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INFRARED SPECTRA OF DECABORANE AND ITS DEUTERIO DERIVATIVES

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Eight symmetrically deuterated derivatives of decaborane were prepared and their infrared spectra measured in the region $4000-400$ cm^{-1}. An approximate assignment of the bridge and terminal B—H bonds based on isotopic shifts was performed.

In the previous paper[1] we have published empirical dependences serving for the determination of the substituent position on the decaborane skeleton, using infrared spectroscopy. The assignment of the bands in the spectrum of $B_{10}H_{14}$, which are specifically affected by the substituent positions, was only approximate. A detailed analysis of the infrared spectrum of the $B_{10}H_{14}$ molecule based on calculation methods cannot be performed owing to the complexity and low symmetry (C_{2v}) of the molecule. A very crude classification of vibrations using the topological distribution of boron atoms, not regarding the real bonding conditions, has been given by Keller and Johnson[2]. Other authors[3-4] restricted themselves only to the simplest assignment of the stretching vibrations of the bridge B—H$_b$ and terminal B—H$_t$ bonds.

We prepared therefore symmetrically deuterated derivatives of $B_{10}H_{14}$, *viz.* μ-$B_{10}H_{10}D_4$**(*I*); 1,2,3,4-$B_{10}H_{10}D_4$ (*II*); μ-1,2,3,4-$B_{10}H_6D_8$ (*III*); 5,7,8,10-$B_{10}H_{10}D_4$ (*IV*); 1,2,3,4,5,7,8,10-$B_{10}H_6D_8$ (*V*); μ-1,2,3,4,5,7,8,10-$B_{10}H_2D_{12}$ (*IV*); μ-6,9-$B_{10}H_8D_6$ (*VII*); and 6,9-$B_{10}H_{12}D_2$ (*VIII*), resp., and attempted at a more accurate assignment of some spectral bands from their isotopic shifts.

II can be prepared by electrophilic substitution of decaborane by DCl in the presence of AlCl$_3$ (ref.[5,6]). If the reaction is carried out under increased pressure, exchange proceeds also in the positions 5,7,8,10 with the formation of *V*, yielding *IV* when treated with HCl under normal pressure and in the presence of AlCl$_3$ (ref.[7]). Bridge-deuterated *I* is formed by the exchange reaction between $B_{10}H_{14}$ and D_2O in the

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**   The symbol μ is used for the substitution in bridge positions.

medium of ethers[4,8-10] or DCl in dioxane[3]. The authors, however, never isolated that substance. During our attempts at isolation of I according to the first method, a dangerous decomposition of the reaction mixture occured. The exchange carried out according to the second method did not proceed even after 240 h under increased pressure of DCl or after one month under normal pressure, if dioxane was perfectly dried. Deuteration described[3] was obviously due to the presence of traces of moisture in dioxane, *i.e.* to the attack of B—H$_b$ by D$_2$O. We have developed a new method for the bridge deuteration of B$_{10}$H$_{14}$ from ist terminally deuterated derivatives, based on the effect of D$_2$O in acetonitrile. By this procedure, D is introduced selectively only into the bridge positions, no migration occurring into the terminal positions.

EXPERIMENTAL

All operations were carried out in the nitrogen atmosphere, in whole-glass equipments or in a dry-box. IR spectra were recorded on a UR 10 (Zeiss, Jena) and a Beckman IR 20 A spectrometer; 5% solutions in tetrachloromethane or carbon disulfide were measured in cells 0·01 cm thick. The content of D in the compounds prepared was determined by decomposing the sample in a quartz tube evacuated to 10^{-2} Torr at 600—700°C. The mixture of H$_2$, HD, and D$_2$ formed was analysed on a mass spectrometer. DCl was prepared by the reaction of D$_2$O with benzoyl-chloride, with the purity of 95% D (IR-spectroscopy). D$_2$O used contained 98% D. Carbon disulfide and acetonitrile were distilled with P$_2$O$_5$ before using. B$_{10}$H$_{14}$ was resublimed at 20°C/10^{-5} Torr. μ-6,9-B$_{10}$H$_{12-x}$D$_{2+x}$ with an undefined content of D in the bridges was obtained by the hydrogenation of bis(dimethyl sulfide) decaborane by D$_2$ in benzene at 90°C and 130 atmospheres[11].

