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The Application of Certain Physical Methods in the Study of the Properties of Carborane-12† and Its Derivatives

V.I.Stanko, V.V.Khrapov, and T.A.Babushkina

The review presents the results of the application of various physical methods (X-ray diffraction analysis, electron diffraction, ^{1}H, ^{11}B, and ^{13}C nuclear magnetic resonance, nuclear quadrupoler resonance, nuclear gamma-resonance, and the dipole moment method) in the study of the geometric and electronic structures of the isomers of carborane-12 and a number of its derivatives. The results obtained with the aid of these methods are compared.
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I. INTRODUCTION

In view of the nature of the bonds in which boron and particularly carbon atoms are involved, which is unusual for classical organic chemistry, and the capacity of carboranes to take part in various chemical reactions such as metallation, electrophilic substitution, and others, their chemistry now constitutes one of the most interesting and vigorously developing fields in the chemistry of organic derivatives of the elements.

However, many problems associated with the reactivity and structure, with the transmission of the influence of substituents via the icosahedral skeleton, with the dynamics of structural rearrangements, etc. are still not entirely clear. The difficulty of solving these problems by the methods of classical chemistry are evident. On the other hand, with the aid of a series of physical methods, it is possible to make a significant approach to an understanding of the phenomena associated with the characteristics of the structure and the nature of the bonds in carborane systems.

Bearing in mind the continuous growth of interest in the chemistry of carboranes (the number of publications has now exceeded 500), the fact that the relevant information is scattered in a wide variety of journals, and also the virtual absence of reviews on the application of physical methods in the study of carboranes, it appeared interesting to compile the available information in a single review. The aim of the present review was to give the fullest possible description of the state of research using a series of familiar physical methods. Since the review deals mainly with the thoroughly investigated *closo*-carborane-12, subsequently the prefix "*closo*" will be omitted.

The numbering of the atoms in the icosahedron differs from that which has been proposed and follows the rule that the 2nd atom is linked to the 7th and 8th atoms, the second carbon atom in the isomers corresponding to the 2nd atom for *ortho*-carborane, the 7th atom for *meta*-carborane, and the 12th atom for *para*-carborane‡.

† Dicarba-*closo*-dodecaborane(12) [Ed. of Translation].

‡ *o*-, *m*-, and *p*-Carboranes are 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaboranes(12) [Ed. of Translation].

The following abbreviations have been adopted: NMR = nuclear magnetic resonance; NGR = nuclear gamma-resonance [Mössbauer spectroscopy]; CS = chemical shift in NMR spectra; IS = isomer shift in Mössbauer spectra; QS = quadrupole splitting in Mössbauer and NQR spectra; SSIC = spin–spin interaction constant in NMR spectra; LCAO – MO = method of molecular orbitals with linear combination of atomic orbitals; SCF = self-consistent field method; NEMO = non-empirical molecular orbital method; CNDO/2 = method of complete neglect of differential overlap.

Table 1. The bond lengths (Å) in *o*-, *m*-, and *p*-carboranes (according to X-ray and electron diffraction studies).

o-$B_{10}H_{12}C_2$ [27]		*o*-$B_{10}H_{10}C(CH_2Br)_2$ [3]		*o*-$B_{10}Br_2H_{10}C_2$ [6]		*o*-$B_{10}Br_4H_8C_2$ [7]		*o*-$B_{10}Cl_4H_8C_2$ [1]		*o*-$B_9C_2H_{12}AlEt$ [19]	
C—C (1,2)	1.65	1.64		1.64		1.65		1.67		C—Al	1.561
B—C (2,3)	1.708	1.71	av. 1.72	1.71	av. 1.72	1.73	av. 1.72	1.73	av. 1.715	B—C	1.697
(2,7)		1.73		1.73		1.71		1.70		B—B	1.777 (av.)
B—B (3,7)	1.800	1.78	av. 1.783	1.76	av. 1.773	1.78	av. 1.78	1.81	av. 1.803	Al—B	2.137
(7,11)		1.79		1.80		1.78		1.79		Al—C	2.173
(6,10)		1.76		1.73		1.77		1.75			
(10,11)		1.75		1.74		1.79		1.78			
(11,12)	1.787	1.75	av. 1.761	1.76	av. 1.754	1.76	av. 1.779	1.76	av. 1.781		
(10,12)		1.77		1.78		1.79		1.81			
(9,12)		1.81		1.73		1.78		1.81			

m-$B_{10}H_{12}C_2$ [27]		*m*-$B_{10}Br_2H_{10}C_2$ [14]		*m*-$CH_3CB_{10}H_9Br_2CH$ [16]		*p*-$B_{10}H_{12}C_2$ [26]	
B—C (1,2)	1.719	1.64		B (9)—Br (9)	2.04	1.719	
(1,4)		1.68	av. 1.676	B (10)—Br (10)	1.99		
(1,5)		1.74		B (12)—Br (12)	1.99		
B—B (2,3)	1.828	1.89		B—C av.	1.73	1.792 (in the band of C atoms)	
(2,6)	1.790	1.72	av. 1.775	B—B av.	1.73	1.772	
(4,5)	1.83	1.83				(connecting two pentagonal pyramids)	
(6,11)		1.81					
(5,9)		1.70	av. 1.763				
(6,10)	1.816	1.80					
(9,10)		1.77					

II. X-RAY AND ELECTRON DIFFRACTION STUDIES

Numerous X-ray[1-21] and electron[22-28] diffraction studies on carborane-12 confirmed Hoffman and Lipscomb's view[29] that these systems have the icosahedral structure. Table 1 lists the bond lengths for some of these molecules. The observed bond lengths and angles agree fairly well with the icosahedral structure. The icosahedral structure of carboranes persists also on substitution of one boron atom in *o*-carborane by another heteroatom[19] (Table 1). Available data show that: (1) derivatives of carborane-12 have an almost regular icosahedral skeleton; (2) the carbon and boron atoms in these molecules have a coordination number of six (five neighbours in the molecular skeleton and one hydrogen atom), which is unusual for the familiar carbon and boron compounds; (3) the bond lengths in the icosahedron vary in the following sequence: B–B > B–C > C–C.

Unfortunately it is impossible to investigate the structures of labile carborane systems and the dynamics of their various transformations by X-ray and electron diffraction methods. For this reason, an increasing amount of structural information about carborane-12 derivatives has been obtained in recent years by other procedures—primarily by microwave and optical spectroscopic methods.

III. THEORETICAL CALCULATIONS

Carboranes having the general formula $C_2B_nH_{n+2}$ have electron-deficient molecules in which the number of valence electrons of the atoms forming the molecular skeleton is insufficient to link all the atoms by covalent (two-electron) bonds. Thus in carborane-12 thirteen electron pairs are involved in the formation of thirty bonds. To account for the structure of polyhedral molecules and also for the unusual valence state of the carbon atom, the concept of many-centre bonds is resorted to. On the basis of these ideas, Hoffman and Lipscomb[29] proposed in 1962 a nearly icosahedral structure for $C_2B_{10}H_{12}$, which is an example of this series of compounds. Depending on the positions of the carbon atoms in the icosahedral skeleton, three different isomers were suggested. All three isomers of carborane-12 (*ortho*-, *meta*-, and *para*-) have now been synthesised[30-32].

Various methods have been used in the calculations on the structural features of carboranes and their derivatives[6,7,33-41]. Hoffman and Lipscomb were the first to employ the extended Hückel method for the calculation of the charge distribution on the atoms in carborane-12 molecules[29]. Subsequently, in the development of quantum-chemical calculations, various versions of non-empirical methods were used to estimate the electronic structure of carboranes. Thus diagonal matrix elements obtained by the LCAO-MO SCF method for B_2H_4, C_2H_6, and B_4H_4 [3] have been used in the calculations[6,7,33-38]. The coordinates of the atoms and the distances between them were taken from experimental data (mainly from the results of X-ray and electron-diffraction analyses).

The charge distribution in the lower carboranes and in $C_2B_{10}H_{12}$ enabled Lipscomb[6,7] to formulate the rule of substitution in carboranes, which states that "electrophilic reactions should proceed at the boron atoms furthest away from the carbon atoms". This rule was confirmed in studies on the electrophilic halogenation of *o*- and *m*-carboranes.

Subsequently Lipscomb and coworkers[29,40] applied the non-empirical NEMO method. The matrix elements were taken from results of calculations by the SCF method on the small molecules of the simplest lower carboranes, for example $B_4C_2H_6$. The charges on the carbon and boron atoms in various carboranes were estimated by the NEMO methods[40] (Table 2).

Table 2. The calculated charges of the boron atoms in *o*-, *m*-, and *p*-carboranes and the pK_a values for all the isomeric carboranols-12.

