated by the microwave method[13]. These results have not been included in the Table because of their low accuracy.

***The values for two types of C–B bonds in *ortho*-carbaborane and its derivatives (Nos.23–40) are presented: C(1)–B(3) and C(1)–B(4) (the atoms are always numbered in accordance with Bohn and Bohn[3]) or average values are given. The values for seven types of B–B bonds are quoted: B(3)–B(4)(g); B(4)–B(5)(d); B(3)–B(8)(c); B(4)–B(8)(b); B(4)–B(9)(b); B(8)–B(9)(a); B(9)–B(12)(a); otherwise the average values for some of them are given.

****The values for three types of C–B bonds in *meta*-carbaborane and its derivatives (Nos.41–49) are quoted: C(1)–B(2), C(1)–B(4), and C(1)–B(5), or their average values are given. Seven types of B–B bonds are quoted: B(2)–B(3)(i); B(2)–B(6)(h); B(4)–B(5)(d); B(4)–B(8)(f); B(4)–B(9)(b); B(5)–B(9)(b); B(9)–B(10)(a); otherwise the average values of some of them are given.

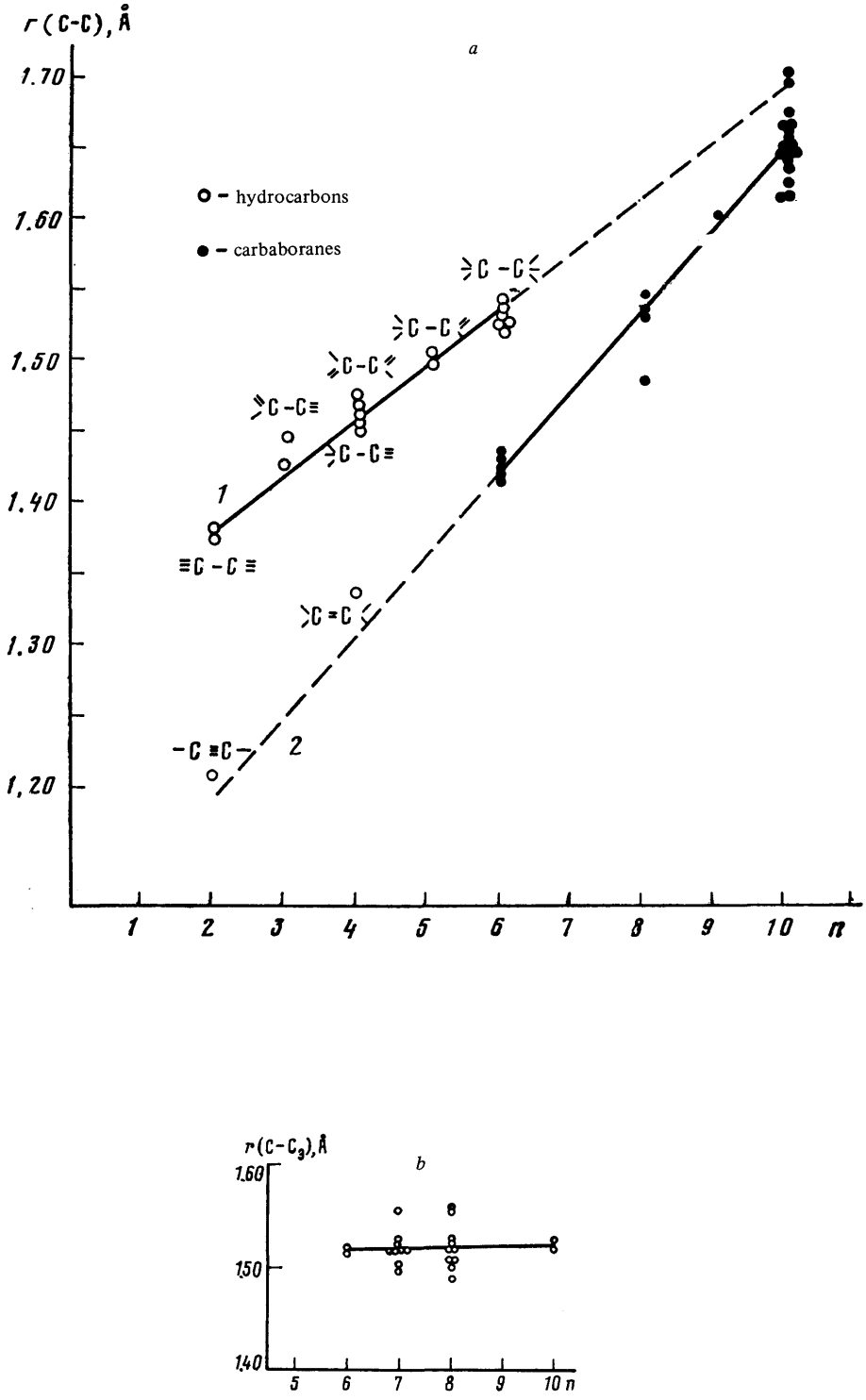


Figure 1. Variation of the C–C bond lengths in carbaboranes and hydrocarbons with the number *n* of neighbouring bonds: *a*) continuous line *1* corresponds to the variation of the bond lengths in hydrocarbons [see Eqn.(1)] and line *2* corresponds to the variation of the polyhedral distances in carbaboranes [see Eqn.(2)]; the dashed line represents the extrapolation of Eqn.(1) to the region of high C.N. of the carbon atom and the extrapolation of Eqn.(2) to the region of low C.N. of the carbon atom; *b*) variation of the exopolyhedral distances in carbaboranes [see Eqn.(3)].

the deviations from the latter, which in the case of *closo*-carbaboranes are indicated in Fig.2.

