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CORRELATION BETWEEN SOME SPECTRAL AND CHEMICAL PROPERTIES OF C—H BONDS IN CARBORANE MOLECULES

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Summary

Some spectral and chemical properties of CH bonds in "small", "medium" and "large" carborane molecules are compared. The increase in coordination number of the carbon atoms in carboranes is shown to lead to a successive decrease in the CH stretching frequency. While an increase in the positive charge on the carbon atoms brings about an increase in the intensity of the corresponding infrared band and an increase of the CH acidity and of the energy of hydrogen bond formation.

Previously we recorded vibrational spectra of "large" *o*-, *m*-, and *p*-$B_{10}H_{10}C_2H_2$ carboranes and their borondecachloroderivatives [1—4] and of "medium" *p*-$B_8H_8C_2H_2$ carborane [5]. Intensities of the CH stretching bands in the infrared spectra of these compounds were measured [6] and their ability to form C—H..L type hydrogen bonds with various L bases was established and quantitatively described [7—10]. Vibrational spectra of "small" *p*-$B_3H_3C_2H_2$ and *p*-$B_4H_4C_2H_2$ carboranes are presented in [11]. Comparison of the results of our studies with published data makes it possible to establish certain correlations between the spectral and chemical properties of CH bonds in carboranes depending on their structure.

Several spectral and chemical characteristics of CH bonds in "large", "medium" and "small" carboranes are presented in Table 1. First of all, the frequency of the CH stretching mode, ν(CH), is very high (above 3100 cm^{-1}) for "small" carboranes and decreases by about 50 cm^{-1} with an increase of one in the coordination number of carbon atoms in the carborane molecule *.

The CH stretching vibration being well localised, the variation of the corresponding frequency reflects the variation of elastic properties of the CH bond.

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* A similar dependence of ^{13}C NMR chemical shifts of carboranes on the coordination number of the

TABLE 1

SEVERAL PROPERTIES OF C—H BONDS IN CARBORANES

Carborane	Coordination number of carbon atoms	Vibrational frequency ν(C—H) (cm^{-1})	^{13}C Chemical shifts δ (ppm) [12]	Spin coupling constant $J(^{13}C—H)$, in CH_2Cl_2 [19]	Charge on carbon atoms [23]	Infrared intensity A(C—H) in CCl_4 (10^3 l mol^{-1} cm^{-2})	Enthalpy ΔH of hydrogen bond with DMSO (kcal/mol)	Acidity pK_a
1,5-$C_2B_3H_5$	4	3165 [11]	90,4 (in CS_2)		—0,4	0 [11]		
1,6-$C_2B_4H_6$	5	3110 [11]	115,6 (acetone)		—0,05	0 [11]		
1,10-$C_2B_8H_{10}$	5	3106		188		0,70	1,7	27,3 [24]
1,12-$C_2B_{10}H_{12}$	6	3060	123,9 (acetone)	163	+0,15	0,75	2,2	26,8 [24]
1,7-$C_2B_{10}H_{12}$	6	3064	137,4 (acetone)	179	+0,15	1,2	2,5	25,6 [24]
1,2-$C_2B_{10}H_{12}$	6	3071	137,3 (acetone)	195	+0,3	1,6	2,8	22,0 [24]
1,12-$C_2B_{10}Cl_{10}H_2$	6	3016				7,5		
1,7-$C_2B_{10}Cl_{10}H_2$	6	3037				8,4	~7	9,19 [25]
1,2-$C_2B_{10}Cl_{10}H_2$	6	3046		198		10,0	~8	6,89 [25]

The high ν(CH) values are usually due either to the high *s*-character of hybridized carbon orbitals (ν(CH) $\simeq$ 3300 cm^{-1} for acetylene compounds and ~3050 cm^{-1} for ethylenic and aromatic compounds) or to the electron acceptor effect. Thus, substituents with a strong —*I* effect increase the ν(CH) frequency, even in alkanes, to about 3000 cm^{-1} (for instance, the ν(CH) frequency of trinitromethane is 3008 cm^{-1} [4]). Obviously, the inductive effect of the carboranyl group plays a secondary role in carboranes since the electron-acceptor effect of "small" carboranes is weaker than that of "large" carboranes [13] while the direction of the ν(CH) frequency variation is reversed. Besides, when going from $B_{10}H_{10}$-C_2H_2 carboranes to their borondecachloroderivatives a spectacular increase in electron-acceptor properties of the nucleus is observed [14] but the ν(CH) frequency decreases.

If we were considering systems with a "classical" carbon atom it could have been concluded from the presented data that carbon orbitals in carborane molecules have a high *s*-character which is primarily responsible for the observed CH stretching frequency values. The ν(CH) values of "small" and "medium" carboranes would then indicate hybridization intermediate between *sp* and *sp*^{2} and of "large" carboranes: hybridization close to *sp*^{2}.