Carborane	The numbering system for the carborane atoms according to the data of the authors of the review	Numbering used in Refs.29,40, and 41	Hückel method (Ref.29)	CNDO/2 (Ref.41)	NEMO-1 (Ref.40)	NEMO-2 (Ref.40)	$\Delta\nu$, cm^{-1}	pK_a for carboranols*		
								expt.	found from correlation equations (I) and (II)	
									(I)	(II)
ortho-	3,6	3,6	0.081	0.05	0.36	0.10	410	22.6±0.4	21.0	22.3
	4,5,7,8	4,5,7,11	−0.027	0.03	0.32	0.08	320	25.6±0.2	26.7	26.2
	9,11	8,10	−0.162	0.02	0.13	−0.08	245	24.7±0.3**	31.8	29.4
	10,12	9,12	−0.158	0.02	0.12	−0.09	230	30.5±0.5	32.3	30.0
meta-	2,6	2,6	0.101	0.04	0.38	0.12	370	24.3±0.2	23.5	24.0
	3,5,8,11	4,5,8,11	−0.030	0.04	0.32	0.08	300	28.4±0.3	28.0	27.1
	4,12	5,12	−0.026	0.03	0.31	0.07	310	27.8±0.3	27.3	26.6
	9,10	9,10	−0.162	0.01	0.10	−0.10	260	29.6±0.3	30.4	28.8
para-	2	2	−0.031	0.03	0.29	0.06	310	27.7±0.3	27.3	26.6

* The pK_a were determined by potentiometric titration with Bu_4NOH in CH_3CN and spectroscopically. (I) pK_a = 46.90 − 0.0632$\Delta\nu$ ± 0.8; (II) $\Delta\nu$ = 1088.95 −28.64 pK_a ± 23; r = 0.9; within the limits of the series of *o*- and *m*-carboranols, the correlation coefficient reaches 0.98.
** *o*-Carboranol-9 undergoes degradation during titration in CH_3CN.

The total energies of carboranes calculated by these workers show that the stability of the carborane-12 isomers should vary in the sequence *meta* > *ortho* > *para*. This is in conflict with experimental data, which suggest that *p*-carborane is more stable but comparable to *m*-carborane and that both are more stable than *o*-carborane. Thus the total energies obtained by the NEMO methods cannot predict accurately the small differences between the energies of the carborane-12 isomers. The dipole moments calculated for the carborane-12 isomers by the NEMO method[40] exceed the experimental values approximately by a factor of 2.5 with retention of the sequence of changes in the triad.

The laborious nature and certain disadvantages of the non-empirical methods for calculations on carborane systems make it necessary to resort to the semi-empirical LCAO-MO methods in which the integrals in the matrix elements which are most difficult to evaluate are approximated by experimental data.

With these assumptions, the CNDO/2 method was employed[41] to estimate the B–B bond lengths in various carboranes, the stability of the molecules, the atomic charge distribution in carborane skeletons, and the effects of substituents as well as in the calculation of intermediate states and dipole moments.

Examination of the methods used to calculate the structural characteristics of carboranes-12 and comparison of the results with X-ray diffraction and electron diffraction data as well as those derived by the dipole moment method

shows that the results obtained by semi-empirical computational methods are of greatest interest for the experimental chemist.

Certain information concerning the charge distribution on the boron atoms was obtained recently[42] by determining the pK_a or of all possible *B*-carboranols (Table 2). Although the introduction of a hydroxy-group at a boron atom in the carboranes-12 can lead to certain deviations from the charge distribution in the unsubstituted molecules, nevertheless the overall sequence and the calculated charges should be correlated with the changes in the pK_a. Table 2 shows that the charges on the boron atoms calculated theoretically are only of qualitative significance.

IV. DIPOLE MOMENTS

X-Ray diffraction studies on carboranes-12 and their *C*- and *B*-derivatives showed that a nearly icosahedral structure is retained in all the compounds.

The dipole moment method in conjunction with microwave spectroscopic methods (NMR and NQR) yields extremely valuable information about the structures of derivatives of carborane-12 isomers and particularly their *B*-halogeno-derivatives. This method, developed by a number of investigators[43-49], proved to be very convenient for the determination of the positions of the halogen atoms in *o*-, *m*-, and *p*-carboranes. It is based on a comparison of experimental and calculated dipole moments of various isomers of carborane-12, the calculated values being obtained as a rule with allowance for the differences between the B–B and the B–C bond lengths and some distortion of the valence angles. This is caused both by the infringement of the ideal symmetry of the icosahedral skeleton and by some steric hindrance between the hydrogen atoms attached to neighbouring boron atoms (the B–B–Hal angle is 122° instead of the ideal value of 120°). The calculations were based on the following dipole moments of the B–Hal bond: 1.67 D for *o*-carborane and 1.61 D for *m*-carborane. When the molecules of the halogeno-derivatives of *o*- and *m*-carboranes are regarded as ideal icosahedra, the B–Hal dipole moments are 1.59 D for *o*-carborane and 1.58 D for *m*-carborane. Since the dipole moment of *p*-carborane is zero, that of 2-chloro-*p*-carborane should in fact be equal to the B–Cl bond moment. It has been found[47] that the dipole moment of 2-chloro-*p*-carborane is 1.47 D.

Table 3 lists the experimental dipole moments of various carboranes and heterocarboranes-12 and Table 4 gives a compilation of the experimental and calculated dipole moments of a series of *B*-halogenocarboranes. It is interesting to note that, in the presence of boron–halogen and carbon–halogen bonds respectively, the dipole moment is higher and lower than that of unsubstituted carboranes[43]. This is evidence that the carbon and boron atoms form the positive and negative poles of the dipole respectively. All these considerations apply equally to *o*-, *m*-, and *p*-carbaphosphaboranes and carba-arsaboranes[58,59].

In a series of chemical and structural studies[50-53] it has been shown that, in the electrophilic halogenation of *o*-carborane, four halogen atoms enter the boron skeleton. The first and second halogen atoms enter preferentially the 10- and 12-positions, involving to some extent, depending on the halogenation conditions, also the boron atoms in the 9- and 11-positions of the *o*-carborane nucleus[54]. The third and fourth halogen atoms enter the 9- and 11-positions. In electrophilic halogenation two halogen atoms enter the *m*-carborane nucleus in the presence of $Fe(FeX_3)$ and four and more atoms in the presence of $AlCl_3$.[52,54,55] The first and second atoms enter mainly the 9- and 10-positions. The sites of the third and particularly the fourth halogen atoms could not be determined in this case from the number of the isomers formed (the principle first applied to carboranes by Wiesboeck and Hawthorne[56]). This was done with the aid of the dipole moment method and it was shown that one of the isomers has the 3(5, 8, 11), 9, 10-structure and the other the 4(12), 9, 10-structure[44,57].

Table 3. The dipole moments of the isomeric carboranes-12 and their derivatives.

Compound	μ_{exp}, D			
	in benzene	references	in cyclohexane	references
m-Carborane	2.76	44,45	2.78	43
	2.85	48		
9(10)-Chloro-*m*-carborane	4.22	44,45		
9(10)-Bromo-*m*-carborane	4.24	44,45		
9(10)-Iodo-*m*-carborane	4.20	44,45		
9,10-Dichloro-*m*-carborane	5.37	44,45		
9,10-Dibromo-*m*-carborane	5.40	44,45	5.14	43
9,10-Di-iodo-*m*-carborane	5.43	44,45		
3,4,9,10-Tetrachloro-*m*-carborane	5.86	44,45		
3,4,9,10-Tetrabromo-*m*-carborane	6.26	44,45		
B-Decachloro-*m*-carborane	6.29	44,45		
	4.39	44,45	4.31	
o-Carborane	4.45	44,45	4.49	43
	4.53	48		46
10(12)-Chloro-*o*-carborane	5.93	44,45		
3-Bromo-*o*-carborane	3.69	60		
4-Bromo-*o*-carborane	4.47	60		
9-Bromo-*o*-carborane	5.48	60		
10(12)-Bromo-*o*-carborane	5.90	44,45		
	5.98	60		
10(12)-Iodo-*o*-carborane	5.96	44,45		
10,12-Dichloro-*o*-carborane	6.98	44,45		
10,12-Dibromo-*o*-carborane	7.18	44,45	7.21	43
10,12-Di-iodo-*o*-carborane	7.02	44,45		
B-Decachloro-*o*-carborane	6.36	44,45		
1-Methyl-*o*-carborane	4.75	46		
1-Chloro-*o*-carborane	3.45	46	3.10	46
1-Bromo-*o*-carborane	3.34	60	3.36	46
2-Chloro-1-methyl-*o*-carborane	3.57	46	3.65	46
2-Bromo-1-methyl-*o*-carborane	3.80	46	3.80	46
p-Carborane	0.00	47,48		
2-Chloro-*p*-carborane	1.47	47		
1,2-Dibromo-*o*-carborane			2.82	43
1,7-Dibromo-*m*-carborane			1.64	43
Bis(chloro-*o*-phosphacarborane)			0.73	49
o-Phosphacarborane	3.87	58		
m-Phosphacarborane	2.39	58		
p-Phosphacarborane	0.68	58		
o-Arsacarborane	4.83	59		
m-Arsacarborane	2.76	59		
p-Arsacarborane	0.5	59		

Thus owing to the geometry of carborane-12, the dipole moment method is an effective procedure for the determination of the site of the substituent in the icosahedral skeleton of the molecule.

