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treatment of scattering by an angle-dependent potential (together with the problem of rotational energy transfer) is, however, a formidable one, beyond the scope of the present work.

CONCLUSIONS

(1) The cross sections for the elastic scattering of CsCl beams by *nonpolar* molecules may be predicted with fair accuracy from the Massey-Mohr formula, using the Slater-Kirkwood approximation for the dispersion term and the Debye equation for the induction force.

(2) The influence of the dipole-dipole force upon the scattering is appreciable and may be directly observed. The scattering cross sections for the *dipolar* molecules are large and decrease significantly with increasing temperature.

(3) Owing to the large magnitude of the dipole-dipole interaction with the CsCl beams, the approximate theoretical treatment accounts only semiquantitatively for the experimental observations.

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Infrared Spectra of Alkyldiboranes. III. 1,2-Dimethyl- and 1,2-Diethyldiboranes

Walter J. Lehmann,* Charles O. Wilson, Jr.,† and I. Shapiro*

Research Laboratory, Olin Mathieson Chemical Corporation, Pasadena, California

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The infrared spectra of three isotopic variants of 1,2-dimethyldiborane—$(CH_3B^{10}H_2)_2$, $(CH_3BH_2)_2$, $(CH_3BD_2)_2$—and of five 1,2-diethyldiboranes—$(C_2H_5B^{10}H_2)_2$, $(C_2H_5BH_2)_2$, $(C_2H_5BD_2)_2$, $(C_2D_5BH_2)_2$, $(C_2D_5BD_2)_2$—are reported and frequency assignments are made. 1,2-Dialkyldiboranes are very stable with respect to decomposition, but on prolonged standing rearrange to 1,1-dialkyldiboranes. Appearance of absorptions at ca 2100 and 1550 cm^{-1} is the first indication of the presence of 1,1-dialkyldiborane impurity. Although not conclusive, the evidence favors existence of predominantly cis configurations.

INTRODUCTION

In the monoalkyldiboranes[1,2] the vibrational character of diborane is partly preserved, in that one end of the molecule has retained both terminal hydrogens. This is not true in the 1,2-dialkyldiboranes, i.e., the sym-dialkyldiboranes, which have only a single terminal hydrogen at each end. In some respects one might expect simpler spectra for these molecules, in which both ends are alike, than for monoalkyldiboranes. However, it must be remembered that the corresponding vibrations of the two ends are not independent; they "couple," i.e., they interact with each other, producing "in-phase" and "out-of-phase" vibrations. This "splitting" may be quite considerable for some vibrations, but still, the average of the two frequencies should be relatively close to the value expected for the vibration of a single isolated unit.[3] Quite often the intensity of one member of a pair may be so weak as to escape detection or assignment as a fundamental vibration, but if we should fail to correlate properly such a split pair of frequencies, then the apparent shifts (up or down) from the single value may become quite puzzling.

The complexity of the problem is increased because the ratio of cis to trans isomers is not known in the 1,2-dialkyl compounds. Raman spectra, if available, would probably resolve the dilemma by virtue of the difference of selection rules. For cis compounds of this sort, e.g., *cis*-2-butene,[4] all vibrations are Raman active and all but one species (A_2) are infrared active, yielding a large number of "coincidences." However, in trans compounds (which have a center of symmetry) infrared and Raman activities are mutually exclusive,[3] allowing us to observe only one vibration of each pair.

EXPERIMENTAL

1,2-Dialkyldiborane can be prepared by direct interaction of trialkylborane with excess diborane, but the yield is so low that it is difficult to separate it from the much more abundant 1,1-dialkyldiborane. We found it more convenient to prepare 1,2-dialkyldiborane by the

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* Present address: Hughes Tool Company—Aircraft Division, Culver City, California.

† Present address: National Engineering Science Company, Pasadena, California.