μ-*Tetradeuteriodecaborane* (*I*): 20 ml D$_2$O was added to the solution of 3·0 g (24·5 mmol) B$_{10}$H$_{14}$ in 30 ml acetonitrile. After 20 min shaking the acetonitrile layer was separated and evaporated at 20°C/10^{-5} Torr. 2·2 g (71%) substance *I* with the content of 3·7 (93%) D was obtained by the sublimation of the residue at 20°C/10^{-5} Torr.

1,2,3,4-*Tetradeuteriodecaborane* (*II*): A total amount of 45 l DCl was introduced into the solution of 20 g (163 mmol) B$_{10}$H$_{14}$ and 5·0 g (37 mmol) anhydrous AlCl$_3$ in 250 ml CS$_2$ under stirring during 24 h. Then the solvent was evaporated *in vacuo*, the residue extracted with pentane, and the fraction soluble in the latter was sublimed at 80°C/10^{-2} Torr. 19·5 g (93%) substance *II*, purity 2·9 (72·5%) D was obtained.

1,2,3,4,5,7,8,10-*Octadeuteriodecaborane* (*V*): 0·1 g (0·82 mmol) B$_{10}$H$_{14}$ and 0·1 g (0·75 mmol) anhydrous AlCl$_3$ was placed in an ampoule. After attaching to a vacuum line and cooling to −190°C, 4 ml CS$_2$ and 2200 ml (92 mmol) DCl were condensed in the ampoule. The ampoule was sealed off, heated slowly to room temperature, and left for 7 days. Then it was cooled to −190°C, attached to the vacuum line, and after opening to vacuum the content was evaporated to dryness. The evaporation residue was extracted with pentane; after sublimation at 20°C/10^{-5} Torr the fraction yielded 0·1 g (94%) substance *V*, purity 5·7 (71·5%) D.

5,7,8,10-*Tetradeuteriodecaborane* (*IV*): The solution of 0·25 g (1·12 mmol) substance *V* and 0·1 g (0·75 mmol) anhydrous AlCl$_3$ in 15 ml CS$_2$ was bubbled through by dry HCl for 36 h. Then the mixture was filtered and the solid fraction extracted with carbon disulfide; after sublimation at 20°C/10^{-5} Torr, the combined extracts yielded 0·19 g (79%) substance *IV* with the content of 4·1 (104%) D.

μ-1,2,3,4-*Octadeuteriodecaborane* (*III*): 15 ml D_2O was added to the solution of 0·7 g (5·5 mmol) substance *II* in 15 ml acetonitrile and the mixture was shaken vigorously for 20 min. The aceto-nitrile layer was separated and the solvent distilled off at $20°C/10^{-2}$ Torr. After sublimation at $20°C/10^{-5}$ Torr, the residue yielded 0·5 g 69% substance *III*, containing 6·7 (83·6%) D.

μ-1,2,3,4,5,7,8,10-*Deuteriodecaborane* (*VI*): 5 ml carbon disulfide and 2500 mmol (104 mmol) DCl were condensed in a vacuum line to a mixture of 0·35 (2·8 mmol) substance *I* and 0·2 g (1·5 mmol) anhydrous $AlCl_3$ in an ampoule cooled to −190°C. The ampoule was sealed, heated to room temperature, and left for 6 days. After the evaporation of the volatile fractions at 20°C / : 10^{-1} Torr, the residue was extracted with pentane. After sublimation at $20°C/10^{-5}$ Torr, the extracts gave 0·35 g (93%) substance *VI*, with the content of 9·5 (79·5%) D.

μ-6,9-*Hexadeuteriodecaborane* (*VII*): A mixture of 5 ml acetonitrile, 0·2 g (1·59 mmol) μ-6,9--$B_{10}H_{12-x}D_{2+x}$, and 3 ml D_2O was shaken for 20 min, the acetonitrile layer was separated and the solvent distilled off at $20°C/10^{-2}$ Torr. By sublimation of the residue, 0·13 g (63·5%) *VII* was obtained.

