

CHEMISTRY OF BORANES. XXVI.*

INFRARED SPECTRA OF MONOSUBSTITUTED DECABORANES

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Received July 5th, 1971

The frequencies of B-H deformation vibrations in the region of 800 – 650 cm⁻¹ and the frequencies of B–H bridge deformation vibrations in the region of 1600–1300 cm⁻¹ in the infrared spectra of monosubstituted decaboranes were found to be characteristic for the site of decaborane skeleton substitution.

Soon earlier we have pointed out the importance of the 1600 – 1400 cm⁻¹ region in the infrared spectra of 5- and 6- substituted decaboranes, allowing a direct correlation between the shifts of the bands in these regions and the substituent position¹. To generalize the nature of these shifts, we extended our study using the newly prepared 6-substituted decaboranes (6-isothiocyanatodecaborane, 6-acetoxycydecaborane², 6-phenyldecaborane³, 6-bromodecaborane) and a series of 1- and 2-halogenodecaboranes⁴, respectively. The complication in the interpretation of infrared spectra of decaborane and its derivatives arise from two main factors. First of them is the low symmetry of the molecule with respect to the large number of atoms involved (C_{2v} in the case of decaborane, C_s in the case of 1-, 2-, and 6-substitution, and C₁ in the case of 5-substitution). The second factor is the exceptional nature of the bonds in borane molecules. Both these factors complicate the problem in such an extent that the exact assignment and the theoretical analysis of the spectra are limited to the first member of the borane family (diborane) and its alkyl derivatives^{5–17}. The empirical assignment only is known for pentaborane (9)^{7,18}, pentaborane (11), hexaborane (10), hexaborane(12)¹⁹, and tetraborane and its methyl derivatives²⁰. The wave-numbers only are reported for substituted pentaboranes (9)^{21–24}. No information concerning the interpretation of the infrared spectra of decaborane and its derivatives can be found in the literature except the assignment of the B–H terminal and bridge stretching vibrations^{25,26}.

In the presented work we try to explain some trends in the infrared spectra on the basis of following simplified consideration of decaborane structure: 1. Assuming validity of the Lipscomb's formulation of decaborane⁵, the boron atoms 2 and 4 have the sp²-hybridization whereas the remaining atoms are sp³-hybridized. 2. There are only two normal covalent B–B bonds in this formula – B₂–B₆ and B₄–B₉, respectively; all other boron atoms are connected by three-center bonds. 3. The

* Part XXV: This Journal 37, 2696 (1972).

boron atoms 5, 6, 7, 8, 9, 10 carry both the terminal B—H_t and the bridge bond B—H_b. Atoms 6 and 9 carry each two bridge bonds symmetrically arranged, whereas the atoms, 5, 7, 8, and 10 have each only one bridge bond. The substitution at these atoms can therefore directly affect the strength or the polarity of the B—H_b bonds, respectively.

EXPERIMENTAL

All manipulations were performed in nitrogen atmosphere in whole-glass apparatuses or in a dry-box, respectively. The melting points (uncorrected) were taken in a sealed capillary. The mixture of 1- and 2-halogenodecaboranes, respectively, was prepared by direct halogenation of decaborane under conditions of Friedel-Crafts reaction and was separated on a silica gel column pre-treated by acetic acid⁴. In the case of iododecaboranes this procedure failed to yield the isomers of sufficient purity and therefore was combined with fractional crystallization from the cyclohexane-pentane mixture. The 5- and 6-halogenodecaboranes were prepared by reaction of 6,9-bis(dialkylsulphido) decaborane with halogen hydride according to the earlier described method²⁷; 6-acetoxy- and 6-isothiocyanatodecaborane were prepared by reaction of the same compound with mercury(II) acetate or mercury(II) thiocyanate, respectively². The preparation of 6-phenyldecaborane will be reported later. The purity of all compounds was checked by thin-layer chromatography. Melting points (°C) were: 1-Cl 74–75, 2-Cl 86.5–88, 6-Cl 31–32, 1-Br 92–93, 2-Br 108–109.5, 5-Br 48–49, 6-Br 32–34, 1-I 98.5–100, 2-I 117.5–119, 5-I 70–70.5, 5-F 67.5–69, 6-CH₃COO 138–140, 6-NCS 83–86. Decaborane was purified by multiple sublimation *in vacuo* (10⁻³ Torr) and had m.p. 99.5°C. Infrared spectra were measured on a Zeiss (Jena) UR 10 spectrophotometer as 5% solutions in carbon tetrachloride and carbon disulfide, respectively. The sample path length was 0.01 cm. The wavenumber scale was calibrated by indene-cyclohexanone-camphor mixture²⁸.