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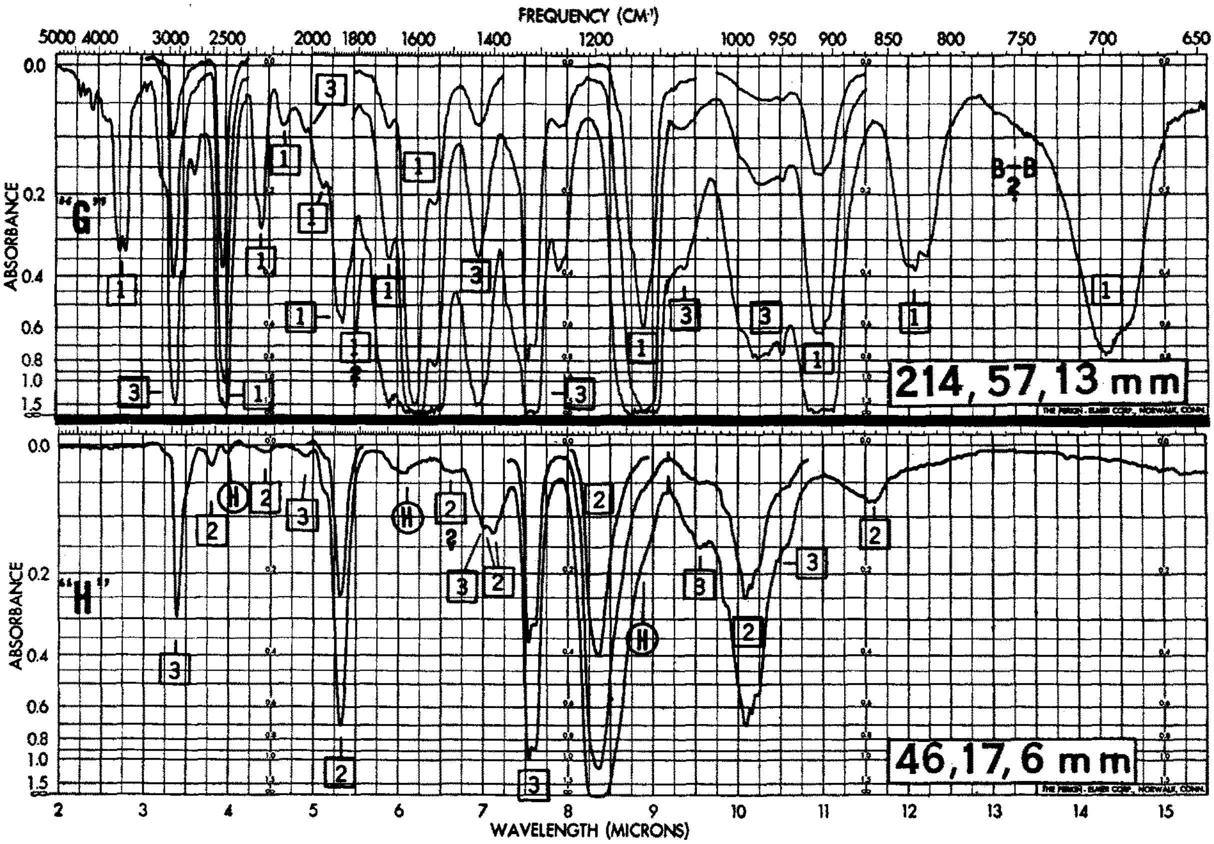

FIG. 1. Infrared spectra of 1,2-dimethyldiboranes; pressures reported for 5-cm cells. "G": $(CH_3BH_2)_2$; "H": $(CH_3BD_2)_2$. [1]:–B_2H_4 bands; [2]:–B_2D_4 bands; [3]:–CH_3 bands. (H): protium-impurity bands; B—B: stretching.

disproportionation of monoalkyldiborane[1,2] according to the reaction

$$2RB_2H_5 \leftrightarrows (RBH_2)_2 + B_2H_6.^5$$

1,2-Dimethyldiborane was purified by distillation through a −115°C bath and condensation in a −120°C bath, while the corresponding temperatures for 1,2-diethyldiborane were −72° and −80°C. Mass spectrometric analysis indicated negligible impurities. The vapor pressure of the ethyl compound was 36.4 mm at 0°C, in agreement with a previously reported value.[6]

Contrary to earlier reports,[7] our experience as well as that of other investigators[6] has shown that the 1,2-dialkyldiboranes decompose or disproportionate more slowly than any other alkyldiborane. Even after pure 1,2-dimethyldiborane had been stored at room temperature for several months we found very little infrared spectral evidence of disproportionation (formation of other methyldiboranes) and no evidence of decomposition (evolution of hydrogen accompanied by formation of polymeric solids). Very little disproportionation of 1,2-diethyldiborane was evident after two weeks storage at room temperature, but after several months most of the compound had rearranged to 1,1-diethyldiborane as well as small amounts of triethyldiborane and probably some monoethyldiborane. A similar result was obtained by heating a sample at 80°C for less than a half-hour. We surmise that the previously reported instability[7] was due to the catalytic effect of an impurity. The ultimate conversion of 1,2-dialkyldiborane to the 1,1- isomer and the fact that there is no evidence that this rearrangement is reversible indicate that the latter compound is more stable *thermodynamically*, even though the former can be stored for longer periods of time.

The infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer equipped with sodium chloride optics. The spectra of $(CH_3BH_2)_2$ and $(CH_3BD_2)_2$ are reproduced in Fig. 1, and those of $(C_2H_5BH_2)_2$, $(C_2H_5BD_2)_2$, $(C_2D_5BH_2)_2$, and $(C_2D_5BD_2)_2$ are shown in Fig. 2. The spectrum of $(C_2H_5BH_2)_2$ agrees well with a previously published (weaker) spectrum.[6] Our measured frequencies, including those of $(CH_3B^{10}H_2)_2$ and $(C_2H_5B^{10}H_2)_2$, are listed in Tables I and II. For brevity, the designations "F", "G", and "H" will henceforth be used for the above methyl compounds, and "F_1" through "J_1" for the ethyl com-

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[5] We use the form $(RBH_2)_2$ for the 1,2-dialkyldiboranes to distinguish them from the 1,1-dialkyldiboranes, $R_2B_2H_4$.

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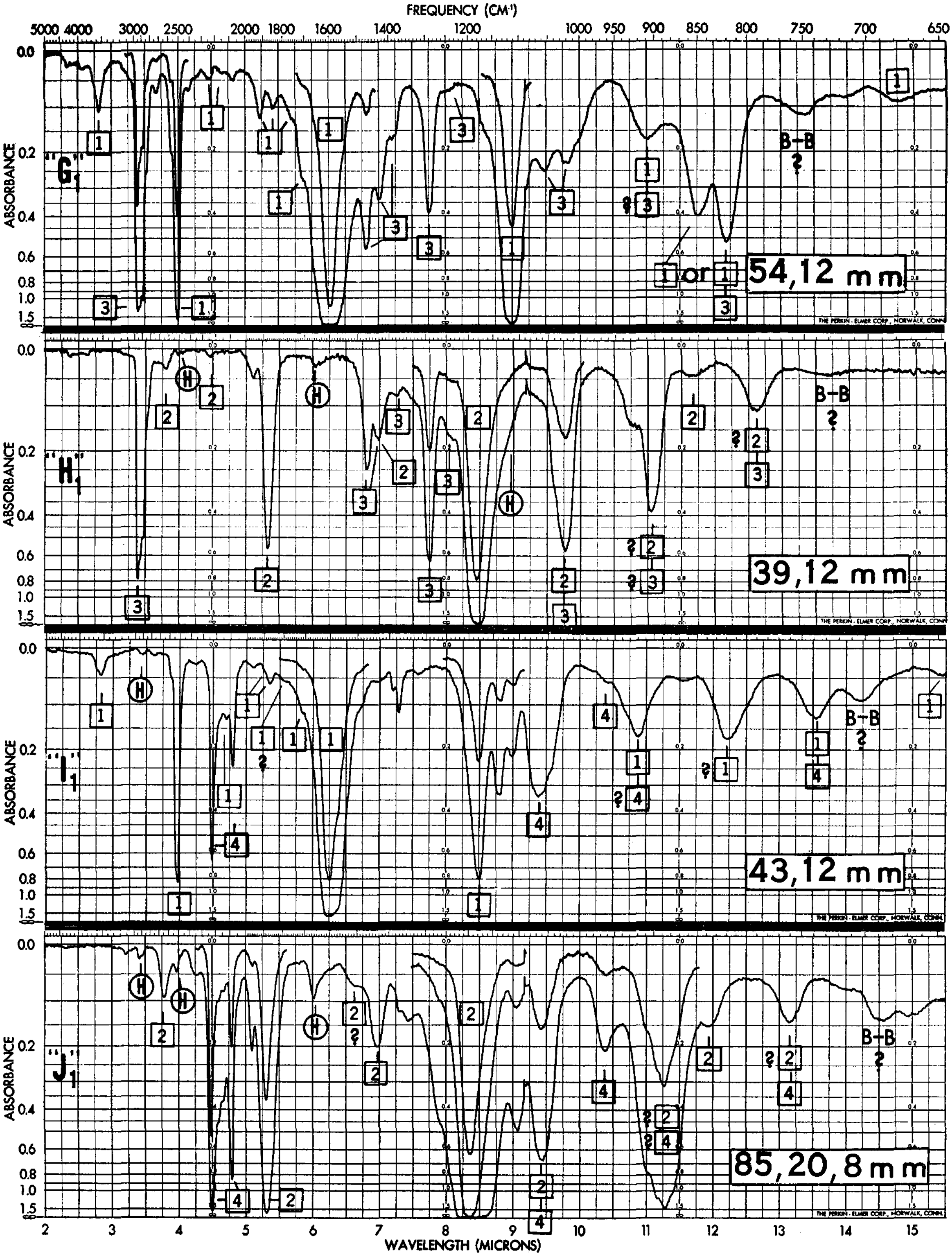