IV. POLYHEDRAL B–B BONDS

The uncertain role of the C.N. of the boron atom in C–B bonds becomes still more appreciable on passing to B–B bonds even in the simplest *closo*-carbaboranes with the following skeletons:

C_2B_3	C_2B_4	C_2B_5		C_2B_8	C_2B_{10}
(5) — (5)	(5) — (5)	(5) — (5)	(5) — (6)	(6) — (6)	(6) — (6)
1.853 (2)	1.724 (9)	1.659 (10)	1.772 (11)	1.850 (5)	1.792 (7)
			1.852 (11)	1.829 (4)	1.772 (13)

(for the corresponding references, see Table). The B–B bond lengths apparently depend to a large extent on electronic factors which are weakly related (or not related at all) to the C.N. One may note, by analogy, that in the stereochemistry of organic compounds not all the changes in C–C bond lengths depend on the C.N.: the most evident exceptions are cyclic hydrocarbons and sterically hindered molecules[54].

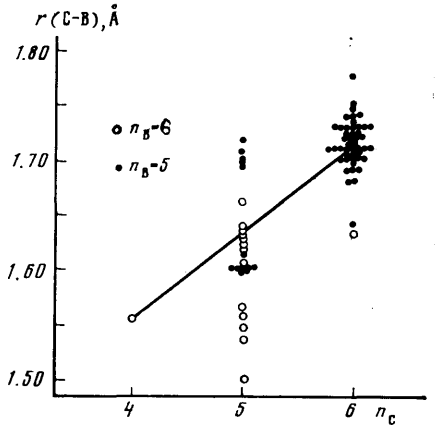


Figure 2. Variation of the C–B bond lengths in *closo*-carbaboranes with the C.N. of the carbon atom n_C. Different designations have been used for different C.N. of the boron atom (n_B). The straight line corresponds to Eqn.(4).

The anomalously long B–B bond in 1,5-$C_2B_3H_5$ [6] agrees with the quantum-chemical description of this molecule[55], which is represented as a bicyclic system consisting of three C–B–C bonds and without B–B bonds. For the remaining cases, a gradual increase of the B–B distances with increasing C.N. of the boron atoms can be seen. This agrees qualitatively with the proposed[53] atomic radii of boron with different coordination, but quantitative estimates are relatively inaccurate even in those cases where the geometry has been optimised[55,56].