V. NMR SPECTROSCOPY

There are two main aspects to the application of nuclear magnetic resonance in the study of carboranes-12: in the study of the electronic properties of the carborane system and in the determination of the structures of newly synthesised compounds.

The elucidation of the electronic properties of carborane systems behaving as substituents and the transmission effects in carboranes are important for the determination of the nature of the bond in polyhedral molecules. Hawthorne et al.[61] investigated the electronic properties of 1,2- and 1,7-dicarbadodecaboranes and determined the σ constants by Taft's method[62] from the ^{19}F chemical shifts of the *m*- and *p*-fluorophenyl derivatives of *o*- and *m*-carboranes. They showed that the negative inductive effect ($-I$) of the *C*-substituted *o*-carbonyl group is close to that for halogens and that its resonance effect in the ground state is close to zero. A smaller inductive effect and a very small resonance (electron-donating) effect are characteristic of the *C*-substituted *m*-carbonyl group. It was found that in cyclohexane $\sigma_I = +0.375 \pm 0.010$ and $+0.194 \pm 0.010$ and $\sigma_R = +0.003 \pm 0.005$ and -0.039 ± 0.05 for the 1,2- and 1,7-carboranyl groups respectively.

Table 4. Comparison of the calculated and experimental dipole moments[44,46,47] of halogeno-derivatives of *o*-, *m*-, and *p*-carboranes.

Compound	μ_{exp}, D	Possible positions of halogen atoms in ring	μ_{calc}, D
10,12-Dichloro-*o*-carborane	6,98	9,10	6,27
10,12-Dibromo-*o*-carborane	7,18 cp. 7,08	10,12	7,28
10,12-Di-iodo-*o*-carborane	7,02	9,11	6,07
B-Decachloro-*o*-carborane	6,36	3,4,5,6,7,8,9, 10,11,12	6,23
9,10-Dichloro-*m*-carborane	5,37	9,10	5,50
9,10-Dibromo-*m*-carborane	5,40 cp. 5,40	4,12	4,41
9,10-Di-iodo-*m*-carborane	5,43	9(10), 4(12) 3,9	5,21 4,83
B-Decachloro-*m*-carborane	4,39	2,3,4,5,6,7,8, 9,10,11,12	4,41

The difference between the electronic properties of the carborane system depending on the atom involved in the formation of a bond with the fluorophenyl substituent was demonstrated for 1-substituted and 3-substituted *o*-carborane derivatives[63]. It was shown that the chemical shifts of the fluorine atoms relative to fluorobenzene in chloroform are $\delta_p^F = -2.51$ and -2.22 p.p.m. and $\delta_m^F = -2.22$ and -0.35 p.p.m. Hence $\sigma_I = +0.40$ and $+0.13$ and $\sigma_R = +0.01$ and $+0.06$ were calculated for 1-substituted and 3-substituted *o*-carboranes respectively.

The dependence of electronic properties on the type of solvent was also investigated by Taft's method on the basis of the ^{19}F chemical shifts of the 1-*o*-, 3-*o*-, and 1-substituted *m*-carborane derivatives with *m*- and *p*-fluorophenyl substituents[64].

The study of the influence of substituents at the carbon atoms in *o*- and *m*-carborane systems on their electronic properties[65] demonstrated that Taft's method cannot be used to estimate the properties of *C*-substituted *o*-carboranyl groups. This is in all probability due to the specific "cisoid" disposition of the substituent X and the fluorophenyl ring, which leads to a marked dependence of the ^{19}F chemical shifts on the magnetic anisotropy of the substituent. The influence of the unusual "*ortho*-effect" was also noted in the ^{35}Cl NQR spectra of 1-CH_2Cl-2-X-*o*-carboranes[66].

The most complete investigation of the electronic properties of carborane systems, their anions, and metallocarboranes was made by Adler and Hawthorne[67]. They give a kind of compilation of the available data on the electronic properties of carborane molecules. They note that the $-I$ effect for *C*-substituted *o*-carboranes is greater than for *m*-carboranes. The decrease of σ_I for 3-substituted *o*-carboranes (almost to zero) confirms that the transmission of the electrostatic Coulombic effect of carbon atoms diminishes fairly rapidly with distance. Carboranes with substituents at the boron atoms furthest away from the carbon atoms should have an appreciable $+I$ effect.

A second important problem involved in the understanding of the nature of the bond in carboranes is that of the transmission of the electronic influence of substituents via the carborane nucleus. An attempt was made to solve it[68] by investigating methylmercuri-derivatives of *o*- and *m*-carboranes, namely 1,7-R-$CB_{10}H_{10}$.CHgMe and 1,2-R-$CB_{10}H_{10}$CHgMe. The HgMe group served in this case as an indicator of the influence of the substituent characterised by the spin–spin interaction constant $J_{^{199}Hg\text{-}C\text{-}^1H}$. It was shown that, depending on R, $J_{^{199}Hg\text{-}C\text{-}^1H}$ in *o*-carborane varies very significantly (137.2–149.0 Hz in CCl_4). In *m*-carboranes the influence of R is greatly reduced: in weakly solvating solvents $J_{^{199}Hg\text{-}C\text{-}^1H}$ remains constant within the limits of the error of the measurements (135.9–136.3 Hz in CCl_4). For *o*-carboranes in highly solvating solvents (dioxane, pyridine, dimethyl sulphoxide) and CH_2Cl_2, a satisfactory correlation

$$J^R_{Hg-Me} = J^0_{Hg-Me} + m\sigma^*$$

was found for all R, except R = $PhCH_2$, $MeOCH_2$, or H. For these substituents R, the authors[68] suggest an intramolecular coordination. The above relations indicate a change in the shape of the electron cloud in the Hg–Me bond as a function of the inductive properties of the substituent R. Unfortunately the transmission of effects by the *o*-carborane nucleus ($C_2B_{10}H_{10}$) is difficult to assess from these results, since they reflect the transmission through the *o*-R–C–$B_{10}H_{10}$–C–Hg–Me system only.

Table 5. The ^1H chemical shifts in the spectra of *C*-monosubstituted *o*-, *m*-, and *p*-carboranes in carbon tetrachloride relative to HMDS*.[69,70]

R(C)	σ_I	σ_R	σ^*	Carboranes		
				o-	*m*-	*p*-
CH_2Cl	0.14	−0.03	1.05	3.93		
CH_2Br	—	—	1.00	3.96		
CH_2I	—	—	0.85	3.88		
Cl	0.40	−0.18	2.9	3.91	2.91 (2,93)	2.55
Br	0.44	−0.16	2.8	3,85	2.87 (2,91)	2.71
I	0.44	−0.14	2.36	3,72	2.87 (2,85)	2.91
Et_3Sn	—	—		3.26	2.88	2.62
Me_3Sn	—	—		3.06	2.89	2.67
H	0.0	0.0	0.49	3.50	2.85	2.68
Me	−0.08	−0.15	0.00	3.68	2.80	2.45

* Possibly hexamethyldisiloxane [Ed. of Translation].

Evidently direct information about the transmission of effects through carborane nuclei can be obtained in studies on the chemical shifts of the protons in the C–H bond with different R at the second carbon atom[69] (Table 5). The introduction of a halogen atom at one of the carbon atoms in *o*-carborane causes a shift of the signal due to the proton in the C–H bond involving the second atom to a lower field,

the chemical shifts varying in parallel with the σ* constants of the halogens (Table 5), which reflect the variation of their electron-accepting properties. In *C*-halogeno-substituted *p*-carboranes, whose carbon atoms are located at the opposite corners of the icosahedron, the C–H proton chemical shifts and the σ* constants of the halogen atoms were found to vary in opposition.

The transmission of effects through icosahedral molecules containing three-centre bonds is difficult to describe in terms which are at present generally accepted; nevertheless the variation of the chemical shifts of the C–H protons in *C*-monohalogeno-substituted *o*- and *p*-carboranes indicates two opposed effects of the halogen atoms on the electron density at the second carbon atom. For *C*-halogeno-substituted *m*-carboranes, these effects cancel out to such an extent that the chemical shift of the C–H proton hardly changes regardless of the nature of the halogen.

The introduction of substituents into the carborane ring at the boron atoms alters the chemical shifts of the C–H protons and the form of the ^{1}H NMR spectra[70]. Thus a doublet structure associated with the non-equivalence of the C–H bonds is observed in the spectra of *10*-monosubstituted *o*-carboranes and also of the spectra of *B*-substituted *m*- and *p*-carboranes permits conclusions concerning the symmetry of the molecules of these compounds. The appreciable change in the C–H proton chemical shifts is evidence for a ready transmission of the effect of the substituent in carborane nuclei (Table 6).

Table 6. The chemical shifts of the protons in the C–H bonds of *B*-substituted *o*-, *m*-, and *p*-carboranes[69,70].