RESULTS AND DISCUSSION

Boron-Substituent Stretching Vibrations

Perec and Becka²⁹ have assigned the band at 1402 cm⁻¹ in the spectrum of difluoroborane HBF₂ to the B—F stretching vibration, *i.e.* the value very close to the B—H_b—B deformation vibration in decaborane. The assignment of the B—F stretching in 5-FB₁₀H₁₃ will be therefore very difficult owing to the strong interaction of this vibration with the B—H_b—B vibration and the F—B—H deformation vibration, respectively. The bands in this region appear (as expected) in the form of poorly resolved quadruplet having maxima at 1212, 1239, 1266 and 1281 cm⁻¹, that can be assigned to the coupled F—B—H_b—B vibrations or to the F—B—H_b deformation vibrations respectively. A similar complication was noted by Burg²³ in the spectrum of 2-FB₅H₈ (*i.e.* in an analogous case, where the boron atom is shared by the strongly electronegative fluorine atom and the hydride bridge). In contradistinction to the preceding case, the assignment of B—Cl stretching vibration presents no problems even for the 6-isomer in which the coupling with the B—H_b—B vibration is very

small owing to the greater mass of the chlorine atom and the greater frequency difference between these two vibrations. We assigned the following bands to the $^{10}\text{B}-\text{Cl}$ and the $^{11}\text{B}-\text{Cl}$ stretching vibrations: 1- $\text{ClB}_{10}\text{H}_{12}$ 1011, 1024; 2- $\text{ClB}_{10}\text{H}_{13}$ 1055, 1068; 6- $\text{ClB}_{10}\text{H}_{13}$ 1046, 1064 cm^{-1} . The assignment for $\text{H}^{10}\text{BCl}_2$ and for $\text{H}^{11}\text{BCl}_2$ is 1100 and 1089 cm^{-1} , respectively³⁰. With chlorodiborane $\text{B}_2\text{H}_5\text{Cl}$ were to the $\text{B}-\text{Cl}$ stretching vibration assigned³¹ the bands at 1095 and 1075 cm^{-1} . Similarly to the iodo derivatives, the bands of $\text{B}-\text{Br}$ stretching vibrations appear in the very complex region of decaborane „fingerprint” between 1000 and 700 cm^{-1} . Using the analogy with the $\text{B}-\text{Br}$ stretching vibrations in the spectrum of BBr_3 (820 and 865 cm^{-1})³², we propose the following assignments: 1- $\text{BrB}_{10}\text{H}_{13}$ 827, 847; 2- $\text{BrB}_{10}\text{H}_{13}$ 885, 898; 5- $\text{BrB}_{10}\text{H}_{13}$ 850, 871,; 6- $\text{BrB}_{10}\text{H}_{13}$ 868, 880 cm^{-1} . The bands at 704 and 731 cm^{-1} in the spectrum of BI_3 were assigned to the $\text{B}-\text{I}$ stretching vibration³². Similarly can be assigned to this vibration the bands at 797 and 787 cm^{-1} in the spectra of 1- $\text{IB}_{10}\text{H}_{13}$ and 2- $\text{IB}_{10}\text{H}_{13}$, respectively. However, this vibration cannot be assigned with certainty in the spectrum of 5- $\text{IB}_{10}\text{H}_{13}$. The doublet at 1106 and 1140 cm^{-1} in the spectrum of 6- $\text{CH}_3\text{B}_{10}\text{H}_{13}$ can be assigned to the $\text{B}-\text{C}$ stretching vibration and the bands at 1320 and 1343 cm^{-1} to the symmetric deformation of the methyl group³³. The antisymmetric deformation vibration of the methyl group is overlapped by strong bands due to the $\text{B}-\text{H}-\text{B}$ deformation vibrations at 1500–1400 cm^{-1} . The band at 1434 cm^{-1} in the spectrum of 6- $\text{C}_6\text{H}_5\text{B}_{10}\text{H}_{13}$ can be assigned to the benzene ring stretching, the bands at 1228 and 1248 cm^{-1} can be assigned to the $\text{B}-\text{C}_6\text{H}_5$ stretching vibration, the band at 751 cm^{-1} to the CH wagging vibration and the band at 697 cm^{-1} to the benzene ring bending vibration. The $\text{B}-\text{N}$ and the $\text{B}-\text{O}$ stretching vibrations in isothiocyanato- and acetoxydecaboranes were assigned earlier².