6,9-*Dideuteriodecaborane* (*VIII*) was obtained from *VII* by the same procedure by a quantita-tive reverse exchange with H_2O. 0·1 g (0·78 mmol) *VII* gave 0·07 g (72·2%) *VIII*.

Attempts at the bridge deuteration of decaborane. A. 20 ml D_2O was added to the solution of 3·3 g (24·6 mmol) decaborane in 15 ml dioxane or tetrahydrofuran, and the mixture was left for 72 h in nitrogen atmosphere. During that time, the decomposition of the reaction mixture with the evolution of hydrogen was apparent. A spontaneous decomposition of the re-action mixture proceeded after the evaporation of the volatile fractions. *B.* 1 100 ml (46 mmol) DCl was condensed into an ampoule containing the solution of 0·1 g (0·82 mmol) decaborane in 4 ml dioxane, in a vacuum line at −190°C. After heating up to room temperature, the ampoule was left for 240 h opened into vacuum and the volatile products were evaporated. Unreacted decaborane was recovered quantitatively by the sublimation of the residue at $20°C/10^{-5}$ Torr.

RESULTS AND DISCUSSION

If the molecular symmetry C_{2v} is assumed for decaborane, then 20 of the total of 66 vibrational modes belong to the species A_1, 14 to A_2, 15 to B_1, and 17 to the species B_2; only the species A_1, B_1, and B_2, however, are IR active. In the first approxim-ation, the division by Keller and Johnson[2] can be accepted and the vibrational modes described as idealized vibrations of the various B—H bonds and of the boron skeleton. 24 vibrations of the boron skeleton, 10 B—H_t stretching vibrations, 20 B—H_t bending vibrations (10 of them parallel with and 10 perpendicular to the C_2 axis), and 12 B—H—B vibrations can be then expected for the molecule of $B_{10}H_{14}$. Regard-
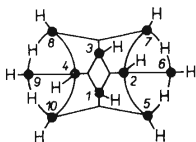

FIG. 1
Arrangement of the Molecule $B_{10}H_{14}$

ing the quite exceptional arrangement of the bonds in hydroboron molecules, several different types of boron atoms can be considered for the molecule of decaborane[12] (Fig. 1).

These types were discussed in the previous paper[1], and although in the last time there is some doubt about the existence of the open three-center bond[13] between the atoms $B_{(5)}$, $B_{(2)}$, $B_{(7)}$ and $B_{(8)}$, $B_{(4)}$, $B_{(10)}$, resp., we shall consider the arrangement of the bonds according to Fig. 1 in this work.

Stretching vibrations B—H$_t$. The band at $2590\ cm^{-1}$ was attributed to this vibration[2-4]. In terminally deuterated derivatives, the band corresponding to the B—D$_t$ stretching vibration lies at $1930\ cm^{-1}$ $(\nu_H/\nu_D = 1\cdot34)$ with a distinct shoulder in the case of substances *III* and *IV*. In the bridge-deuterated *I* the position of the band is not affected, which indicates a pure terminal vibration with no coupling with the B—H$_b$ stretching vibration. As stated, however, in the previous paper[1], that band represents the overlap of four bands with the maxima at 2552, 2570, 2582 and $2595\ cm^{-1}$. In order to examine the dependence of those bands upon the deuteration position, we carried out a numerical separation of the bands of the B—H$_t$ stretching vibration fo deuterated decaboranes on a computer. The results are listed in Table I.

From the results of the separation it is apparent that the sum of the integral intensities of the bands is linearly dependent on the number of deuterium atoms in the molecule. An increase of those values appears for the bridge-deuterated compounds in comparison with the terminally deuterated compounds, approximately by 13,

TABLE I

Parameters of Separated Bands of Stretching Vibration of the Terminal B—H Bonds: Positions of the Maxima (cm^{-1}) and Molar Integrated Intensities ($mol^{-1}\ l\ cm^{-2}$, in parentheses)

$B_{10}H_{14}$	I	II	III	IV	V	VI
2 552	2 552	2 557	2 557	2 552	2 553	2 557
(1 325)	(2 080)	(380)	(1 650)	(1 520)	(120)	(1 050)
2 570	2 570	2 574	2 576	2 569	2 573	2 575
(7 045)	(7 320)	(3 550)	(6 620)	(5 750)	(750)	(2 450)
2 582	2 583	2 587	2 589	2 583	2 588	2 593
(15 060)	(14 470)	(11 980)	(9 890)	(5 350)	(5 030)	(6 110)
2 595	2 596	2 597	2 600	2 596	2 600	2 605
(6 800)	(8 750)	(3 450)	(4 230)	(5 320)	(2 490)	(830)

