A STUDY OF THE TRANSFER OF THE ELECTRONIC INFLUENCE OF SUBSTITUENTS IN o-CARBORANES BY NUCLEAR QUADRUPOLE RESONANCE

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The ^{35}Cl NQR spectra of 2-substituted 1-chloromethyl-o-carboranes and of 1-chloromethyl-9,12-dihalogeno-o-carboranes have been investigated. The anomalous influence of two halogen atoms present in positions 9 and 12 of the carborane nucleus on the electron density of the chlorine atom in the CH_2Cl group is explained by the combined action of their −I and +M effects, and also by the effect of p → d conjugation. The comparatively high ^{35}Cl NQR frequency for o-$ClCH_2CB_{10}H_{10}CH$ is due to the large −I effect of the carboranyl group. The induction constants of a number of groups attached to the carborane ring have been evaluated. In the molecules of the 2-substituted 1-chloromethyl-o-carboranes spatial interaction between X and Cl clearly appears. The substituents X in compounds of this series can be divided into three types according to their electronic influence: 1) electron-donating substituents, 2) substituents containing a mobile hydrogen atom (capable of forming a hydrogen bond), and 3) substituents possessing an unshared pair of electrons capable of passing into the vacant 3d orbital of a chlorine atom.

An investigation of compounds of the carborane series by nuclear quadrupole resonance (NQR) [1-4] has shown that the carborane nucleus as a substituent in the benzene ring is an electron acceptor, and one which is stronger than fluorine and chlorine atoms or a COOH group but weaker than an NO_2 group, and that the transmission through the carborane system of the influence of substituents present in position 1 and 2 is greater than the transmission through an aromatic nucleus or through a $-C \equiv C-$ group.

We have studied the ^{35}Cl NQR spectra of 2-substituted 1-chloromethyl-o-carboranes o-$ClCH_2CB_{10}H_{10}CX$ and also of 1-chloromethyl-9,12-dihalogeno-o-carboranes (see Table 1).

The ^{35}Cl NQR frequency in the spectrum of $ClCH_2CB_{10}H_{10}CH$ is high − 36.044 MHz − which is due to the greater −I effect of carboranyl group due to the considerable s-nature of the carbon atoms of the carborane nucleus. If we assume that the correlation equation connecting the values of ν_m^{77} and σ^* for molecules of the RCH_2Cl series ($\sigma^* = 0.806 \cdot \nu_m^{77} - 26.615$) and the RCl series ($\sigma^* = 0.365\ \nu_m^{77} - 12.14$) [5] are applicable to 1-chloromethyl-o-carborane, it is possible to evaluate the Taft σ^* constant for the o-carboran-1-yl and the o-carboran-1-ylmethyl groups, which prove to be +2.4 and +1.0, respectively.

The value of σ^* obtained for the o-carboran-1-yl group (+2.4) is in good agreement with the values of σ^* determined from the ionization constant of o-carborane-1-carboxylic acid (σ^* = 2.10) [6].

As was to be expected, the introduction of two halogen atoms into positions 9 and 12 of the carborane nucleus lowers the electron density on the chlorine atom in the chloromethyl group in position 1. However, bromine atoms act in this direction more strongly than chlorine or iodine atoms (the ^{35}Cl NQR frequency when bromine atoms are present in the carborane nucleus is higher than when chlorine or iodine atoms are present). At the same time, chlorine atoms act more strongly than iodine atoms. This transmission of the influence of halogen atoms through the carborane nucleus does not correspond to their electronegativities (Cl 3.15; Br 2.90; I 2.68 [7]) or their Taft or Hammett constants.

The anomalous change in the influence of halogen atoms on the electron density of the chlorine atom is also characteristic for other series of di- and polyhalogeno derivatives. Thus, for example, in the XCH_2Cl series (X = F, Cl, Br, I), the ^{35}Cl NQR frequency falls in the following sequence of changes in the atom X: Cl > I > Br > F, in the X_2CHCl series Cl > Br > F, and in the p-XC_6H_4Cl series F > Br > I ≈ Cl [8]. Such an unusual behavior of the halogens, which has also been detected by other methods [9-11], and this also in the carborane nucleus [12], must be ascribed to the possibility of the superposition of the effect of p → d conjugation with the participation of the vacant d-orbitals of the chlorine, bromine, or iodine atoms combining with the −I and +M effects of the halogen.

