INFRARED AND RAMAN SPECTRA OF HYDRAZINE-BIS(TRIHYDROBORANE)

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Infrared spectra of hydrazine-bis(trihydroborane) and its B-deuterio and perdeuterio derivatives, resp., were measured in the region of 4000—400 cm^{-1}. The bands were assigned by using the isotopic shifts and the Raman spectrum of hydrazine-bis(trihydroborane) in the region of 3400 to 200 cm^{-1}.

Diborane reacts readily with nitrogen-containing compounds like ammonia, amines, imides, nitriles, and nitrogen-containing heterocycles under the formation of coordination compounds with the dative B—N bond. Hydrazine and its derivatives possess two lone electron pairs, and theferore they can coordinate with one or two BH_3 molecules under the formation of $NH_2NH_2BH_3$ (*I*) (ref.[1]) and $H_3BNH_2NH_2BH_3$

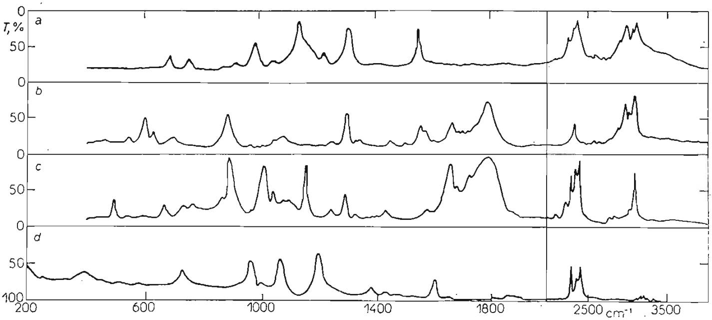

FIG. 1

Infrared Spectra of Hydrazine-bis(trihydroborane) (KBr disks)

a $N_2H_4.2\,BH_3$ (*II*), *b* $N_2H_4.2\,BD_3$ (*III*), *c* $N_2D_4.2\,BD_3$ (*IV*), *d* Raman spectrum of solid *II*.

(*II*) (ref.[2,3]). The infrared spectrum of the compound *I* was assigned tentatively[1], for the compound *II* the data are missing[4]. In relation to the study of vibrations of the dative B—N bond in various types of compounds we assigned the bands of the infrared and Raman spectra of *II*, based on the band shifts in the spectra of the isotopomers $D_3BNH_2NH_2BD_3$ (*III*) and $D_3BND_2ND_2BD_3$ (*IV*), respectively.

EXPERIMENTAL

The infrared spectra were measured on a spectrometer UR 10 (Zeiss, Jena) in the form of KBr disks, Florube mulls, or solutions in diethyl ether. The Raman spectrum of *II* was measured in the solid state on a spectrometer Coderg PHI equipped with a He–Ne laser. The compound *II* was prepared by the reaction of $(N_2H_6)SO_4$ with $NaBH_4$ in diethyl ether[3]. The same reaction was used with $(N_2D_6)SO_4$ and $NaBD_4$ for the preparation of the isotopomers *III* and *IV*. The use of diethyl ether is more advantageous due to easy desolvation of the etherate of *II* formed, although the yields decrease considerably. $(N_2D_6)SO_4$ was prepared by a fourfold crystallization from deuterium oxide (98·8% D); its D-purity was checked by infrared spectroscopy. The D-purity of $NaBD_4$ was 95%, with the total of 98.2% active hydrogen. All operations were carried out in whole-glass equipments or in a dry-box.

The Raman spectrum of *II* and the infrared spectra of *II*, *III*, and *IV*, resp., are represented by Fig. 1.

DISCUSSION

An isolated molecule of *II*, with the BH_3 or NH_2 groups in a mutual *trans*-arrangement, possesses the symmetry C_{2h}. From this it follows that of the 36 normal vibrations, 11 belong to the class A_g, 7 to the class B_g (both Raman-active), 8 to the class A_u, and 10 to the class B_u (both IR-active). This distribution should be considered only informative, as the crystal structure is not known. For that reason, the effect of the crystal field, which can perturb the symmetry of the isolated molecule and thus to change the distribution of vibrations, cannot be included in the over-all symmetry considerations. These effects are, in our case, apparent for the NH stretching vibration, whereas for the B—H stretching vibration no difference in the intensity and number of bands occurs between the solution of *II* in diethyl ether and the solid state.

NH_2 *stretching vibrations*. In comparison with the spectrum of free hydrazine[5], the NH_2 stretching vibrations in its coordination compounds with transition metal halides[6-8] are shifted to lower wavenumbers. In the spectrum of *II* we attributed the infrared bands at 3001, 3074, 3161, and 3214 cm^{-1} to those vibrations; in the spectrum of the compound *IV* the corresponding bands are found at 2252, 2309, 2370, and 2415 cm^{-1}. The vibrations appear at 3115, 3172, and 3205 cm^{-1} in the Raman spectrum of *II*. The molecular symmetry C_{2h} obviously decreases due to the effect of the crystal field; therefore four bands appear in the infrared spectrum, although only two bands of the vibrations of the classes B_u and A_u would be expected.