TABLE II

Approximate Assignment of IR Bands (cm^{-1}) of $B_{10}H_{14}$ and Its Deuterio Derivatives

$B_{10}H_{14}$[a]	I	II	III	IV	V	VI	VII	VIII	Assignment
707 ms	704 ms	645 ms	643 ms	532 ms	508 ms	526 ms	703 s	710 sh	δB—H$_t$
722 vs	739 vs	552 ms	553 ms	559 ms	525 w	540 s		722 s	δB—H$_t$
743 w		563 sh	586 w	571 ms	553 w	550 w	739 vs	744 ms	δB—H$_t$
772 ms	773 ms	766 s	—	774 ms	770 ms	773 ms	780 ms	768 ms	νB—B
811 s	810 w	695 sh	643 ms	643 ms	620 s	620 w	680 w	812 w	δB—H$_t$
822 ms	690 sh	821 ms	750 ms	730 vs	640 ms	640 ms	690 w	694 w	+δB—H$_b$[b]
860 ms	739 vs	853 s	872 w	670 ms		675 w	734 vs	859 ms	δB—H$_b$[b]
899 ms	895 s	886 ms					895 s	902 ms	δB—H$_t$
922 vs	704 vs	930 s	706 ms	703 ms		705 ms	703 s	923 sh	δB—H$_t$
935 s	935 s	944 s	954 ms	965 ms	959 ms	944 w	955 s	966 ms	+δB—H$_b$[b]
965 ms	957 ms	955 s	984 s	818 s	796 s	793 s	1 005 s	1 009 vs	νB—B
1 009 vs	993 ms	984 ms	995 s	835 sh	826 s	825 s	1 017 vs	1 029 sh	δB—H$_t$
—	1 009 vs	998 ms	757 sh	845 sh		1 025 w			
1 042 ms	1 015 vs	1 037 w	836 sh	1 033 s	1 033 s				
1 100 ms	1 100 w	1 107 w	1 128 sh						
1 470 sh	1 131 sh	1 484 sh	1 160 vs	1 493 sh	1 480 sh	1 122 sh	1 128 sh	1 475 sh	νB—H$_b$ out-of-phase
1 500 ms	1 148 sh	1 503 sh	1 177 sh	1 506 sh	1 502 vs	1 143 vs	1 164 vs	1 502 sh	
1 512 vs	1 166 vs	1 516 vs	1 396 sh	1 515 vs	1 520 sh	1 174 sh	1 182 sh	1 515 vs	
1 576 ms	1 184 ms	1 583 ms	1 418 ms	1 576 sh	1 572 s		1 409 ms	1 568 s	
1 855 sh	1 402 sh	1 869 sh	1 463 w	1 860 sh	1 875 sh	1 418 ms	1 468 w	1 888 ms	νB—H$_b$ in-phase
1 885 ms	1 416 ms		1 516 ms	1 885 s,sh		1 460 mw	1 515 vs		
1 930 sh	1 480 sh	1 927 vs	1 929 ms	1 930 vs	1 929 vs	1 520 ms	1 941 ms	1 935 s	
1 966 ms	1 516 ms		1 946 sh	1 945 sh		1 936 ms			
2 590 vs	2 575 vs	2 588 vs	2 590 vs	2 580 vs	2 590 vs	2 599 vs	2 580 vs	2 580 vs	νB—H$_t$
—									
—									