The Taft constants for the 9,12-dihalogenocarboranyl groups calculated [5] from the ^{35}Cl NQR results are 3.10 for 9,12-diiodo-, 3.20 for 9,12-dichloro-, and 3.30 for 9,12-dibromo-o-carborane. These figures show a marked increase in the electron-accepting nature of the o-carboranyl group on the addition of halogen atoms to the boron atom in it.

An unusual NQR spectrum was obtained for 8,9,10,12-tetrachloro-1-chloromethyl-o-carborane. The echo signal was observed in the 25-42 MHz range (the actual width of the line is obviously still greater), the intensity of the signal being very high over the whole range. (For 8,9,10,12-1-chloromethyl carborane, $\nu^{77} = 37.04$ MHz is given in the literature [4]). The integral intensities ($I_{CH}^{1/2}$) of the absorption bands of the stretching vibrations of the C−H bonds in the IR spectra of o-$XCB_{10}H_{10}CH$ [12] and the spin-spin coupling constants I_{Hg-CH_3} in the NMR spectra of o-$XCB_{10}H_{10}CHgCH_3$ [13] are connected by linear relations with the induction constant σ_I. This shows that the transmission of the influence of a substituent through a C−C bond of the o-carborane nucleus takes place by an induction mechanism.

In contrast to this, the ^{35}Cl NQR frequencies in $ClCH_2CB_{10}H_{10}CX$ correlate neither with the σ_I values nor with the σ^* values, nor with any other σ constants at all (see figure). The ^{19}F chemical shifts in the NMR spectra of the 2-substituted 1-(fluorophenyl)-o-carboranes containing fluorine atoms both in the para and in the meta positions [14], and the pK_a values of 2-substituted 1-carboxy and 1-methoxycarbonyl-o-carboranes [6] behave similarly. This has been explained by the steric interaction of the substituent with the reaction center.

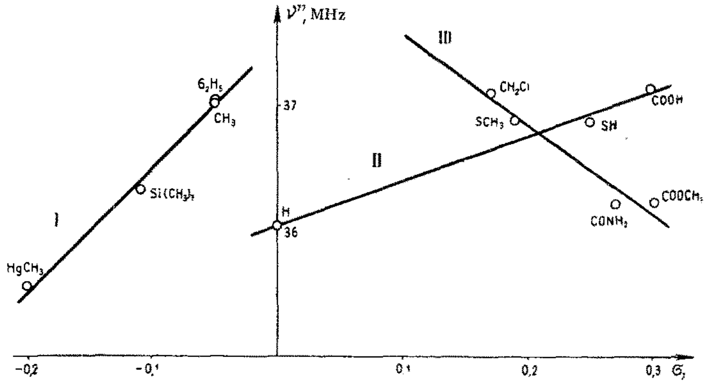

Fig. 1. Connection between the ^{35}Cl NQR frequencies (ν^{77}) of of the 2-substituted 1-chloromethyl-o-carboranes o-$ClCH_2 \cdot CB_{10}H_{10}CX$ with the induction constant σ_I of the substituents X.

The figures in Table 1 show that the C-derivatives of o-carborane $ClCH_2CB_{10}H_{10}CX$ containing the substituents X = CH_3, C_2H_5, CH_2Cl, SCH_3, SH, and COOH, which possess different electronic effects, have practically the same ^{35}Cl NQR frequency (37.0 ± 0.2 MHz; the observed deviations (± 0.5%) are within the limits due to the crystal effect). The closeness of the ν^{77} values of the compounds mentioned above lead to the assumption of the absence of a transfer to the chlorine atom of the induction effect of the substituent X through the three carbon atoms in the $-CB_{10}H_{10}CCH_2-$ system. In favor of this hypothesis is the fact that even the 3-carbon system $-CH_2CH_2CH_2-$ scarcely transmits the induction effect of substituents. Consequently, for example, the values of the ^{35}Cl NQR frequencies of compounds of the $X(CH_2)_nCl$ series with $n \geq 3$ remain practically constant (33.05 ± 0.25 MHz) at any value of X, i.e., they do not depend on the induction constant of the substituent. In addition to this, for compounds of the $ClCH_2CB_{10}H_{10}CX$ series, where X = $HgCH_3$, $Si(CH_3)_3$, H, $COOCH_3$, and $CONH_2$ considerable deviations in the NQR frequencies from 37.0 MHz are observed, which shows the influence of these substituents on the p-electron environment of the chlorine atom.