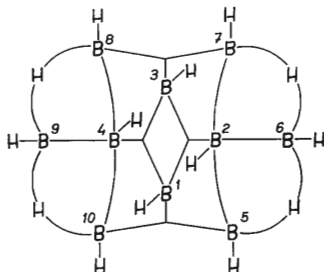


FIG. 1
Structural Formula of $\text{B}_{10}\text{H}_{14}$

B-H Stretching Vibration

It can be stated, that except an apparent intensity decrease of the $\text{B}-\text{H}_\beta$ stretching bands in monosubstituted decaboranes in comparison with decaborane, no repro-

ducible dependency of the frequency on the substituent position can be found. The 5-FB₁₀H₁₃ is again an exception, since in this compound the coupling with the B—F stretching takes place (similarly to the B—H_b deformation vibration) and therefore a shift of the B—H_b stretching bands to the values 1875 and 1912 cm⁻¹ accompanied by their intensity increase is observed. A similar effect of even greater magnitude can be found in 6-SCNB₁₀H₁₃, in which four anomalous very strong bands appear at 1870, 1892, 1950, and 1970 cm⁻¹. This fact remains unexplained yet. However, we suppose that it is due to an increase of the B—H_b bond polarity due to the —N=C=S group.

The assignment of B—H_t stretching vibrations (c. 2600 cm⁻¹) is usually straightforward since these bands are the most intense ones and appear in the region where no other bands occur. Closer examination of the shape of these bands revealed their unsymmetric character and suggested a shoulder at the side of lower wavenumbers. This asymmetry is well apparent on the appropriate band of decaborane itself. The results of numerical band separation of the B—H_t stretching bands of decaborane, 1-, 2-, 5-, and 6-bromodecaborane (*i.e.* in the series containing all four possible sites of substitution) are given in the Table I. The calculations were performed on a digital computer using the method of damped least squares^{35,36}. In agreement with

TABLE I

Parameters of the Separated Bands of the B—H Stretching Vibrations in Decaborane B₁₀H₁₄ and its Derivatives X-B₁₀H₁₃

X	ν_{\max}^a	E_{mol}^b	B ^c	X	ν_{\max}^a	E_{mol}^b	B ^c
H	2 552	53	1 325	5-Br	2 558	56	1 855
	2 570	193	7 046		2 572	174	5 158
	2 582	380	15 059		2 582	216	7 589
	2 595	180	6 797		2 596	198	8 226
1-Br	2 563	14	313	6-Br	2 553	61	1 839
	2 580	178	5 746		2 571	199	7 688
	2 590	222	7 357		2 583	323	13 145
	2 600	198	7 877		2 597	185	6 884
2-Br	2 560	47	1 000				
	2 572	54	1 415				
	2 583	211	7 731				
	2 596	288	12 555				

^a Band maximum cm⁻¹; ^b molar extinction coefficient mol⁻¹ l cm⁻¹; background correction introduced; ^c molar integrated intensity [mol⁻¹ l cm⁻²].

the assumption made at the beginning of this paper, the B—H_i stretching band is a superposition of the four bands assignable to the B—H_i vibrations of four