FIG. 2. Infrared spectra of 1,2-diethyldiboranes; pressures reported for 5-cm cells. "G_1": $(C_2H_5BH_2)_2$; "H_1": $(C_2H_5BD_2)_2$; "I_1": $(C_2D_5BH_2)_2$; "J_1": $(C_2D_5BD_2)_2$. [1]:—B_2H_4 bands; [2]:—B_2D_4 bands; [3]:—C_2H_5 bands; [4]:—C_2D_5 bands; (H) protium-impurity bands; B—B: stretching.

TABLE I. Infrared bands of 1,2-dimethyldiboranes.

"F"	"G"		"H"		
$(CH_3B^{10}H_2)_2$	$(CH_3BH_2)_2$		$(CH_3BD_2)_2$		
cm^{-1}	cm^{-1}	intensity[a]	cm^{-1}	intensity[a]	Assignment[b]
3636	3636	(31)			$-B_2H_4$ (combination)
3534	3546				
3077	3077	sh	3077	sh	
2958	2958	(140)	2958	(130)	CH_3 stretch. asym.
2841	2857	pip	2857	sh	CH_3 stretch. sym.
2755	2755	(15i)			$-B_2H_4$ (combination)
			2632	(12)	$-B_2D_4$ (combination)
2519	2519	(∼450)	2512	(5)	B—H stretch. (protium imp. in "H")
	2299	sh			
2288	2268	(25)			$-B_2H_4$ (combination)
			2257	(4)	$-B_2D_4$ (combination)
2137	2137	(8)			B—H′ sym. in-phase
	2028	(9i)	2032	(7)	$-CH_3$
1955	1949	(18i)			B—H′ sym. out-of-phase
			1953	ssh	MeB_2D_5 and/or $Me_2B_2D_4$ imp.
			1880	(300)	B—D stretch.
1869	1862	(54) C?			$-B_2H_4$
	1835	sh			
1792	∼1780	wsh			$-B_2H_4$ (B—H′ asym. out-of-phase?)
1706	1695	(125)			$-B_2H_4$
			1653	(15)b	B—H′ (single) asym. (protium imp.)
1615	1610	(2300)			B—H′ asym. in-phase
∼1558	1555	(330i)			partly $Me_2B_2H_4$ impurity?
			1510	(15)b	B—D′ sym. in-phase?
1433	1437	(120)	1428	(52i)	CH_3 def. asym. and B—D′ sym. out-of-phase
			1404	(56i)	$-B_2D_4$ (combination)
1360	1360	sh			
1328	1328	(280)	1328	(∼400)	CH_3 def. sym.
1316	1315	(250) B?	1316		
1269	1269	(35i)			
1258	1255	sh			
			1198	(1300)	B—D′ as. in-phase
(1160)	(∼1163)	sh			BH in-plane bend.
1152	1143	A?			
(1138)	(1125)	(920)			
			1124	wvbsh	protium impurity
1129 A?	...	A?			
(1121)	(1115)	sh			
1081	1067	(35i)	1049	(66i)	CH_3 rock.
			1015	sh	
1010	998	sh	993−	(∼300)	BD in-plane bend.
976	976	(75)	−985		CH_3 rock.
954	950	(71)	∼952	sh	
924	∼917−	(230)			BH bend. out-of-plane
915	−904				
			∼865	(35)	$-B_2D_4$ (BD out-of-plane bend.?)
829	828	(36) A			$-B_2H_4$
758	746	bsh			B—B stretch.?
∼690	∼690	(72) A?			$-B_2H_4$

[a] Approximate intensities expressed as absorbance$\times 10^5$ divided by cell length in cm and sample pressure in mm. Abbreviations: w: weak, s: strong, sh: shoulder b: broad, v: very; i: apparent intensity increased by overlap with other band(s); A, B, C: apparent band types.

[b] B—H′ and B—D′ refer to bridge stretchings.

pounds (see headings of Tables I and II), continuing the scheme introduced for the monoalkydiboranes.[1,2]

Incidentally, the most sensitive areas for detection of 1,1-dimethyldiborane impurity in "G" are at 2100 and 1550 cm^{-1} (appearance of a shoulder), revealing the presence of a minimum of ca 2% of the 1,1- isomer, while the 2570-cm^{-1} region is not good for spotting less than ca 10% of this impurity. The corresponding sensitive frequencies for the ethyl compounds are 2080 and 1540 cm^{-1}.