This anomalous influence of substituents on the ^{35}Cl NQR frequencies of $ClCH_2CB_{10}H_{10}CX$ is apparently connected with the possibility of a steric interaction of certain substituents X with the chlorine atom, which is favored by their cisoid arrangement in the o-carborane nucleus. Steric factors interfere with the evaluation of the Taft constants of the 2-substituted o-carboranyl groups by the equation given above [5]. Thus, for example, the σ^* values of the $-CB_{10}H_{10}CCH_3$ and $-CB_{10}H_{10}CCOOH$ groups proved to be the same (~ 3.20), which is in contradiction to the electronic properties of the methyl and carboxyl groups. The Taft constants of the $-CB_{10}H_{10}CSi(CH_3)_3$ group ($\sigma^* = 2.7$) and of the $-CB_{10}H_{10}CCOOCH_3$ group ($\sigma^* = 2.9$) are just as close, although the trimethylsilyl group is an electron-donating and the methoxycarbonyl group an electron-accepting substituent.

Table 1. ^{35}Cl NQR Frequencies at 77°K (ν^{77}) of 2-Substituted 1-Chloromethyl-o-carboranes and 1-Chloromethyl-9,12-dihalogeno-o-carboranes

Compound	ν^{77}, MHz	σ_I X[16]
$ClCH_2CB_{10}H_{10}CCOOH$	37,122*	+0,28
$ClCH_2CB_{10}H_{10}CCH_2Cl$	37,106†	+0,17
$ClCH_2CB_{10}H_{10}CC_2H_5$	37,026	−0,05
$ClCH_2CB_{10}H_{10}CCH_3$	37,02	−0,05
$ClCH_2CB_{10}H_{10}CSCH_3$	36,881	+0,19
$ClCH_2CB_{10}H_{10}CSH$	36,874	+0,25
$ClCH_2CB_{10}H_{10}CSi(CH_3)_3$	36,349	−0,12
$ClCH_2CB_{10}H_{10}CCOOCH_3$	36,232	+0,30
$ClCH_2CB_{10}H_{10}CCONH_2$	36,207	+0,27
$ClCH_2CB_{10}H_{10}CH$	36,044‡	0,0
$ClCH_2CB_{10}H_{10}CHgCH_3$	35,565	−0,20
$ClCH_2CB_{10}H_8Cl_2CH$	37,044‡	
$ClCH_2CB_{10}H_8Br_2CH$	37,358	
$ClCH_2CB_{10}H_8I_2CH$	36,848	

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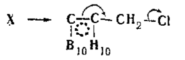
*Mean frequency of the quadruplet 37.756, 37.070, 36.865, and 36.796 MHz.

†Mean frequency of the quadruplet 37.407, 37.345, 37.010, and 36.665 MHz. Approximately the same frequency is given in the literature [4].

‡The same frequency is given in the literature [4].