Compound	δ relative to TMS*	Compound	δ relative to TMS*
o-Carborane	3.50	10-Iodo-*m*-carborane	3.03
10-Chloro-*o*-carborane	3.40; 3.54	9,10-Dichloro-*m*-carborane	2.85
10-Bromo-*o*-carborane	3.42; 3.53	9,10-Dibromo-*m*-carborane	2.98
10-Iodo-*o*-carborane	3.67; 3.87	9,10-Di-iodo-*m*-carborane	3.14
10,12-Dichloro-*o*-carborane	3.42	4,9,10-Trichloro-*m*-carborane	2.78; 3.19
10,12-Dibromo-*o*-carborane	3.63	3,4,9,10-Tetrachloro-*m*-carborane	3.07
10,12-Di-iodo-*o*-carborane	3.94	*p*-Carborane	2.68
m-Carborane	2.85	2-Chloro-*p*-carborane	2.79; 3.15
10-Chloro-*m*-carborane	2.87	2-Bromo-*p*-carborane	2.76; 3.13
10-Bromo-*m*-carborane	2.94	2-Iodo-*p*-carborane	2.74; 3.09

* Tetramethylsilane [Ed. of Translation].

Hitherto all that has been said referred to the ^{1}H NMR of the protons linked to the carbon atoms in the carborane system. Fairly numerous studies have been made on ^{11}B NMR and ^{1}H NMR of the protons linked to the boron atoms[14,36,69,71–79]. In most of these investigations the second aspect of the problem was solved—the determination of the structure of newly synthesised compounds.

The ^{1}H NMR spectra of the protons linked to boron atoms are always greatly complicated both by quadrupole broadening (owing to the nuclear quadrupole moment of ^{11}B) and by the ^{1}H–^{11}B spin–spin interaction. The ^{1}H NMR spectra are greatly simplified when ^{1}H–{^{11}B} heteronuclear resonance is employed with the application of the frequency at the resonance value for ^{11}B. The chemical shifts of the protons at the boron atoms and also the spin–spin interaction constants $J_{^{11}B-^1H}$ for *o*-, *m*-, and *p*-carboranes and their organotin derivatives have been determined[69] (Table 7).

The difficulties associated with the employment of ^{11}B NMR spectroscopy are due mainly to two causes: (1) the broadening of the NMR line owing to the quadrupole moment of the ^{11}B nucleus and (2) due to the fact that in the usually employed NMR spectrometers (frequencies of 19, 124, and 32.08 MHz) the spin–spin interaction constants $J_{^{11}B-^1H}$ are of the same order of magnitude as the ^{11}B chemical shift. This hinders the assignment of the ^{11}B frequencies to the structurally non-equivalent boron atoms in the complex molecules of carboranes and their derivatives. The method of ^{11}B–{^{1}H} heteroresonance has been used recently in the study of the ^{11}B NMR spectra in conjunction with a noise generator to suppress the ^{11}B–^{1}H spin–spin interaction.

Table 7. The chemical shifts of the protons at the boron and carbon atoms in certain carboranes[69].

Compound	Equivalent protons	^{1}H chemical shift δ relative to TMS*, p.p.m.
o-Carborane	1,2	3.50
	3,6	2.12
	4,5,7,8	2.12
	9,11	2.09
	10,12	2.09
m-Carborane	1,7	2.85
	2,6	2.65
	3,5,8,11	2.20
	4,12	2.20
	9,10	2.20
p-Carborane	1,12	2.68
	2—11	2.16
o-Triethylstannylcarborane	2	3.26
	3,6	2.29
	4,5	2.29
	7,8	2.29
	9,10	2.08
	10,12	2.08
m-Triethylstannylcarborane	7	2.88
	2,6	2.52
	3,5	2.21
	4	2.21
	8,11	2.21
	9,10	2.21
	12	2.21
p-Triethylstannylcarborane	12	2.63
	2,3,4,5,6	2.30
	7,8,9,10,11	2.21

* Tetramethylsilane (Ed. of Translation).

Some of the results of the authors of the review (see Refs. 71 and 79) for ^{11}B NMR of carborane-12 isomers and a number of its derivatives are presented in Table 8. On the basis of the structure of the carborane-12 isomers, it is possible to postulate the number of equal-intensity lines which should comprise the ^{11}B–{^{1}H} NMR spectrum of the given compound. Thus in the spectra of unsubstituted *o*- and *m*-carboranes there are four types of structurally non-equivalent boron atoms and in the ^{11}B–{^{1}H} NMR spectra of each of these compounds there should be four lines with the intensity ratios 2 : 4 : 2 : 2, which is in fact observed experimentally. Since all the boron atoms in *p*-carborane are equivalent, the ^{11}B–{^{1}H} spectrum of this compound consists of one line. The ^{11}B–{^{1}H} spectra of 2-halogeno-*p*-carboranes and 10-halogeno-*o*-carboranes should consist of six lines with the intensity ratios 2 : 2 : 2 : 2 : 1 : 1 and the spectra of 9-halogeno-*m*-carboranes should consist of seven lines with the intensity ratios 2 : 2 : 2 : 1 : 1 : 1 : 1. Although Table 8 shows that the

Table 8. The parameters of the $^{11}B-\{^1H\}$ NMR spectra of the isomeric carboranes-12 and their *B*-monohalogeno- and *BB*-dihalogeno-derivatives [in tetrahydrofuran and carbon tetrachloride solutions; $(MeO)_3B$ standard].

Unsubstituted carboranes				Chlorocarboranes				Bromocarboranes				Iodocarboranes			
Atom	δ, p.p.m.	$J_{^{11}B-^1H}$, Hz	rel. int.	Atom	δ, p.p.m.	$J_{^{11}B-^1H}$, Hz	rel. int.	Atom	δ, p.p.m.	$J_{^{11}B-^1H}$, Hz	rel. int.	Atom	δ, p.p.m.	$J_{^{11}B-^1H}$, Hz	rel. int.
o-carborane				10-chloro-*o*-carborane				10 bromo-*o*-carborane				10-iodo-*o*-carborane			
B(10, 12)	21.4	150	2	B(10)	11.5	0	1	B(10)	16.7	0	1	B(12)	20.1	160	1
B(9, 11)	28.5	160	2	B(12)	20.6	140	1	B(12)	20.0	190	1	B(9, 11)	26.5	165	2
B(3, 4, 5, 6, 7, 8)	32.8	170	6	B(9, 11)	26.9	165	2	B(9, 11)	27.4	185	2	B(3, 4, 5, 6, 7, 8)	32.5	140	6
				B(3, 4, 5, 6, 7, 8)	32.7	170	6	B(3, 4, 5, 6, 7, 8)	33.2	150	6	B(10)	36.1	0	1
				10,12-dichloro-*o*-carborane				10,12-dibromo-*o*-carborane				10,12-di-iodo-*o*-carborane			
				B(10, 12)	11.4		2	B(10, 12)	18.2		2	B(9, 11)	24.0		2
				B(9, 11)	26.5		2	B(9, 11)	25.6		2	B(3, 4, 5, 6, 7, 8, 10, 12)	31.8		8
				B(4, 5, 7, 8)	33.4		4	B(4, 5, 7, 8)	32.6		4				
				B(3, 6)	36.0		2	B(3, 6)	35.0		2				
m-carborane				9-chloro-*m*-carborane				9-bromo-*m*-carborane				9-iodo-*m*-carborane			
B(9, 10)	25.5	150	2	B(9)	17.0	0	1	B(4, 10, 12)	24.3	155	3	B(4, 12)	24.3	185	2
B(4,12)	29.3	170	2	B(4, 12)	24.2	120	2	B(9)	27.0	0	1	B(10)	26.7	150	1
B(3; 5, 8,11)	31.5	160	4	B(10)	27.2	180	1	B(5, 11)	30.0	170	2	B(3, 5, 8, 11)	31.0	165	4
B(2, 6)	35.5	180	2	B(5, 11)*	30.6	160	2	B(3, 8)*	31.7	165	2	B(2)*	35.1	186	1
				B(3, 8)*	31.6	120	2	B(12)*	35.5	155	1	B(6)*	37.4	180	1
				B(2)*	35.3	150	1	B(6)*	38.9	165	1	B(9)	42.5	0	1
				B(6)*	39.1	170	1								
				9,10-dichloro-*m*-carborane				9,10-dibromo-*m*-carborane H				9,10-di-iodo-*m*-carborane			
				B(9, 10)	17.8		2	B(4, 9, 10, 12)	24.0		4	B(4, 12)	22.4		4
				B(4, 12)	24.1		2	B(3, 5, 8, 11)	31.4		4	B(3, 5, 8, 11)	29.9		4
				B(3, 5, 8, 11)	32.3		4	B(2, 6)	39.6		2	B(2, 6)	36.9		2
				B(2, 6)	41.4		2					B(9, 10)	38.4		2
p-carborane				2-chloro-*p*-carborane				2-bromo-*p*-carborane				2-iodo-*p*-carborane			
B(2, 3, 4, 5, 6, 7, 8, 9, 10, 11)	33.2	165	1	B(2)	22.9	0	1	B(2)	30.5	0	1	B(3, 4, 5, 6, 7, 8, 9, 11)	32.0	165	8
				B(3, 4, 5, 6, 7, 8, 9, 11)	34.0	170	8	B(3, 4, 5, 6, 7, 8, 9, 11)	33.4	165	8	B(10)	36.2	150	1
				B(10)	39.0	130	1	B(10)	39.5	120	1	B(2)	46.4	0	1

* Assignment not determined. For explanation, see text.

experimental spectra differ from the theoretical spectra both as regards the number of lines and their intensities (owing to the overlapping of lines with close chemical shifts), nevertheless the results[79] permit the assignment of the lines in the ^{11}B NMR spectrum of each compound. This assignment is unambiguous for *B*-monohalogeno-derivatives of *o*- and *p*-carboranes, although there are certain difficulties for the analogous *m*-carborane derivatives. Thus the assignment of the lines in the spectra of 9-halogeno-*m*-carboranes for the B(5, 11) and B(3, 8) atoms and also for B(2) and B(6) is fairly difficult without additional data and the ^{11}B chemical shifts quoted in Table 8 for these groups may have to be interchanged.