ASSIGNMENTS

Simple comparison of the spectra enables us in many instances to assign bands to the molecular groups.

TABLE II. Infrared bands of 1,2-diethyldiboranes.

“F_1” $(C_2H_5B^{10}H_2)_2$	“G_1” $(C_2H_5BH_2)_2$		“H_1” $(C_2H_5BD_2)_2$		“I_1” $(C_2D_5BH_2)_2$		“J_1” $(C_2D_5BD_2)_2$		
cm^{-1}	cm^{-1}	intensity[a]	cm^{-1}	intensity[a]	cm^{-1}	intensity[a]	cm^{-1}	intensity[a]	Assignment[b]
3571	3546	(40)			3534	(20)			$-B_2H_4$ (combination)
							3106	(3)	
3077	3077	sh							
2950	2950	(600)	2958	(400)					CH_3 stretch. asym.
2915	2915	sh	2924	sh	2915	(5)b	2924	(6)	CH_2 stretch. asym.; protium imp. in “I_1” and “J_1”
2882	2882	sh	2882	sh			2882	sh	CH_3 stretch. sym.
2841	2841	wsh	2841	sh					CH_2 stretch. sym.
2730	2725	(27i)			2755	(5)b			$-B_2H_4$ (combination)
			2646	(15)			2646	(22)	$-B_2D_4$ (combination)
2577	2577	sh			2584	sh			$Et_2B_2H_4$ impurity
2512	2506	(670)	2506	(5)	2512	(400)	2519	(11)	B—H stretch; protium imp. in “H_1” and “J_1”
2421	2398	(26i)							
2342	2342	sh							
					2353	(10)b	2353	(12i)b	$-C_2D_5$
2257	2247	(18)							$-B_2H_4$ (combination)
			2247	(7)					$-B_2D_4$ (combination)
					2227	(300)	2227	(520)	CD_3 stretch. asym.
					2174	sh	2179	sh	CD_2 stretch. asym.
							2151	sh	
wb?	2137	w			2128	(60i)			B—H′ sym. in-phase (“breathing”)
					2083	(110)	2088	(200)	CD_3 and CD_2 stretch. sym.
∼2105	2075	w							part. $Et_2B_2H_4$ imp.
			1961	(50i)			1961	(50i)	$Et_2B_2D_4$ imp.
					1953	(14)			
1927	1916	(46)			∼1905	sh			B—H′ sym. out-of-phase
			1876	(290)			1883	(360)	B—D stretch.
1852	1845	(20)			1869	(28)			$-B_2H_4$
1764	1760	wsh			1786	bsh			$-B_2H_4$ (B—H′ asym. out-of-phase?)
1709	1706	sh			1709	sh			$-B_2H_4$
			1658	(15)			1661	(22)	B—H′ (single) asym. (protium imp.)
1595	1595	(2000)			1600	(1350)			B—H′ asym. in-phase
							1508	(16)b	B—D′ sym. in-phase?
					1492	bsh			
1466	1466	(210i)	1468	(130)					}CH_3 asym. and CH_2 def.
1426	1426	(125i)	1433	(95i)			1435	(47)	}B—D′ sym. out-of-phase
					1428	wb			
∼1389	∼1391	sh	1377	(65)					CH_3 def. sym.
					1389	(33i)			
					1374	(55)	1370	sh	
							1351	(33)	part. $(C_2D_5)_2B_2D_4$ imp.
			1333	bsh	1321	(20)			impurity?
1292	1289	(145)	1289	(330)					}CH_2 wag. and/or twist.
1242	1242	bsh	1242	bsh			1266	sh	}
			1183	(1400) A?			1198	(1600)	B—D′ asym. in-phase
					1178	(380)			BH def. in-plane (“I_1”)
	1175	sh							sl. B_2H_6 imp.
1168	1163	sh							sl. $Et_2B_2H_4$ imp.
					1136	(150)			also BH def. in-plane?
1122	1112	(750)							BH def. in-plane (“F_1” and “G_1”)
					1111	(100i)	1102	(120i)	
					1066	(160)	1059	(160)	CD_3 asym. and CD_2 def. and BD def. in-plane
1060	1055	(93)							}CH_3 rock.
1024	1020	(85)							}
			1024	(300) A?					BD def. in-plane and/or B—C stretch.
					1047	sh			