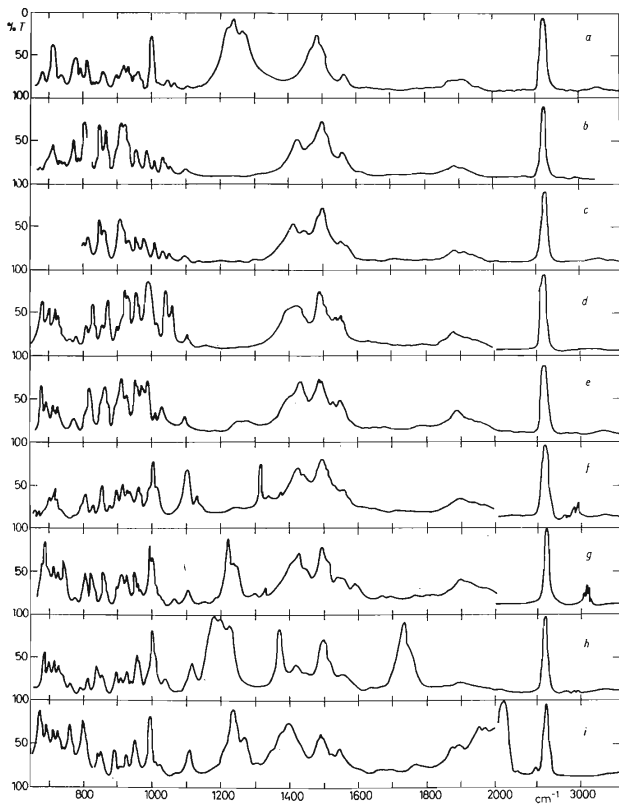


FIG. 2

Infrared Spectra

a 5-FB₁₀H₁₃, *b* 5-BrB₁₀H₁₃, *c* 5-IB₁₀H₁₃ *d* 6-ClB₁₀H₁₃, *e* 6-BrB₁₀H₁₃, *f* 6-CH₃B₁₀H₁₃
g 6-C₆H₅B₁₀H₁₃, *h* 6-CH₃COOB₁₀H₁₃, *i* 6-SCNB₁₀H₁₃.

non-equivalent boron atoms. However, this assumption is not justified by the parameters of the separated bands. Whereas the 6-substitution nearly does not affect the position and the intensity of these bands, the positions and the intensities of the first three bands in 1-bromodecaborane are evidently changed. On the second hand, the band positions in 2- or 5-bromodecaborane agree mutually well and also their integrated intensities. However, the abnormal intensity of the 2596 cm^{-1} band in the spectrum of 2-bromodecaborane is striking.

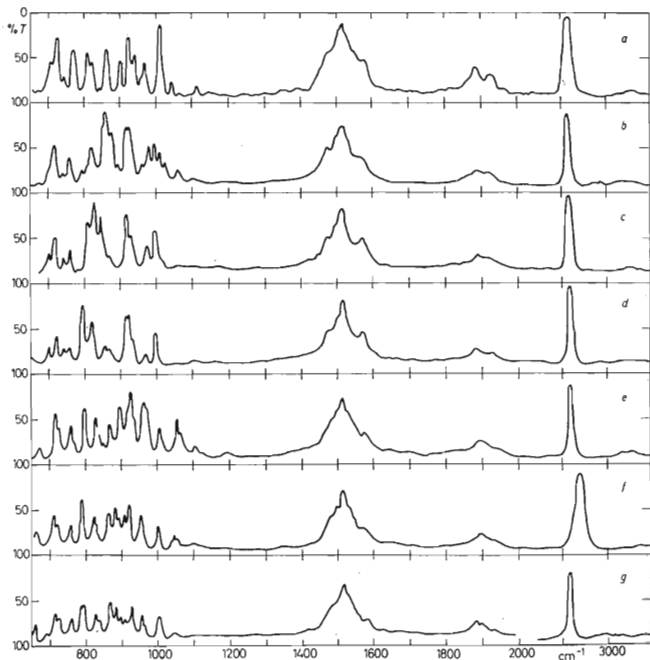


FIG. 3

Infrared Spectra

a $\text{B}_{10}\text{H}_{14}$, *b* $1\text{-ClB}_{10}\text{H}_{13}$, *c* $1\text{-BrB}_{10}\text{H}_{13}$, *d* $1\text{-IB}_{10}\text{H}_{13}$, *e* $2\text{-ClB}_{10}\text{H}_{13}$, *f* $2\text{-BrB}_{10}\text{H}_{13}$,
g $2\text{-IB}_{10}\text{H}_{13}$.