[a] w weak, ms medium strong, s strong, vs very strong, sh shoulder, ν stretching, δ bending; [b] together with δB—H$_t$.
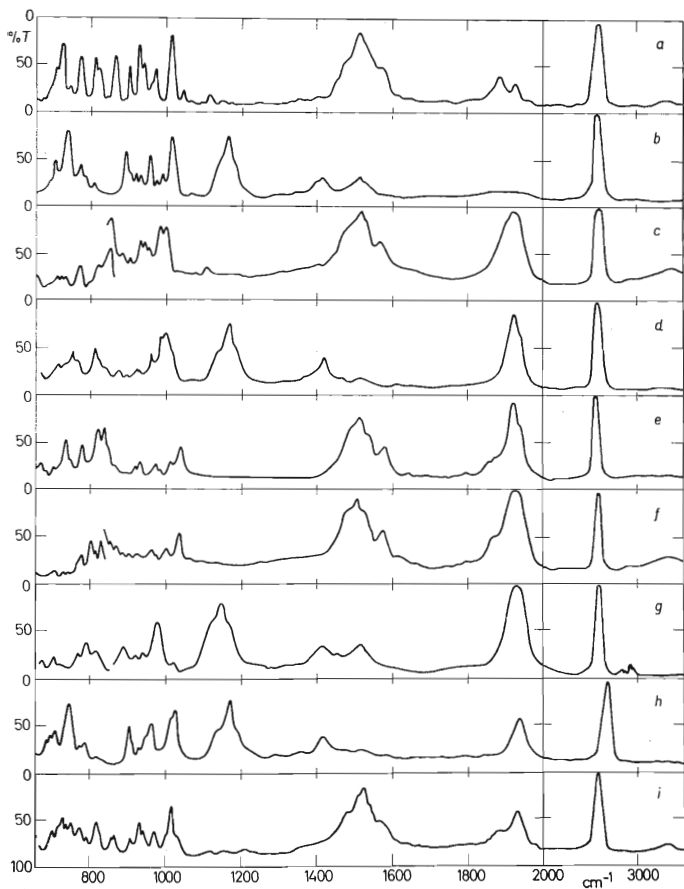
FIG. 2

Infrared Spectra

a $B_{10}H_{14}$; b μ-$B_{10}H_{10}D_4$ (*I*); c 1,2,3,4-$B_{10}H_{10}D_4$(*II*); d μ-1,2,3,4-$B_{10}H_6D_8$(*III*); e 5,7,8,10-$B_{10}H_{10}D_4$ (*IV*); f 1,2,3,4,5,7,8,10-$B_{10}H_6D_8$ (*V*); g μ-1,2,3,4,5,7,8,10-$B_{10}H_6D_8$ (*VI*); h μ-6,9-$B_{10}H_8D_6$ (*VII*); i 6,9-$B_{10}H_{12}D_2$ (*VIII*).

15 and 22% for *I*, *III*, and *VI*, resp. This increase can be explained by the mass effect of the remainder of the molecule. The highest effect appears with the compound *IV*, where the boron atom is common to the bridge as well as to the terminal deuterium. The comparison of the integral intensities of the various bands of the terminally deuterated compounds shows the maximum affecting for the band at $2582\ cm^{-1}$, which is the most intense in the quadruplet analyzed. Its intensity is lowered by 20, 65, and 67% in *II*, *IV* and *V*, resp., with respect to $B_{10}H_{14}$; in the case of *I*, the decrease is only 4%. Thus the band can be attributed to the stretching vibration of the peripheral atoms $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$ together with the atoms $B_{(1)}$ and $B_{(3)}$, lying in the xz plane. This assignment agrees with the consideration – following from the symmetry of the molecule – that the highest change of the vibrational dipole moment of the $B-H_t$ bond can be expected at the four peripheral atoms. Similarly, the comparison of the integral intensity of the band at $2595\ cm^{-1}$ of decaborane and its deuterated derivatives *I*, *II*, *IV* and *V*, resp., suggests the assignment of that band to the stretching vibration of the terminal hydrogens at the atoms $B_{(6)}$, $B_{(2)}$, $B_{(4)}$ and $B_{(9)}$, lying in the yz plane. This vibration should be less intense than that of the terminal hydrogens at the peripheral atoms, since change of the vibrational dipole moment occurs only in the components M_y and M_z, which is in accordance with the observed intensity of the band at $2595\ cm^{-1}$.