TABLE II.—*Continued.*

"F_1"	"G_1"		"H_1"		"I_1"		"J_1"		
$(C_2H_5B^{10}H_2)_2$	$(C_2H_5BH_2)_2$		$(C_2H_5BD_2)_2$		$(C_2D_5BH_2)_2$		$(C_2D_5BD_2)_2$		
cm^{-1}	cm^{-1}	intensity[a]	cm^{-1}	intensity[a]	cm^{-1}	intensity[a]	cm^{-1}	intensity[a]	Assignment[b]
					962	sh	963	(50)	CD_3 rock.
			926	bsh					$Et_2B_2D_4$ imp.
							909	sh	
915	910	(63)			920	(80)			BH out-of plane bend. } C—C stretch?
			905	(200)			887	(320)	$-B_2D_4$? } C—C stretch?
					866	wb			
			858	(25)b			838	(35i)	$-B_2D_4$ (BD out-of-plane bend?)
858	849	(150i)			818	(80)			$-B_2H_4$?
826	820	(195i)	794	(56)					CH_2 rock. ($-B_2H_4$ in "F_1", "G_1"?)
					738	(60)	760	(33)	CD_2 rock.
765	750	(45)	734	wb					B—B stretch?
							714	w	$(C_2D_5)_2B_2D_4$ imp.
					702	(40)	690	(33)	B—B stretch.?
725	717	w							
678	678	(35)			~640	. . .[c]			$-B_2H_4$
							667	(32)	

[a] Approximate intensities expressed as absorbance$\times 10^5$ divided by cell length in cm and sample pressure in mm. Abbreviations: w: weak, s: strong, sh: shoulder, b: broad, v: very; i: apparent intensity increased by overlap with other band(s); A, B, C: apparent band types.

[b] B—H′ and B—D′ refer to bridge stretchings.

[c] Beyond limit of chart.

However, particularly for these 1,2- compounds, many correlations are not immediately apparent and depend on a more detailed analysis. The final group assignments to $-B_2H_4$, $-B_2D_4$, $-CH_3$ or $-C_2H_5$, and $-C_2D_5$ are indicated by [1] to [4] in Figs. 1 and 2.

In general, the detailed assignments follow readily from comparison with the corresponding monoalkyldiboranes.[1,2] As expected, there are the fairly strong C—H (and C—D) stretching absorptions near 3000 (and 2100–2200) cm^{-1} and the very strong B—H′ (and B—D′) bridge stretching bands at 1600 (and 1200) cm^{-1}.

The 1,2-dialkyldiboranes can readily be distinguished[8] from the 1,1-dialkyldiboranes by their single strong B—H (and B—D) terminal stretching absorption at about 2510 (and 1880) cm^{-1}. For trans structures only the B—H (terminal) out-of-phase vibration is infrared active, but for cis compounds both the in-phase and out-of-phase vibrations are infrared active. Thus the shoulders at ca 2580 (and 1960) cm^{-1} might be assigned to the second B—H (and B—D) vibration. However, such large splitting of frequencies, ca 70–85 cm^{-1}, would indicate considerable coupling between the two ends of the molecule. We know that this situation does not exist, because deuterium substitution on only one end of the molecule does not appreciably affect the B—H vibration of the other end (see H, H_1, J_1). Similar lack of coupling has been observed in ethylenes.[9] As a consequence we conclude that the 2580- and 1960-cm^{-1} shoulders do ***not*** represent a second B—H or B—D vibration of 1,2-dialkyldiboranes, but rather are due to impurities, probably 1,1-dialkyldiborane.

The BH in-plane bending vibrations are located at ca 1110–1150 cm^{-1}. Their great intensity clearly links them with the stronger of the two bands in the same region in monoethyldiborane.[2] In the latter compound, the two bands in the 1150-cm^{-1} region were thought to belong to the BH and the BH_2 bendings, but there had been a tendency to assign the more intense member of that pair to the BH_2 deformation, in view of the great intensity of the BH_2 relative to HBD deformation in B_2H_5D.[10] It should be remembered, however, that in B_2H_5D the strong *A*-type 1178-cm^{-1} vibration actually represents BH_2 deformations in the *two* compounds present in the mixture—terminally and bridge-deuterated B_2H_5D. As in the monoalkyldiboranes, the BH frequency shifts *upward*, for some odd reason, in the carbon-deuterated compound ("I_1"). Other bands or shoulders in that region could possibly represent another of the BH bendings (if the compound is cis or if cis compound is present).