The application of ^{13}C NMR in the study of carboranes is so far extremely limited. There have been only two communications[80,81] on the ^{13}C NMR chemical shifts of carborane isomers and some of their analogues (Table 9). Presumably the ^{11}B and ^{13}C chemical shifts in similar chemical environments are influenced by the same factors. It was noted that on substitution the change in the chemical shifts of these nuclei in carboranes is in the same direction.

The observation of ^{31}P NMR spectra of carbaphosphadodecaborane derivatives[82] has been only mentioned.

Hitherto we have spoken of high-resolution NMR spectra for the nuclei of various atoms forming the carborane skeleton. The application of broad-line NMR and the spin–echo method, which permit the investigation of the geometry of relative positions, molecular mobility, exchange processes, and the dynamics of the motions in solids, are extremely promising. Only one study has been published[83] in which broad-line NMR was used in conjunction with calorimetric and X-ray diffraction data in the study of molecular mobility in crystalline *o*- and *m*-carboranes. All the results support the view that the reorientational disorder in crystalline carboranes has a kinetic basis. A phase transition was observed in the *o*-isomer at 4.0° ± 3.0°C. The measurement of the second moments of the proton lines in the NMR spectra of carborane isomers as a function of temperature showed that molecular reorientational motions occur down to −130°C. It is difficult to overestimate the value of these first experimental data, which lead to new fields in the study of the characteristics of the crystal structures of carboranes and to the understanding of the dynamics of the molecular motions in solids.

VI. NQR SPECTROSCOPY

NQR data constitute a completely new type of information about molecular structures and permit the determination of the type of electron distribution in space near the nucleus of the given atom.

Although the nuclei of the boron atoms forming the carborane skeleton do have quadrupole moments, purely NQR studies have been made not on boron nuclei (owing to experimental difficulties) but on halogen nuclei (^{35}Cl, ^{79}Br, and ^{127}I) in various derivatives of *o*-, *m*-, and *p*-carboranes[53,84-92] (Table 10). ^{35}Cl and ^{79}Br NQR spectroscopy was applied to halogenocarboranes for the first time[84] in 1965 to elucidate the nature of the carborane nucleus as a substituent in the systems *o*-

$HCB_{10}H_{10}C-C_6H_4-Y$ and *o*-$HCB_{10}H_{10}C-(CH_2)_nCl$ (I), where

$n = 1, 2, 3, 4 \ldots$ (series I) and to investigate the transmission of effects via the carborane nucleus in the system *o*-$Y-CH_2C_2B_{10}H_{10}CH_2-Y$ (II) (series II, Y = Cl or Br).

Table 9. ^{13}C chemical shifts of certain carboranes in acetone[80,81].

Compound	^{13}C chemical shifts relative to CS_2, p.p.m.	Compound	^{13}C chemical shifts relative to CS_2, p.p.m.
1,2-$B_{10}C_2H_{12}$	137.3	1,7-$Me_3SiCB_{10}H_{10}CSiMe_3$	125.4
1,7-$B_{10}C_2H_{12}$	137.4	1,7-$MeSCB_{10}H_{10}CSMe$	120.1
1,7-$B_{10}C_2Br_2H_{10}$—9,10-dibromo	139.7	1,12-$B_{10}C_2H_{12}$	129.3

It was found that the *o*-carborane system exhibits powerful electron-accepting properties, occupying an intermediate place between the NO_2 and COOH groups. The Hammett σ constant for the *o*-carboranyl substituent was estimated from the NQR frequencies as 0.4 ± 0.2, which agrees well with the estimates of the σ_I and σ_R constants from NMR spectra. The decay coefficient for the transmission of the effect of a substituent X in a chain consisting of methylene groups in series I (see above) has also been determined[84] and found to be 0.44 ± 0.01. The study of the transmission of effects through the carborane nucleus itself by comparing the ^{35}Cl NQR frequencies in series II for Y = Cl and in series I for $n = 1$ with the frequencies for $ClCH_2-C\equiv C-CH_2Cl$ and $HC\equiv C-CH_2Cl$ showed that the carbon atoms in the carborane ring do transmit effects. The powerful electron-accepting properties of the $CH_2-C_2B_{10}H_{11}$ and $Ph-C_2B_{10}H_{10}$ substituents follow also from the investigation of the 79Br and ^{81}Br NQR of the corresponding halogen-containing organomercury compounds[88]. Comparison of the ^{35}Cl and ^{127}I frequencies of 2-halogeno-*p*-carboranes, 9-halogeno-*m*-carboranes, and 10-halogeno-*o*-carboranes[86,87] showed that the polarity of the boron–halogen bond decreases in the series *o*-carborane > *m*-carborane > *p*-carborane, which is consistent with the variation of the reactivity of these isomers.

A number of studies have been made[66,90-93] on the ^{35}Cl NQR spectra of the *o*-$XC-B_{10}H_{10}-C-CH_2Cl$ system, where X = H, $ClCH_2$, Et, Me, SMe, HS, $SiMe_3$, MeOOC, NH_2CO, MeHg, Cl, Br, I, Ph, ClCO, or COOEt.

To elucidate the transmission of the effects of substituents in this system, the entire set of ^{35}Cl NQR data were examined[66]. Problems of this kind are usually solved by establishing a correlation between the changes in the characteristics investigated in the given method (NQR frequency, chemical shift, or the spin–spin interaction constant for NMR, etc.) and the Taft–Hammett constants of the substituents in the given series of molecules. It has been shown[66] that in the *o*-$X-C-B_{10}H_{10}C-CH_2Cl$ system the two-parameter correlation of the ^{35}Cl NQR frequencies with the σ constants of the substituents is absent as well as the one-parameter correlation. This is probably evidence for the important role of the steric factors due to the specific disposition of the substituent and the CH_2Cl group, which are in the cisoid positions relative to one another in the *o*-carborane system (a kind of *"ortho"* effect). It appears evident that in the study of the transmission of the electronic influence of substituents in the *o*-carborane series there is no point in subdividing the substituents in accordance with the type of the electronic effect (this was attempted, for example, by Voronkov et al.[91]), since steric interactions are of decisive importance in the behaviour of both NQR frequencies and the NMR chemical shifts in these systems.

NQR spectroscopy is one of the physical methods for the determination of the structural characteristics, identification, and determination of the purity[53,85,86] of the *B*-halogenocarboranes-12 which have been synthesised. Thus it has been shown by ^{35}Cl NMR spectroscopy that the monochloro-derivatives of *o*-, *m*-, and *p*-carboranes are individual compounds and not mixtures of structural isomers, i.e. they are respectively 10-chloro-*o*-carborane, 9-chloro-*m*-carborane, and 2-chloro-*p*-carborane. Similar conclusions concerning the structures of the isomers have been reached[85] for di-, tetra-, octa-, and decachloro-derivatives of *o*- and *m*-carboranes. It is interesting to note that the ^{35}Cl NQR spectrum of 9, 10, 11, 12-tetrachloro-*o*-carborane consists of two doublets, the difference between the average frequencies of which gives a clear idea about the differences between the electron densities in the 10, 12- and 9, 11-positions. The higher frequency is due to the chlorine atoms in the 9- and 11-positions. This finding agrees with the postulated sequence of the electrophilic halogenation of *o*-carborane. The complex structure of the ^{35}Cl NQR spectra of the decachloro-derivatives of *o*- and *m*-carboranes suggests that the molecules of these substances do not have the ideal icosahedral structure[85,89,90]. Broad ^{35}Cl NQR lines are characteristic of decachloro-*o*-carborane, while in the ^{35}Cl NQR spectrum of decachloro-*m*-carborane there are narrow lines, which suggest a high degree of order in its crystals. The presence of an asymmetric broad line[85] in the ^{35}Cl NQR spectrum of 4(12), 9, 10-trichloro-*m*-carborane is evidence for a slight difference between the ^{35}Cl NQR frequencies of the chlorine atoms in the 9- and 10-positions on the one hand and in the 4(12)-position on the other and may be caused by a statistical disorder in the distribution of molecules in the crystals of this substance.