Stretching vibrations $B-H_b$: The bands at 1855 (shoulder), 1885, 1930, and $1966\ cm^{-1}$, shifted to 1402, 1416, 1480 and $1516\ cm^{-1}$, resp., in the bridge-deuterated derivatives (Table II, Fig. 2), were assigned to those vibrations. The value of the isotopic ratio v_H/v_D varies between $1.30-1.33$, which implies that these vibrations are not coupled with the $B-H_t$ vibrations. In our previous paper[1] we attributed the band group in the range $1300-1600\ cm^{-1}$ to the bending vibrations of the $B-H-B$ bond, although no sufficient argument occured for so high wavenumber values of angle deformations. The shifts of some of those bands on the substitution of the atoms $B_{(5)}$ or $B_{(6)}$ was independent of the nature of the substituent[1], though a dependence on its polarity would be expected. These facts raised doubts of the correctness of our assignment. For bridge-deuterated derivatives of decaboranes, the bands are shifted from the range $1300-1600\ cm^{-1}$ to the values 1131, 1148, 1166 and $1184\ cm^{-1}$ with the isotopic ratio v_H/v_D varying between $1.30-1.33$. This indicates again "pure" vibrations $B-H-B$, which cannot be expected for the $B-H-B$ bending vibrations. The boron atoms bound by the bridge $B-H_b$ bonding carry simultaneously also the terminal $B-H_t$ bond (Fig. 1); for this reason, a considerable coupling of the bending vibrations of the two types of $B-H$ bonds can be expected. We attribute therefore the bands in the range $1300-1600\ cm^{-1}$ to the out-of-phase $B-H_b$ stretching vibrations and those in the range $1800-2000\ cm^{-1}$ to the $B-H_b$ in-phase stretching vibration. This is in accordance with the assignment of that type vibrations for diborane[14,15], tetraborane[16],

and pentaborane[17]. It can be assumed that the coordinates of the peripheral atoms $B_{(5)}$ and $B_{(6)}$ remain practically constant during the out-of-phase stretching vibrations, therefore the substitution at those atoms caused only small shifts of the bands, almost independent of a bulky substituent.

Bending vibrations B—H_t *and* B—H_b: These vibrations can be placed in the very complicated region below 1100 cm^{-1}. Considerable coupling between the vibrations of the B—H_t and B—H_b, and B—H_b and skeletal B—B bonds can be expected *a priori*. This cancels to a high extent the advantages of the utilization of the isotopic shifts, since the ratios v_H/v_D are not characteristic in the case of coupled vibrations. Nevertheless we have done a preliminary attempt at the assignment, as given in Table II. We did not attribute the skeletal vibrations, because we expect their presence mainly in the region below 600 cm^{-1}. Still two of those vibrations appear probably in the range discussed here: they correspond to the bands at 772 and 965 cm^{-1}, which are practically not affected by the introduction of deuterium in the molecule.

The crude assignment of the B—H_t and B—H_b bending vibrations follows from Table II; therefore we restrict the discussion to some interesting effects. In the previous work we have found a dependence of the bands at 707, 722, 743 and 772 cm^{-1} on the substituent position, similarly to the out-of-phase stretching vibrations at $1300 - 1600$ cm^{-1}. The bands at 707, 722, and 743 cm^{-1} can be attributed to the B—H_t bending vibrations with a very low coupling with the B—H_b bending vibration. It can be assumed that the band at 707 cm^{-1} belongs probably to the vibration with a predominating character of vibrations of hydrogens at the peripheral atoms of the type $B_{(5)}$ and the basal atoms of the type $B_{(1)}$. The bands at 722 and 743 cm^{-1} belong, on the contrary, to the vibrations with the character of B—H_t at basal atoms of the type $B_{(2)}$ with a contribution of the peripheral type $B_{(6)}$. The band at 860 cm^{-1} can belong to the bending B—H_b vibration coupled with the bending vibration of the peripheral atoms of the type $B_{(5)}$, as apparent from the band positions, 739, 853 and 640 cm^{-1} for *I*, *II* and *VI*, resp. The very intense band at 1009 cm^{-1}, whose intensity is lowered on the 1-, 2-, or 5- substitution[1], can be attributed to the B—H_t bending vibration of the out-of-plane peripheral atoms of the type $B_{(5)}$ and of the atoms $B_{(1)}$, $B_{(3)}$, lying in the *xz* plane.

The assignment of some bands of the spectrum of decaborane, given in this work, can be considered to be very approximate; it can serve, however, as a starting point for further refinement.

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