A small B^{10} shift of ca 10 cm^{-1} indicates that the boron atoms participate to some extent in the BH bending motion. Therefore, in considering the corresponding BD motion, the BH/BD frequency ratio should be less

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than the "normal" 1.35 value.[8,10–12] Both the 1024- and 905-cm^{-1} absorptions in "H$_1$" would qualify (ratios of 1.09 and 1.23). It is conceivable that these bands represent the two BD bending vibrations. However, examination of "H" (where the only logical candidate is at 990 cm^{-1}) and comparison with monomethyl- and monoethyldiboranes (where ca 1050 cm^{-1} has been assigned to this vibration) persuades us to the former assignment only. In the completely deuterated compound, "J$_1$", this band seems to be hidden under a CD$_3$ vibration at 1059 cm^{-1}, although the intensity of that band does seem rather weak (as in $CD_3B_2D_5$ and $C_2D_5B_2D_5$).

The CH$_3$ asymmetric- and symmetric-deformation bands of the methyldiboranes are found as expected in the 1430- and 1325-cm^{-1} regions. It is not clear whether the latter bands appear as doublets, due to the two methyl groups, or whether we are observing poorly resolved rotational envelopes. The ethyl compounds have their CH$_3$ asymmetric and CH$_2$ deformations at ca 1470 (medium) and 1430 cm^{-1} (weak), and the symmetric CH$_3$ deformations at ca 1380 cm^{-1} (weak). The corresponding CD$_3$ asymmetric and CD$_2$ deformations in "I$_1$" and "J$_1$" are shifted to 1060 cm^{-1} (frequency ratio of ca 1.37). As for monoethyldiborane, we are unable to find an assignment in "I$_1$" and "J$_1$" for the CD$_3$ symmetric deformations.

The 1290 cm^{-1} bands with the 1240 cm^{-1} shoulders in the $-C_2H_5$ compounds represent CH$_2$ wagging and twisting modes. In monoethyldiboranes this frequency is less stable, varying from 1310 cm^{-1} in $C_2H_5B_2{}^{10}H_5$ to 1285 cm^{-1} in $C_2H_5B_2D_5$. In both boron-deuterated compounds this absorption is enhanced to more than double the intensity in the corresponding isotopically normal compounds. In the 1,2-diethyldiboranes, as for the monoethyldiboranes, no good assignment is found for the corresponding CD$_2$ vibrations.

Assignment of bands in the 900–920-cm^{-1} region to BH out-of-plane bending follows directly from comparison with the monoalkyldiboranes.

In monoethyldiboranes, CH$_2$ rocking was assigned to 826 ($C_2H_5B_2{}^{10}H_5$), 816 ($C_2H_5B_2H_5$), and 800 cm^{-1} ($C_2H_5B_2D_5$); CD$_2$ rocking, to 742 ($C_2D_5B_2H_5$) and 760 cm^{-1} ($C_2D_5B_2D_5$). The corresponding assignments in the 1,2-diethyldiboranes are thus reasonable: 826, 820, and 794 cm^{-1} to CH$_2$ rocking in "F$_1$", "G$_1$", and "H$_1$"; 738 and 760 cm^{-1} to CD$_2$ rocking in "I$_1$" and "J$_1$".

Although a number of fairly strong bands remain unassigned in the various spectra, their classification into groups [1] to [4] is not readily evident (see Figs. 1 and 2). This means that these bands are not really *characteristic* bands in the narrow sense of the word, but they nevertheless can be correlated with certain molecular vibrations. To arrive at assignments, extensive comparison is made with the monoalkyldiboranes[1,2] and other alkyldiboranes[13] as well as trialkylboranes.[14–16]

In the monomethyldiboranes CH$_3$-rocking motions have been assigned to the 950–975-cm^{-1} region. Similar bands are available for this assignment in compounds "F", "G", and "H". The $-CH_3$ bands in the 1050–1080-cm^{-1} region of "F", "G", and "H" have no analog in the monomethyldiboranes, but they appear in other alkyldiboranes[13] with increasing intensity. Hence, assignment to CH$_3$ rocking is reasonable.

In spectrum "G" there is a prominent A-type band at 828 cm^{-1}, having no obvious analog in "H". It possibly is a $-B_2H_4$ band of some sort and thus is related to either the 820- and 818- or the 849- and 818-cm^{-1} bands in "G$_1$" and "I$_1$", but the small B^{10}-isotope shift in "F" of only 1 cm^{-1} is puzzling. A similar situation exists for the 640–690-cm^{-1} bands.

The weak bands at about 750 cm^{-1} of the "G" and "G$_1$" could, in view of their relatively large B^{10}-isotope shifts of ca 15 cm^{-1}, represent B—B stretching across the double-hydrogen bridge. This frequency drops to 734 cm^{-1} in "H$_1$" and to 702 and 690 cm^{-1} in "I$_1$" and "J$_1$". No appropriate band is observed in "H". In $B_2{}^{10}H_6$, $B_2{}^{11}H_6$, $B_2{}^{10}D_6$, and $B_2{}^{11}D_6$ this frequency is[17] 816, 788, 721, and 712 cm^{-1}, respectively.