Assuming, as is often done, the value of the interbond angle as a measure of the *s*-character of the carbon orbital of the CH bond, the values of external B—C—H angles in polyhedra, calculated on the basis of literature data, for *p*-$B_3C_2H_5$ 137° [15], *p*-$B_4C_2H_6$ 132° [16], *p*-$B_8C_2H_{10}$ 125° [17] and, finally ~120° for icosahedron carboranes [18] lead us to the same qualitative conclusions as do the ν(CH) values. It should be noted that spin coupling constants in

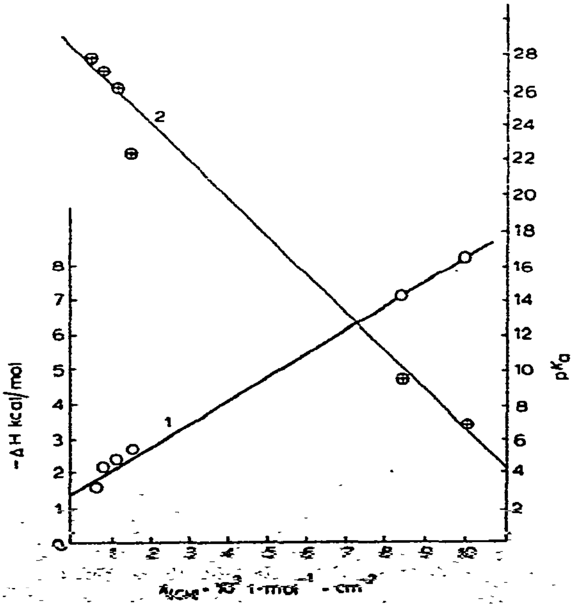

Fig. 1. Correlation between the intensity of the CH infrared stretching band (A(CH)) and: (1) the enthalpy of hydrogen bond formation with DMSO ($-\Delta H$); (2) CH acidity (pK_a) for different carboranes.

^{13}C NMR spectra of icosahedron carboranes are also close to those of molecules with an sp^2-carbon [19].

In classical systems, sp^2-hybridization of the carbon atom presupposes the presence of a π-orbital capable of conjugation with the π-electrons of the substituent. However, as already established [20], this does not hold for the carbon-substituted carborane nucleus. Moreover, field constants in ^{35}Cl NQR spectra, according to data obtained in [21], are close to the corresponding values of compounds in which chlorine is bonded to an sp^3 carbon. The concept of carbon atom hybridization developed within classical organic chemistry should thus be applied with caution to carboranes.

It appears that some other carborane properties are connected with the polarity of CH bonds. Quantum mechanical calculations show that the charge on the carbon atom of carboranes also depends on the size and structure of the molecule. Although different values of the charge are obtained by using different methods of calculation [22], a common feature is observed; the positive charge on the carbon atom increases with its coordination number. According to [23], the charge even changes its sign when passing from "small" to "large" carboranes, i.e., from —0.4 to +0.3 (Table 1). The variations in CH stretching band intensity (A(CH)) in the infrared spectra of carboranes, determined as a square of the dipole moment variation of the CH bond for a given vibration, is in good agreement with these data. No CH stretching infrared band is observed for " small" carboranes (p-$B_3H_3C_2H_2$ and p-$B_4H_4C_2H_2$) [11] while for "medium" carborane (p-$B_8H_8C_2H_2$) the ν(CH) band is sufficiently strong [5] and even strengthens in $B_{10}H_{10}C_2H_2$ carboranes, reaching high values in their decachloroderivatives [6]. The same trend is observed for the acidity of the CH bond [24,25] and for its ability to form hydrogen bonded complexes [8—10]. As can be seen from Fig. 1, there is a linear dependence between A(CH) values (in CCl_4) and ΔH of hydrogen bond formation with DSMO. Similar relationships are observed between A(CH) values and pK_a, and between ΔH and pK_a, which points to the related nature of these quantities. Apparently, they are determined by the same value: the charge on the carbon atom. It should be noted that the point, corresponding to the acidity of o-carborane (22 pK_a units according to [24]) does not fit the straight lines of the last two plots.

Thus, it can be seen from Table 1 that an increase in coordination number of the carbon atoms in carborane molecules leads to a successive decrease in the CH stretching frequency while an increase in the positive charge on the carbon atoms brings about an increase in the intensity of the corresponding infrared band, of CH acidity and of the energy of hydrogen bond formation. This regularity makes it possible to predict qualitatively the properties of CH bonds in carboranes.

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