VII. MÖSSBAUER SPECTROSCOPY

Like NQR spectroscopy, the nuclear gamma-resonance method, based on the Mössbauer effect[94,95] and widely used in studies on properties of various compounds[96,97], has been applied to the study of the nature of the bonds between carbon and elements having Mössbauer nuclei. Studies on the ^{119}Sn Mössbauer spectra of organotin derivatives of carboranes[93,98] (Table 11) showed that the *o*-, *m*-, and *p*-carboranyl groups have a greater electron-accepting effect in relation to the tin atom than all the organic substituents investigated hitherto by this procedure. Comparison of the ^{119}Sn Mössbauer parameters of the Et_3Sn derivatives of *o*-, *m*-, and *p*-carboranes as well as other organotin

Table 10. The parameters of the ^{35}Cl, ^{79}Br, and ^{127}I NQR spectra of halogenocarboranes at 78°K.

Compound	Frequency ν, MHz	Type of bond	References
2-Chloromethyl-*o*-carborane	36,044	C—Cl	84,91
1-Chloroethyl-*o*-carborane	31,41 (calc.)	C—Cl	84
1-(1′-Chloropropyl)-*o*-carborane	33,654	C—Cl	84
1,2-Bis(chloromethyl-*o*-carborane	36,664	C—Cl	84,91
	37,009		
	37,342		
	37,405		
1-(1′-Chloropropyl)-*o*-carborane	33.273	C—Cl	84
1-(*p*-Chlorophenyl)-*o*-carborane	35.442	C—Cl	84
1-Chloro-2-phenyl-*o*-carborane	41.64	C—Cl	85
1,2-Bis(bromoethyl)-*o*-carborane	286.344	C—Br	84
1-(*p*-Bromophenyl)-*o*-carborane	274.404	C—Br	84
	273.945		
1-Chloro-2-chloromethyl-*o*-carborane	37.092	C—Cl	66
1-Bromo-2-chloromethyl-*o*-carborane	37.140	C—Cl	66
2-Chloromethyl-1-iodo-*o*-carborane	36.526	C—Cl	66
1-Chloromethyl-2-phenyl-*o*-carborane	36.33	C—Cl	91
	36.85		
1-Chloromethyl-*o*-carboranecarboxylic acid chloride	36.768	C—Cl	66
1-Chloromethyl-2-ethoxycarbonyl-*o*-carborane	37.488	C—Cl	66
1-Chloromethylcarboranecarboxylic acid	36.788	C—Cl	66
	36.855		
	37.072		
	37.758		
1-Chloromethyl-2-methyl-*o*-carborane	37.02	C—Cl	91
1-Chloromethyl-2-ethyl-*o*-carborane	37.026	C—Cl	91
1-Chloromethyl-2-methylthio-*o*-carborane	36.881	C—Cl	91
1-Chloromethyl-2-mercapto-*o*-carborane	36.874	C—Cl	91
1-Chloromethyl-2-trimethylsilyl-*o*-carborane	36.349	C—Cl	91
1-Chloromethyl-2-methoxycarbonyl-*o*-carborane	36.232	C—Cl	91
1-Chloromethyl-*o*-carboranecarboxylic acid amide	36.207	C—Cl	91
1-Chloromethyl-2-methylmercuri-*o*-carborane	35.565	C—Cl	91
10-Chloro-*o*-carborane	23.06	B—Cl	52,85
10,12-Dichloro-*o*-carborane	23.43	C—Cl	85
10,12-Dichloro-1-methyl-*o*-carborane	23.44	B—Cl	85
	23.48	B—Cl	
10,12-Dichloro-1-chloromethyl-*o*-carborane	37.044	C—Cl	85
	23.34	B—Cl	
	23.52	B—Cl	
10,12-Dichloro-1-vinyl-*o*-carborane	23.61	B—Cl	85
	23.39	B—Cl	
9,10,11,12-Tetrachloro-*o*-carborane	23.74	B—Cl	85
	23.91	B—Cl	
	24.39	B—Cl	
9,10,11,12-Tetrachloro-1-methyl-*o*-carborane	24.495	B—Cl	85
	24.204	B—Cl	
	24.040	B—Cl	
9,10,11,12-Tetrachloro-1-chloromethyl-*o*-carborane	37.20	C—Cl	85
	36.87	C—Cl	
	group of lines 23.8—24.4	B—Cl	
4,5,7,8,9,10,11,12-Octachloro-*o*-carborane	24.440	B—Cl	
	24.784	B—Cl	
	24.968	B—Cl	
	25.128	B—Cl	85
	25.560	B—Cl	
	25.660	B—Cl	
(3-12)-Decachloro-*o*-carborane	25.720	B—Cl	85
	25.125	B—Cl	
	24.950	B—Cl	
	24,695	B—Cl	
[^{79}Br]-2-Bromomercuri-1-methyl-*o*-carborane	137.43	Hg—Br	88
[^{81}Br]-2-Bromomercuri-1-methyl-*o*-carborane	135,64		
[^{79}Br]-2-Bromomercuri-1-phenyl-*o*-carborane	142.54	Hg—Br	88
Bipyridylyl-[^{79}Br]-2-bromomercuri-1-methyl-*o*-carborane	138.72	Hg—Br	88
Bipyridylyl-[^{81}Br]-2-bromomercuri-1-methyl-*o*-carborane	115.88	Hg—Br	88
Bipyridylyl-[^{79}Br]-2-bromomercuri-1-phenyl-*o*-carborane	131.70	Hg—Br	88
Bipyridylyl-[^{81}Br]-2-bromomercuri-1-phenyl-*o*-carborane	127.38	Hg—Br	
9-Chloro-*m*-carborane	23.42	B—Cl	85
	23.62	B—Cl	
9,10-Dichloro-*m*-carborane	23.66	B—Cl	85
9,10-Dichloro-1-methyl-*m*-carborane	23.61	B—Cl	85
4,9,10-Trichloro-*m*-carborane	23.86	B—Cl	85
7-(*m*-Chlorophenyl)-1-phenyl-*m*-carborane	35.41	C—Cl	
	35.11		

Table 10 (Continued...).

Compound	Frequency ν, MHz	Type of bond	References
B-Decachloro-*m*-carborane	24.660	B—Cl	
	25.050	B—Cl	
	25.195	B—Cl	
	25.315	B—Cl	
	25,540	B—Cl	85
	25,605	B—Cl	
	25,640	B—Cl	
	25,965	B—Cl	
	26,060		
B-Decachloro-*m*-carborane*	24.659	B—Cl	
	25.043	B—Cl	
	25.050	B—Cl	
	25.194	B—Cl	89
	25.312	B—Cl	
	25.535	B—Cl	
	25.604	B—Cl	
	25.639	B—Cl	
	25.969	B—Cl	
	26.061		
	(273° K)	B—Cl	
	24.354	B—Cl	
	24.689	B—Cl	
	24.790	B—Cl	
	24.822	B—Cl	89,90
	24.977	B—Cl	
	25.177	B—Cl	
	25.257	B—Cl	
	25.297	B—Cl	
	25.590	B—Cl	
	25.723	B—Cl	
2-Chloro-*p*-carborane	23.94	B—Cl	86
10-Iodo-*o*-carborane	$\nu(\pm^1/_2 \rightleftarrows \pm^3/_2)$192.92; $\nu(^3/_2 \rightleftarrows \pm^5/_2)$ 384.8 η=4.5±0.5%; eQq_{zz}=1283.2	B—I	87
9-Iodo-*m*-carborane	$\nu(\pm^1/_2 \rightleftarrows \pm^3/_2)$ 197.78; $\nu(\pm^3/_2 \rightleftarrows \pm^5/_2)$ 395.5 η=1±1% eQq_{zz}=1318.4	B—I	87
2-Iodo-*p*-carborane	$\nu(\pm^1/_2 \rightleftarrows \pm^3/_2)$204.76; $\nu(\pm^3/_2 \rightleftarrows \pm^5/_2)$405.4 η= 8.9±0.2% eQq_{zz}=1353.6	B—I	87
10,12-Di-iodo-*o*-carborane	$\nu(\pm^1/_2 \rightleftarrows \pm^3/_2)$ 195.72 196.14	B—I B—I	87
		204.22	B—I	
9,10-Di-iodo-*m*-carborane	$\nu(\pm^1/_2 \rightleftarrows \pm^3/_2)$	202.88	B—I	87
		198.36	B—I	
		196.63	B—I	
1,12-Di-iodo-*p*-carborane	$\nu(\pm^1/_2 \rightleftarrows \pm^3/_2)$333.2; $\nu(\pm^3/_2 \rightleftarrows \pm^5/_2)$666.1 η=1.9±0.6 eQq_{zz}=2220.6	C—I	87

* The difference between the spectra quoted by Bryukhova et al.[85] and Smith and Tong[89] is that the signal obtained by the former investigators[85] at 25 050 MHz was resolved by Smith and Tong[89] into two lines at 25 043 and 25 050 MHz.

derivatives shows[93] that in the tin compounds the electron-accepting properties of *o*- and *m*-carboranes exceed those of the C_6F_5, C_6Cl_5, CF_3, C≡CH, and C≡CMe groups and are close to those of the C≡C–Cl, C≡C–Br, and C≡C–Ph groups, while the electronegativity of *p*-carborane is close to that of the C≡C–Me group. In turn, the electron-accepting properties of the carborane isomers vary in the sequence *ortho* > *meta* > *para*, which is consistent with the reactivities of these carborane isomers and with the NQR data (see above).