A more attentive consideration of the, at first sight, chaotic accumulation of points in the figure given above, however, permits the conclusion that, according to their electronic influence, the substituents X in molecules of the $ClCH_2 \cdot CB_{10}H_{10}CX$ series can be divided into three types. If X is an electron-accepting substituent (CH_3, C_2H_5, $Si(CH_3)_3$, $HgCH_3$), a good linear correlation exists between the values of ν^{77} and σ_I (or σ^*) ($\nu^{77} = 9.7\ \sigma_I + 37.51$; $r = 0.99$ and $\nu^{77} = 1.29\ \sigma^* + 37.18$; $r = 0.91$) and, as was to be expected, the ^{35}Cl NQR frequency rises with an increase in the induction constant (straight line I in the figure). The value of ν^{77} for the compounds containing electron-donating substituents that have been considered also has a satisfactory linear correlation with the values of $I_{CH}^{1/2}$ in the IR spectra of $o\text{-}XCB_{10}H_{10}CH$. All this permits the conclusion that the influence of these substituents on the chlorine atom takes place in accordance with their induction effect. It is found that ρ ("the transmission coefficient") characterizing the sensitivity of the chlorine atom to the influence of substituents, i.e., the transmittance of the $-CH_2CB_{10}H_{10}C-$ system, has a comparatively high value ($\rho = 1.29$), while in the $X(CH_2)_nCl$ system with $n = 0\text{–}4$ the values of ρ are, respectively, 2.7, 1.2, 0.4, 0.0, and 0.0.

The high value of ρ in the $-CH_2CB_{10}H_{10}C-$ system cannot be due to the transfer of the influence of the substituent along the valence bonds in this fragment only by an induction mechanism, since even for a single CH_2 group introduced into this system $\rho = 1.2$ (in the $ClCH_2X$ series). In our opinion, the linear correlation between ν^{77} and σ_I with such a high value of ρ in the case of electron-donating substituents can be explained by the transfer of their electron-donating effect to the chlorine atom in $ClCH_2CB_{10}H_{10}CX$ mainly by a p,π conjugation mechanism in accordance with Scheme I.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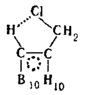
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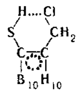
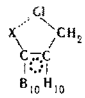

III

The presence of such conjugation in molecules containing π-electronic systems connected with a CH_2Cl group ($C_6H_5CH_2Cl$, $CH_2=CHCH_2Cl$, $HC \equiv CCH_2Cl$, etc.) has been firmly established.

The ^{35}Cl NQR frequency of compounds in which X = H, SH, and COOH, i.e., those in which X is an electron-accepting substituent, containing a mobile hydrogen atom (in this case, the formation by it with the chlorine of an exocyclic hydrogen bond in accordance with Scheme II or III is probable in principle), also shows a linear correlation with σ_I (straight line II). Here, as a rule, the value of ν^{77} rises with an increase in σ_I.

For other electron-accepting substituents in $ClCH_2CB_{10}H_{10}CX$, the ^{35}Cl NQR frequency unexpectedly falls with an increase in σ_I (straight line III). It may be assumed that the cause of this is apparently the superposition of the steric interaction between the vacant 3-d orbitals of the chlorine atom and the unshared pair of electrons of substituent X, raising the electron density on the chlorine atom in accordance with Scheme IV.



IV

The interaction of a chlorine atom and an electron-accepting substituent, which is favored by the comparatively low electron density on the chlorine atom in $ClCH_2CB_{10}H_{10}CX$ must rise with an increase in the induction constant of this substituent X, which also explains the observed anomalous dependence between ν^{77} and σ_I.

In conclusion, it is impossible not to dwell on some inaccuracies tolerated in the literature in the evaluation of the transmission of the induction effect from the results of NQR spectroscopy.

It was mentioned above that according to NQR spectroscopy the transmittance of the system between a substituent X and the atom with the resonating nucleus or (which is the same thing) the relative sensitivity of the chemical shift of the NQR frequency of the resonating nucleus to a change in the nature of the substituent X is characterized by an angle of slope of the correlation line or the parameter ρ ("transmission coefficient") in the linear equation connecting the values of the NQR frequencies and the σ-constants of the substituents.