As a result of structural studies on carbaboranes, attempts have been made to specify the rules concerning the B–B distances.

1. In molecules of *p*-carbaborane 1,1,2-$C_2B_{10}H_{12}$ and its derivatives[3,27,28] and also in 1,10-$C_2B_8H_{10}$ [23] the B–B bonds at the bases of the pyramids are longer than the equatorial bonds.

2. The B–B distance included between two carbon atoms is longest in the molecules of certain small carbaboranes[15–17,22] and also in *m*-carbaborane 1,7-$C_2B_{10}H_{12}$ and its derivatives[3,42,44,45].

3. In the molecules of *o*-carbaborane 1,2-$C_2B_{10}H_{12}$ and its derivatives[3] there is a tendency towards an increase in the length of the B–B bonds near carbon atoms.

Although the proposed rules are not general (exceptions are known[18,19,34,46,48,49]), they are of considerable interest. They can be related to the distribution of charges on the boron and carbon atoms, which obey the so-called inductive rule[57]. According to this rule, boron atoms become electropositive when they are linked to carbon atoms. The inductive rule acquires a geometrical aspect when account is taken of the fact that the bond between two electropositive boron atoms should be weak and long and that an increase of the negative charge on the atoms should be accompanied by a strengthening and shortening of the bonds. Hence it follows that the longest B–B bonds are to be expected in the vicinity of carbon atoms and that the shortest B–B bonds are those at the maximum remove from them.

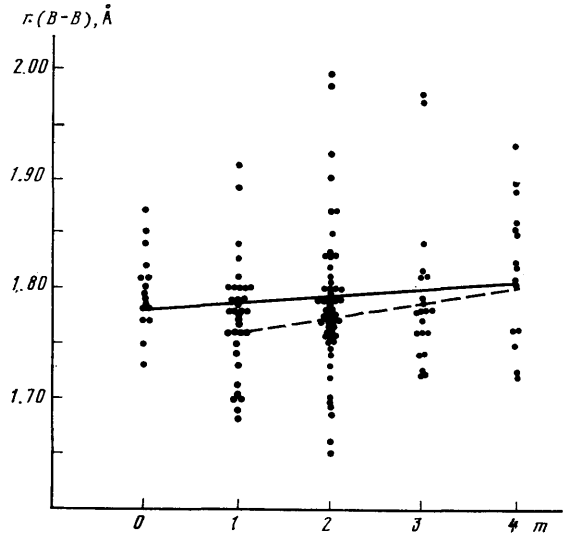
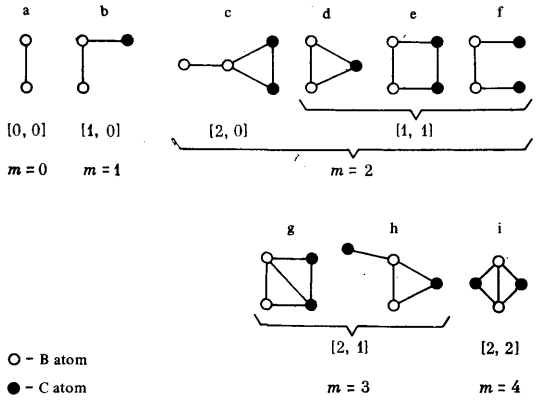


Figure 3. Variation of the B–B bond lengths in *closo*-carbaboranes with the overall number *n* of attached carbon atoms. The continuous line corresponds to Eqn.(5). The dashed line represents the corresponding relation for unsubstituted carbaboranes $C_2B_nH_{n+2}$.

As a result of this approach, it becomes clear that the empirical relations noted above are a direct consequence of a modified inductive rule. Furthermore, there is a possibility of a more detailed quantitative test of the applicability of this rule to the carbaboranes investigated. For this purpose, all the B–B bonds listed in the Table have been classified in terms of the [*k*, *l*[types; the numerals in square brackets show to how many carbon atoms each boron atom is linked.