It is interesting to note a significant difference between the spectra of phenyl-*o*-carboranyltriphenyltin and *o*-carboranyltriphenyltin[98] (Table 11). The difference between the Mössbauer parameters of these compounds cannot be explained from the standpoint of the usual concept of the inductive effect. It is difficult to suppose that the higher electron-accepting capacity of the phenyl-*o*-carboranyl residue compared with the *o*-carboranyl residue is due to the electron-accepting effect of the phenyl group, which

cannot be so large. Possibly the reason for the difference is a specific interaction of the electron systems of the *o*-carborane and benzene rings.

Mössbauer spectroscopy has been used to identify and investigate the electronic structures of new carboranyl derivatives of the elements. Thus it has been shown[98] that ^{119}Sn Mössbauer spectroscopic data provide direct evidence that bis(phenyl-*o*-carboranyl)tin ($Ph-C_2B_{10}H_{10})_2Sn$ contains bivalent tin and is the first example of true organic derivatives of bivalent tin. By measuring the Mössbauer spectra of this substance as a function of time and the presence of oxygen, it is possible, in principle, to investigate the kinetics and mechanism of the polymerisation and oxidation of compounds of this kind. A study of the *B*-iodocarborane derivatives labelled with the ^{125}I radioactive isotope by ^{125}I Mössbauer emission spectroscopy showed[99] that the radioactive breakdown of ^{125}I results in the formation of carboranyl derivatives of tellurium which are isoelectronic with the corresponding iodine compounds. The linear relation[100] between e^2Qq derived from ^{127}I NQR and ^{125}Te Mössbauer spectra: $e^2Qq_{^{125}Te} = 0.60e^2Qq_{^{127}I} - 492.3$ M Hz (with a correlation coefficient of 0.983) confirms the hypothesis that the radioactive breakdown of ^{125}I in the matrices of *B*-iodo-derivatives of *o*-, *m*-, and *p*-carboranes does indeed result in the formation of tellurium derivatives[99,100].

Table 11. The parameters of the ^{119}Sn Mössbauer spectra of certain organotin derivatives of carboranes[93,98].

Compound	Quadrupole splitting in the Mössbauer spectrum, mm s^{-1}	Isomeric shift in the Mössbauer spectrum relative to α-tin, mm s^{-1}
1-(Trimethylstannyl)-*o*-carborane	1.55	−0.97
1-(Triethylstannyl)-*o*-carborane	1.75	−0.63
1-(Tri-n-propylstannyl)-*o*-carborane	1.65	−0.65
1-(Triphenylstannyl)-*o*-carborane	0.95	−0.05
2-Phenyl-1-(triphenylstannyl)-*o*-carborane	1.20	−0.80
1,2-Bis(tri-n-propylstannyl)-*o*-carborane	1.50	−0.65
Bis-(2,3,5,6-*o*-carborano)-1,4-distannacyclohexane	1.60	−0.90
Tri-(1-phenyl-*o*-carboranyl)tin chloride	0.40	−0.90
Bis-(1-phenyl-*o*-carboranyl)tin dichloride	0.90	−0.65
Bis-(1-phenyl-*o*-carboranyl)tin dibromide	0.80	−1.20
Dibutylbis-(1-phenyl-*o*-carboranyl)tin	1.70	−0.90
Bis-(1,2-triphenylstannyl)-*o*-carborane	0.70	−1.15
1-Phenyl-2-(triphenylstannyl)-*o*-carborane	1.50	−0.75
Bis-(1-phenyl-*o*-carboranyl)tin	1.90	0.85
1-(trimethylstannyl)-*m*-carborane	1.37	−0.82
1-(Triethylstannyl)-*m*-carborane	1.50	−0.68
9-Chloro-1-(triethylstannyl)-*m*-carborane	1.44	−0.64
1-(Trimethylstannyl)-*p*-carborane	1.18	−0.73
1-(Triethylstannyl)-*p*-carborane	1.23	−0.75
2-Chloro-1-(trimethylstannyl)-*p*-carborane	1.57	−0.74

VIII. COMPARISON OF THE RESULTS OF VARIOUS PHYSICAL METHODS

It is quite evident that, for a detailed investigation of the electronic properties of carborane systems, it is necessary to adduce and compare the results obtained with the aid of different methods. Consideration of the entire set of different physical methods (NMR, NQR, and Mössbauer spectroscopy) already permits an assessment of the electron-accepting properties of carborane isomers, which vary in the sequence

ortho > *meta* > *para*.

It is interesting to note that the spin–spin interaction constant $J_{^{119}Sn\text{-}Me}$ (from the NMR spectra) and the isomeric shifts and quadrupole splittings in the ^{119}Sn Mössbauer spectra of organotin derivatives of carboranes also vary consistently in the same sequence.

If it is supposed that the Grant–Litchman model[101] proposed for the spin–spin interaction constant $J_{^{13}C\text{-}H}$ is valid also for $J_{^{119}Sn\text{-}Me}$, then the expression for $J_{^{119}Sn\text{-}Me}$ may be written in the form

$$J_{(k)} = \frac{\Delta_{ref}}{\Delta_k}\left(\frac{N_k}{N_{ref}}\right)^2\left(\frac{\alpha_k}{\alpha_{ref}}\right)^2\left(\frac{Z_k}{Z_{ref}}\right)^3 J_{ref.}\ , \qquad (1)$$

where $J_{(k)}$ is the constant $J_{^{119}Sn\text{-}Me}$ for the kth Sn–Me bond, $J_{(ref)}$ is the constant $J_{^{119}Sn\text{-}Me}$ for the compound chosen as the standard, Δ is the average excitation energy, N are normalised coupling constants, α is a quantity proportional to the amount of s character of the bond, and Z is the effective nuclear charge, which can be written in the following form for the 5s orbital of the tin atom:

$$(Z_k/a_0)^{3/2} = (A + Bzr + Cz^2r^2 + Dz^3r^3 + Ez^4r^4)e^{z\cdot r/5}\ , \qquad (2)$$

where α_0 is the first Bohr radius and r the radius of the 5s orbital of the tin atom. The ratios Δ_{ref}/Δ_k and $(\alpha_k/\alpha_{ref})^2$ may be assumed to be unity[102]. On the other hand, the isomer shift for the tin compound is defined by the relation

$$IS = A\cdot\frac{\Delta R}{R}\{|\psi_{5s}(0)|^2_{abs} - |\psi_{5s}(0)|^2_{source}\}\ , \qquad (3)$$

where A and $\Delta R/R$ are constants and the $|\psi_{5S}(0)|^2$ are the 5s-electron densities for the absorber and source of the resonance γ-quanta.

The isomer shift as well as Z^3 (see chapter I of the monograph of Goldanskii and Herber[102]) are proportional to $|\psi_{5S}(0)|^2$, i.e. the isomer shift can be substituted for Z^3 in Eqn. (1) and we obtain

$$J_{(k)} = \frac{\Delta_{ref}}{\Delta_k}\left(\frac{N_k}{N_{ref}}\right)^2\left(\frac{\alpha_k}{\alpha_{ref}}\right)^2\left(\frac{IS_k}{IS_{ref}}\right)J_{(ref)}. \qquad (4)$$

Thus, when there is a linear relation between $J_{^{119}Sn\text{-}Me}$ and the isomer shift for a series of organotin compounds, one can assume that the effective nuclear charge model is valid in this case. Such a relation has been observed[69].

The increase of $J_{^{119}Sn\text{-}Me}$ for a given class of compounds on passing from triethylstannyl derivatives of *p*-carborane to those of *o*- and *m*-carboranes is probably associated with the increase of the 5s-electron density at the tin atom in this series. A similar behaviour obtains also in the trimethylstannyl derivatives of the carborane-12 isomers.

The quadrupole splittings by ^{119}Sn in the spectra of organotin derivatives of carboranes vary in the sequence of the *ortho*-, *meta*-, and *para*-compounds in parallel with the reactivity and the values of $J_{^{119}Sn\text{-}Me}$ and pKa.[63,93] This finding can be explained by a change in the electron populations of the 5p orbitals of tin owing to interaction with the many-centre orbitals of the bonds in the C_2B_{10} icosahedron. In this case the decrease of the screening of the 5s electrons by 5p electrons[103], leading to an increase of the 5s-electron density at the ^{119}Sn nucleus, reflects the electron-accepting properties of the carborane nuclei. Linear relations are observed also between the parameters of organotin derivatives of carboranes, namely between $J_{^{119}Sn\text{-}Me}$ and the isomer shift, between the quadrupole splitting and the isomer shift, and between the

quadrupole splitting and pK_a; there is also a linear relation between ^{127}I eQq_{zz} and the ^{35}Cl NQR frequency for *B*-halogeno-derivatives of *o*-, *m*-, and *p*-carboranes [87]. The latter can be written in the form

$$eQq_{zz}(^{127}I) = \{-638.7 + 83.3\nu(^{35}Cl)\}\ \text{MHz}. \quad (5)$$

This suggests that the asymmetry parameters of *o*-, *m*-, and *p*-*B*-monochlorocarboranes are small as for *B*-monoiodocarboranes. On the other hand, comparison of the electric field gradients along the axis of the B–Hal bond in monohalogenocarboranes showed [87] that the gradients along the bond involving the iodine atom are somewhat higher than for the chlorine atom. This is probably due to certain differences between the polarisations of the boron–iodine and boron–chlorine bonds in carboranes.