Hitherto, the transmission of the carborane system has been evaluated only approximately ($\rho \approx 2.3$). However, the approach to the solution of this question was incorrect in principle. Thus, for example, while Semin et al. [3] compares the difference in the NQR frequencies not of the successive pairs of compounds $ClCH_2CB_{10}H_{10}CH$ and $ClCH_2CB_{10}H_{10}CCH_2Cl$ ($\Delta\nu^{77} = 1.07$ MHz) and $ClCH_2C \equiv CH$ and $ClCH_2C \equiv CCH_2Cl$ ($\Delta\nu^{77} = 0.56$ MHz but of a $ClCH_2CB_{10}H_{10}CCH_3$ and $ClCH_2CB_{10} \cdot H_{11}CCH_2Cl$ ($\Delta\nu^{77} = 0.23$ MHz) and $ClCH_2C \equiv CCH_3$ and $ClCH_2C \equiv CCH_2Cl$ ($\Delta\nu^{77} = 1.01$ MHz), the authors came to the directly opposite conclusion that the transmittance of the carborane nucleus is low and considerably smaller than that of the $-C \equiv C-$ group.

Such contradictory and frequently incorrect conclusions are due to the fact that the mechanisms of the electronic interaction between the substituents in the pairs of compounds considered are by no means the same. While in the acetylenic compounds the transfer of the substituent effect of the chlorine atom is effected mainly through the valence bonds by virtue of the linearity of the acetylene structures, in the o-carborane nucleus the determining factor is the spatial interaction of the substituent with the chlorine atom.

Table 2. Substituted 1-Chloromethyl-o-carboranes

Compound	Mp, °C	Found, %				Empirical formula	Calculated, %			
		C	H	B	halogen		C	H	B	halogen
$ClCH_2CB_{10}H_{10}CCOOCH_3$	53—54	24,34	6,17	43,12	13,49	$C_5H_{15}B_{10}ClO_2$	23,92	5,98	43,20	14,18
$ClCH_2CB_{10}H_{10}CC_2H_5$	72—73	27,71	7,94	49,44	15,35	$C_5H_{17}B_{10}Cl$	27,20	7,70	49,08	16,08
$ClCH_2CB_{10}H_{10}CSH$*	165—166	16,56	6,01	48,33		$C_3H_{13}B_{10}ClS$	16,00	5,83	48,21	
$ClCH_2CB_{10}H_{10}CSCH_3$	47—48	20,72	6,32			$C_4H_{15}B_{10}ClS$	20,10	6,28		
$ClCH_2CB_{10}H_{10}CSi(CH_3)_3$†		27,21	8,21			$C_6H_{21}B_{10}ClSi$	27,26	8,04		
$ClCH_2CB_{10}H_{10}CCONH_2$	139	21,16	6,05			$C_4H_{14}B_{10}ClO$	21,80	6,42		
$ClCH_2CB_{10}H_8Cl_2CH$	86	13,79	4,14	41,52	40,56	$C_3H_{11}B_{10}Cl_3$	13,80	4,23	41,30	40,71
$ClCH_2CB_{10}H_8Br_2CH$	114—115	10,40	3,16	30,93	55,70	$C_3H_{11}B_{10}ClBr_2$	10,28	3,16	30,90	55,72
$ClCH_2CB_{10}H_8J_2CH$	103	8,01	2,33	24,18	65,73	$C_3H_{11}B_{10}ClI_2$	8,10	2,50	24,38	65,83
$ClCH_2CB_{10}H_6Cl_4CH$	184—185	10,99	2,73	32,77	53,73	$C_3H_9B_{10}Cl_5$	10,91 10,91	2,75	32,85	53,70

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*Found %: S 14.53. Calculated %: S 14.23.

†Bp 145-146°C (2 mm).

Thus, the evaluation of the transmission properties of a particular system by comparing the NQR frequencies of a number of compounds of analogous structure is permissible only where there is not doubt that the mechanisms of the electronic influence of the substituents on the resonating nucleus are the same and are characteristic for the whole of the given series.

EXPERIMENTAL

The ^{35}Cl NQR spectra were taken on a pulse NQR apparatus [15] at 77°K. The resonance frequency was measured by means of a Ch4-9 heterodyne frequency meter. All the 2-substituted 1-chloromethyl-o-carboranes were synthesized from the lithium derivative of 1-chloromethyl-o-carborane by the general method used in the chemistry of the carboranes. The 1-chloromethyl-B-halogeno-o-carboranes were obtained by the electrophilic halogenation of 1-chloromethyl-o-carborane. The physical constants and analytical results for the compounds studied are given in Table 2.

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