Weak absorptions in the 838–865 cm^{-1} region of the BD compounds are caused by some sort of $-B_2D_4$ motion, possibly BD out-of-plane bendings (BH/BD frequency ratios of 1.05 to 1.10).

The intense bands at 905 cm^{-1} in "H$_1$" and 887 cm^{-1} in "J$_1$" possibly are $-B_2D_4$ bands even though no counterpart is seen in "H". (It must be remembered that replacement of methyl groups by ethyls may alter the symmetry and thus affect the selection rules.) Possibly bands in the 887–920-cm^{-1} region of all the 1,2-diethyldiboranes could (additionally?) represent C—C stretching modes, assigned tentatively to 850–943 cm^{-1} in monoethyldiboranes.

CH$_3$- and CD$_3$-rocking modes follow almost exactly the pattern of the monoethyldiboranes. In "G$_1$" these are assigned to 1020 and 1055 cm^{-1} (ca 1015 and 1065 cm^{-1} in $C_2H_5B_2H_5$; B^{10}-isotope shift of ca 5 cm^{-1} in all cases). In "H$_1$", as in $C_2H_5B_2D_5$, these bands are masked by the more intense BD-bending absorption. In "I$_1$" and "J$_1$" we assign ca 963 cm^{-1} to CD$_3$ rocking (ca 945 cm^{-1} in $C_2D_5B_2H_5$ and $C_2D_5B_2D_5$).

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As for the previous alkyldiboranes, no assignment is proposed for the B—C-stretching modes.

In each spectrum there remain some higher-frequency bands, most of which can readily be assigned to groups (see Figs. 1 and 2). They represent either combinations or overtones or additional bridge-stretching modes. The B—H′ (bridge) symmetric in-phase "breathing" vibration may be assignable to the 2128–2137 cm^{-1} bands. In that case, bands in "H" and "J_1" at ca 1510 may represent the corresponding B—D′ vibration; no such band is found in "H_1." The B—H′ symmetric out-of-phase vibrations are assigned to the 1905–1955-cm^{-1} region. The equivalent B—D′ bands are at 1428–1435 cm^{-1}, superimposed on CH deformations in "H" and "H_1". Very weak shoulders in the 1760–1792-cm^{-1} region may conceivably be identified with the B—H′ asymmetric out-of-phase vibration, although this vibration should be infrared inactive, at least in the methyl compounds. The related B—D′ vibration would be masked by the other bands. The very strong B—H′ and B—D′ asymmetric in-phase vibration has been discussed previously. A small amount of protium in the boron-deuterated compounds is responsible for the B—H′ (single) vibration of the B(HD)B bridges, at ca 1650 cm^{-1}.

MOLECULAR SYMMETRY

With the completed frequency assignment we can now examine whether our compounds are of the cis or the trans type. It might be argued that the relatively small number of infrared absorption bands is an indication that we are dealing with *trans*-1,2-dialkyldiboranes (in which only half the vibrations are infrared active), but we nevertheless feel more disposed to view the compounds as being predominantly of the cis type. A cursory comparison of a number of trans- and cis-disubstituted ethylenes[3,18–20] reveals that both members of a pair have approximately the same number of infrared bands. The small number of bands does, however, indicate that our compounds are composed predominantly of one isomer and not of a mixture of both.

We base our contention in favor of cis structures on the following arguments. In going from BH_2 deformation (scissors motion) in B_2H_6 to BH bending in our 1,2-dialkyldiboranes, the infrared band shifts from 1177 to ca 1112–1140 cm^{-1}. This relatively small shift parallels a similar shift from CH_2 deformation in C_2H_4 (1444 cm^{-1}) to CH bending in various cis-dialkylated ethylenes[21] (ca 1408 cm^{-1}), in contrast to trans-dialkylated ethylenes (ca 1300 cm^{-1}). Further support for cis structures is found in our somewhat hesitant assignments of B—H′ and B—H′ symmetric in-phase frequencies. These vibrational modes would definitely be infrared inactive in *trans*-di*methyl*diborane, and either active or inactive in *trans*-di*ethyl*diborane depending on the orientation of the ethyl groups.

If B—B (i.e., BH_2B) stretching bands are observed in the infrared spectrum—and we tentatively have assigned some bands to this vibration—this would be conclusive proof of the existence of cis isomers, at least for the methyl compounds.

In conclusion, it should be pointed out that the problem of molecular configuration, as well as a number of uncertainties in our assignments, will most likely be resolved when Raman spectra of these substances become available.

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