It follows from the ^{11}B NMR spectra of monohalogeno-substituted isomers of carborane-12 [79] that the chemical shifts of the boron atoms to which the halogen (chlorine, bromine, and iodine) is attached vary in the sequence *para* > *meta* > *ortho* (Table 8). Whereas the ^{11}B NMR data for the isomeric monochloro- and monobromo-carboranes suggest the descreening of the boron atom to which the halogen is attached, in the spectra of the isomeric iodo-derivatives of carborane-12 the signal of the same boron atom undergoes a shift to a higher field (relative to the chemical shifts of the unsubstituted carborane-12 isomers).

On the basis of the general theory of chemical shifts, the screening of nuclei (for which NMR is observed) depends on the ratios of three contributions:

$$\sigma = \sigma_{dia} + \sigma_{para} + \sigma', \quad (6)$$

where σ_{dia} is the diamagnetic screening of the given nucleus, σ_{para} is the paramagnetic contribution to the screening, and σ' is a term which includes the screening due to the other atoms in the given molecule.

The contribution of σ' depends on the anisotropy of the magnetic susceptibilities of the groups of atoms in the molecule remote from the nucleus under consideration. It has been shown [104] that for heavy nuclei, including ^{11}B, σ' amounts in most cases to only several per cent of the observed shift. Therefore in the consideration of the ^{11}B chemical shifts the σ' contribution may be neglected. Moreover a number of investigators have shown [104-106] for ^{13}C and other heavy atoms that the diamagnetic contribution σ_{dia} is usually small and also can be neglected in the interpretation of the chemical shift. For this reason, the paramagnetic term gives the main contribution to the chemical shifts of heavy atoms. In this connection mention should be made of the study by Lipscomb and coworkers [75], who estimated the extent of the diamagnetic and paramagnetic screening for *o*-, *m*-, and *p*-carboranes. The estimates were carried out under the following conditions. The constancy of the average energy for the entire series was assumed. The electrons in the 2*p* orbitals of both the nucleus under consideration and in the bonds involving all other atoms were taken into account. The diamagnetic screening, averaged over all orientations, was calculated from the formula [105]

$$\sigma_{dia} = \alpha/3 \sum_{n=1}^{m} \sum_{b=1}^{m} P_{ab} \langle r^{-1} \rangle_{ab}, \quad (7)$$

where P_{ab} are the elements of the usual charge matrix with respect to all the orbitals *a* and *b* of the centre *A*. The corresponding expression for the paramagnetic screening is

$$\sigma_{para} = -\frac{\alpha^2}{2\Delta E} \langle r^{-3} \rangle_{2p} \left(Q_{AA} + \sum_{A \neq B} Q_{AB} \right) = -\frac{19{,}5}{\Delta E} \left(Q_{AA} + \sum_{A \neq B} Q_{AB} \right). \quad (8)$$

where

$$Q_{AA} = 4/3 [(P_{X_AX_A} + P_{Y_AY_A} + P_{Z_AZ_A}) - 1/2 (P_{X_AX_A} P_{Y_AY_A} + P_{Z_AZ_A} P_{Y_AY_A} + P_{Z_AZ_A} P_{X_AX_A}) + 1/2 (P^2_{X_AY_A} + P^2_{Y_AZ_A} + P^2_{Z_AX_A})], \quad (9)$$

$$Q_{AB} = 2/3 [-(P_{X_AX_B} P_{Y_AY_B} + P_{Y_AY_B} P_{Z_AZ_B} + P_{Z_AZ_B} P_{X_AX_B}) + (P_{X_AY_B} P_{Y_AX_B} + P_{Y_AZ_B} P_{Z_AY_B} + P_{Z_AX_B} P_{X_AZ_B})], \quad (10)$$

α is the fine structure constant and $\langle r^{-3} \rangle_{2p} = K^3/3$ is the one-centre integral, *K* being the Slater 2*p* exponent of the boron atom.

Using the diborane and ethane data [107] obtained by the SCF method for the calculation of the borohydride wave functions, Lipscomb and coworkers [75] calculated Q_{AA}, ΣQ_{AB}, and σ_{dia} for the non-equivalent atoms in all three carborane isomers. It was found that the observed chemical shifts, corrected for the diamagnetic shift ($\delta = \delta_{obs} - \delta_{dia}$), are satisfactorily correlated with the sum $Q_{AA} + \Sigma Q_{AB}$. The changes in σ_{dia} on passing from one atom to another are small (Table 12).

Table 12.

Carborane		Q_{AA}	Q_{AB}	σ_{dia}	δ, p.p.m.	
					obs.	calc.
ortho-	B3 3*	1.211	0.123	187.8	15.2	16.7
	B4 4	1.250	0.128	188.8	13.9	12.5
	B9 8	1.300	0.131	190.0	9.9	7.4
	B10 9	1.300	0.136	190.0	2.7	6.8
meta-	B2 2	1.197	0.123	187.6	17 3	18.2
	B3 4	1.251	0.127	188.8	13.6	12.5
	B4 5	1.252	0.131	188.8	11.0	11.9
	B9 9	1.301	0.132	190.0	7.0	7.2
para-	B2	1.251	0.128	188.8	15.2	12.5

* The numbering is based on the data of Lipscomb and coworkers [75] and the ^{11}B shifts are quoted relative to $Et_2O.BF_3$.

The calculation reflects satisfactorily the effects of the nearest adjacent carbon atom but the influence of the carbon atom is inadequately reflected in calculations on remote boron atoms [cf. B(9) and B(10) in *o*-carborane]. Thus the chemical shifts of the boron atoms in icosahedral carboranes vary mainly owing to the variation of the paramagnetic screening of the boron atoms in different chemical environments. LCAO-MO calculations have shown [108] that the paramagnetic screening can also be formulated by the expression

$$\sigma_{para} = -2/3 (e^2h^2/m^2c^2) (1/\Delta E) \langle 1/r^3 \rangle_{2p} \cdot P_u, \quad (11)$$

where ΔE is the average electronic excitation energy for the molecule or ion, *r* the radius of the 2*p*-electron orbital (in ^{11}B), and P_u a quantity which reflects the electron populations of the 2*p* orbitals, and is proportional to the number of unbalanced *p* electrons.

Thus the degree of descreening of ^{11}B nuclei must depend on the number of unbalanced *p* electrons. It is also known that the NQR frequencies ν and the electric field gradients eQq_{zz} at the halogen nuclei are directly proportional to the number *U*p of unbalanced *p* electrons. According to the Townes–Dailey theory [108], under these

conditions the number of unbalanced p electrons responsible for the electric field gradient at the halogen nuclei is defined by the expression

$$U_P = \frac{N_x + N_y}{2} - N_z, \qquad (12)$$

where N_x, N_y, and N_z are the electron populations of the P_x, P_y, and P_z orbitals of the halogens.

Hence it is reasonable to compare the ^{11}B chemical shift data for the atoms involved in the boron–halogen bond[79] with ^{35}Cl and ^{127}I NQR spectroscopic data for a series of B-halogeno-derivatives of o-, m-, and p-carboranes[86,87]. Since atoms involved in the same bond are considered, the change in U_p for halogen atoms will reflect the change in the number of the unbalanced $2p$ electrons of the corresponding boron atoms.

Comparison of ^{11}B NMR and ^{35}Cl and ^{127}I NQR data shows[79] that, with increase of the number of unbalanced p electrons in the halogen atoms, i.e. with decrease of the number of unbalanced $2p$ electrons in boron, the chemical shifts in the ^{11}B spectra increase. The results confirm that the main contribution to changes in the chemical shifts of the ^{11}B nuclei comes from the paramagnetic term. On the basis of a comparison of ^{11}B NMR and ^{35}Cl and ^{127}I NQR data, Babushkina et al.[79] also postulated that the ^{11}B chemical shifts for the boron atom in carborane-12 linked to halogens should be greatly influenced by the effect of the lone electron pair of the halogen, which causes a high-field shift of the NMR signal due to the boron atom linked to iodine, relative to those of the atom linked to bromine and chlorine.

We shall restrict to these examples the comparison of the results of various physical methods used in the study of the isomers of carborane and its derivatives, assuming that an increase in the number of correlations of this kind will not only make it possible to estimate certain quantities from the results of different investigations but will also allow a new approach to the study of the electronic properties of carborane-12 isomers.

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