B-H Deformation Vibrations

When comparing the regions of $1600-1300\text{ cm}^{-1}$ in the infrared spectra shown in the Figs 2 and 3, we found that the spectra of 1- and 2-substituted decaboranes are nearly identical with that of decaborane whereas the bands in the spectra of 5- and 6-substituted decaboranes are shifted to the region of $1450-1400\text{ cm}^{-1}$. We deduced from the spectrum of bridge deuteriated³⁴ $\text{B}_{10}\text{H}_{10}\text{D}_4$ that the vibrations in this region can be unambiguously assigned to the $\text{B}-\text{H}_b-\text{H}$ deformation vibrations. As a result of the substitution of bridge hydrogen for deuterium, these bands move to $1131, 1166, \text{ and } 1184\text{ cm}^{-1}$, showing an average BH/BD ratio 1.31. Using the conclusions which follow from the Table I for the atoms 5, 7, 8, 10 and for 6 and 9, it can be concluded that the shift of these bands to the region of $1450-1400\text{ cm}^{-1}$ is characteristic for the substitution at boron atoms having a $\text{B}-\text{H}_b$ bond and is not remarkably affected by the nature of the substituent (Table II). The difference between the values for 5- $\text{IB}_{10}\text{H}_{13}$ and for 5- $\text{BrB}_{10}\text{H}_{13}$ can be explained by unbalancing of the $\text{B}-\text{H}_b-\text{B}$ system in which the mass effect of the substituent can play an

TABLE II

Wavenumbers of the Bands^a of the $\text{B}-\text{H}_b-\text{B}$ Deformation Vibrations in 5- and 6-Substituted Decaboranes in the Region of $1450-1400\text{ cm}^{-1}$

Substituent	max. ^b	E_{mol}^b	B^b	Substituent	max. ^c
5 Br	1 412	13.5	1 491	5-F	1 212
	1 423	37.0	1 783		1 239
5-I	1 390	17.7	2 031	6-AcO	1 266
	1 393	21.3	646		1 281
	1 436	7.5	246		1 423
5- CH_3	1 408	18.5	1 246	6-N=C=S	1 460
	1 424	49.0	2 177		1 403
	1 448	25.0	1 225		
6 Cl	1 402	20.0	1 056	6- C_2H_5	1 408
	1 420	26.1	1 041		1 448
	1 438	33.1	1 721		
6-Br	1 406	30.5	2 535		
	1 442	62.4	2 862		

^a For symbols see Table I ^b separated ^c not separated.

important role. To compare the intensities of the bands in this region, we performed the numeric band separation, whose results are shown in the Table II. It is evident that in all cases the intensity of bands rises with increasing volume of the substituent, *i.e.* that the gradient of the B—H_b—B bond vibrational dipole moment increases. It follows from the mentioned facts that an empirical dependence of the band position in this region on the type of decaborane skeleton substitution was found. This dependence allows the application of infrared spectroscopy to the determination of the constitution of this type compounds.

In the region of 1000–650 cm⁻¹ appear the B—H_t deformation vibrations and eventually the B—B skeletal vibrations. Therefore we consider the assignment as approximate and tentative. Even if the B—H_t deformation vibrations and the skeletal decaborane vibrations, respectively, cannot be definitively assigned, it is possible by detailed study of this region to obtain some information about the substituent position supplementing the data from the region of B—H_b—B deformation vibrations. A very strong sharp band at 1009 cm⁻¹ occurs in the spectrum of decaborane. Its intensity is markedly lowered in 1-, 2-, and 5-substituted decaboranes and retains nearly the same intensity in the case of the 6-substitution but shifts from 997 to 1006 cm⁻¹. We claim that this band can be assigned to the vibration of the terminal hydrogen at boron atom 2. The increase of this band intensity will be caused by increased polarity of the B₍₂₎—B₍₆₎ bond due to the electronegative substituent at B₍₆₎.

Similarly to the B—H_b—B deformation vibrations (range of 1600–1300 cm⁻¹), we found an interesting correlation between the band wavenumber and the substituent position in the region of 800–650 cm⁻¹. For 1- and 2-substituted decaboranes, respectively, the following characteristic bands can be found: 704, 720, 742, 763 cm⁻¹ and 668, 715, 729, 763 cm⁻¹. With decaborane, these bands are located at 707, 722, 743 and 770 cm⁻¹. A general rule applies in both cases: the intensity of the bands decreases with increasing mass of the substituent but their separation increases. The 6-substituted decaboranes display these bands at 687, 706, 723 and 735 cm⁻¹. The bands are strong and do not show any apparent changes of the intensity when changing the substituent. They can be most probably assigned to the deformation vibration of the terminal hydrogen atoms at boron atoms B₍₆₎, B₍₄₎ and B₍₉₎. In agreement with this assignment, the 1-substitution does not affect their position whereas the 2- eventually the 6-substitution cause the above discussed changes independent on the nature of the substituent.

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Translated by P. Sedmera.