The comparison of different B–B bonds is based on the overall characteristic $m = k + l$:



The results of a quantitative treatment of data for *closo*-carbaboranes alone are presented in Fig.3 and are described by the equation

$$r(\text{B—B}) = 1.780 + 0.006\,m\,(\text{Å});\ m = 0,\ 1,\ 2,\ 3,\ 4. \qquad (5)$$

For each type of B–B bond, there is a considerable scatter of values, but the average bond length is in all cases close to 1.80 Å. In order to eliminate the possible influence of substituents on the distribution of electron density in the skeleton, a calculation was performed taking into account only data for unsubstituted carbaboranes $C_2B_nH_{n+2}$. The final relation changed insignificantly, as shown by the dashed line in Fig.3.

Thus the analysis showed that the modified inductive rule is of limited applicability, being valid only for some molecules. In the remaining cases there are appreciable infringements of this rule, as a result of which the average B–B distances are almost independent of the distance from the carbon atoms in the molecules of *closo*-carbaboranes.

V. EXOPOLYHEDRAL B–X BONDS

The B–Hal bonds proved to be most thoroughly investigated among the exopolyhedral bonds formed by boron atoms in carbaboranes. Compared with, for example, the C–I bond mentioned above, their specific features consist in the fact that all the B–Hal distances in the carbaboranes investigated[13,30,32–34,42,43–48], where Hal = Cl, Br, or I, are greater by 0.01–0.1 Å than the corresponding distances in the simplest compounds of the type $BHal_3$.[58]# This is consistent with the fact that the electron-accepting properties of the C_2B_{10} carbaborane nucleus are manifested much more weakly in relation to the substituents attached to the boron atoms than in relation to the substituents at the carbon atoms[59]. It is also of interest to note that, in contrast to the C–H bonds (see above), the B–Cl vibration frequencies in carbaboranes are lower than in the B_2Cl_4 and BCl_3 molecules[60].

#The only exception is the B–Cl distance in the $1,7\text{-}C_2H_2B_{10}H_7CH_3ClI$ molecule (1.69 Å),[44] which is somewhat smaller than in BCl_3.

The B–C distances in the four carbaboranes investigated[25,36,39] are 1.55–1.60 Å, which is close to the B–C distances in the $B(CH_3)_3$ (1.578 Å)[61] and $1\text{-}CH_3B_5H_9$ (1.595 Å)[62] molecules and to values expected on the basis of Eqn.(4) (Fig.2) for the polyhedral C–B bonds with $n_C = 4$. For $1,2\text{-}C_2B_{10}$. $.(CH_3)_4H_8$, this distance is significantly longer (1.68 Å).[44]

The B–B distance between the two carbaboranyl systems in $(1,2\text{-}C_2B_{10}H_{11})_2$ is 1.660 Å,[27] which is appreciably smaller than the polyhedral distances of the same type, but is close to the corresponding distance (1.686 Å)[63] between the *closo*-borane fragments in $10,10'\text{-}\{B_{10}H_8[S(CH_3)_2]\}_2$ and to the distance (1.678 Å)[64] in its analogue $2,2'\text{-}(1\text{-}B_9H_8S)_2$.

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It is seen from the foregoing that individual aspects of the geometrical structures of carbaboranes have now been investigated in fair detail. This applies primarily to the structure of *closo*-carbaboranes and especially to the structure of the icosahedral carbaboranes with the C_2B_{10} skeleton. The accumulated data permit a classification of the internuclear distances and make it possible to discover certain rules in the variation of the polyhedral bonds in carbaboranes. The exopolyhedral C–X and B–X bonds have been studied much less, although they undoubtedly merit a special systematic investigation.

During the preparation of this article, two reviews devoted to the chemistry of carbaboranes were published[65,66], which demonstrates yet again the vigorous development of this field of chemistry.

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