BH_3 *stretching vibrations.* We attribute the band at 2282 cm^{-1} to the BH_3 symmetric stretching vibration of the class A_u, and the bands at 2357 and 2391 cm^{-1} to the totally antisymmetric vibration of the class B_u. In the spectrum of *III* the corresponding bands lie at 1668, 1748, and 1794 cm^{-1}, in the spectrum of *IV* they appear at 1668, 1735, and 1790 cm^{-1}. In the Raman spectrum of *II* the bands at 2300 and 2407 cm^{-1} can be ascribed to the totally symmetric vibration of the A_g class and the shoulder at 2369 cm^{-1} to the antisymmetric vibration B_g. In the infrared spectrum of the solution of *II* in diethyl ether, we found bands at 2278, 2328, and 2385 cm^{-1}. This indicates that the BH_3 stretching vibrations are not affected by the crystal field, and the assignment to the symmetry classes can be considered rigorous.

NH_2 *bending vibrations.* The NH_2 antisymmetric bending vibration, with the wavenumbers 1587 and 1628 cm^{-1} in the spectrum of hydrazine vapours[5] (class *B*, symmetry C_2), is lowered, as expected, to the value of 1565 cm^{-1} in the infrared spectrum of *II*. For the isosymmetric compound $F_3BNH_2NH_2BF_3$ (*V*), however, the value of 1610 cm^{-1} was found by Paterson and Onyszchuk[9]. The high wavenumber value of this vibration is due to the high electronegativity of the fluorine atoms of the ligand; a similar effect can be found for $N_2H_6Cl_2$, where the value 1613 cm^{-1} is ascribed to the degenerate antisymmetric E_u vibration[10]. The symmetric A_g vibration cannot be assigned in the spectrum of *II*, since the wavenumber of the Raman band, 1604 cm^{-1}, is too high with respect to the corresponding values in the spectra of hydrazine (1493 cm^{-1})[5] and *V* (1473 cm^{-1})[9]. In the spectrum of *IV* the ND_2 antisymmetric vibration is identified with the band at 1166 cm^{-1}. In our assignment the rocking vibration appears at 1310 and 1025 cm^{-1} in the spectra of *II* and *IV*, resp. (1275 cm^{-1} in the spectrum of hydrazine vapours[5] and 1300 cm^{-1} in that of *V* (ref.[9])). In the Raman spectrum of *II*, the band at 1200 cm^{-1} can be attributed to that vibration of the A_u class.

NH_2 wagging vibration appears at 966, 933 cm^{-1} (class *B*), and 780 cm^{-1} (class *A*) in the spectrum of hydrazine vapours[5]. As found by Sacconi and Sabatini[8] for a series of complexes of hydrazine with transition metal chlorides, the symmetric wagging vibration is very sensitive to the type of the ligand bound to nitrogen, and its wavenumber lies in the range of 682–658 cm^{-1}. For the compound *V*, the band at 775 cm^{-1} was ascribed to the symmetric vibration[9], and for *I*, the bands at 982, 1044 cm^{-1} to the antisymmetric vibration[1]. We attribute the bands at 992, 1052, and 692 cm^{-1} in the spectrum of *II* and those at 768 and 498 cm^{-1} in the spectrum of *IV* to the NH_2 wagging vibrations. In the Raman spectrum of *II*, the bands at 998, 1059 cm^{-1} can be attributed to those vibrations.

BH_3 *bending vibrations.* The BH_3 bending vibration is identified with the highly intense band at 1145 cm^{-1} with shoulders at 1165 and 1189 cm^{-1} in the spectrum of *II*, the band at 893 cm^{-1} in the spectrum of *III*, and the bands at 875, 904 cm^{-1} in the spectrum of *IV*. In the Raman spectrum, the shoulder at 1190 cm^{-1} is attributed to that vibration. The weak band at 925 cm^{-1} in the spectrum of *II* can belong to the BH_3 rocking vibration. The bands of the other BH_3 angle deformation modes, however, do not appear in the spectrum of *II*. Similarly, Goubeau and Ricker[1] have found only the BH bending vibration at 1127, 1152, 1180, and 1263 cm^{-1} in the spectrum of *I*, and Taylor[11] has found the bands at 1175 and 1026 cm^{-1} for BH_3NH_3.

TABLE I

Assignment of Bands (cm^{-1}) of the Infrared and Raman Spectra of Hydrazine-bis(trihydroborane)

IR *II*	Raman *II*	IR *III*	IR *VI*	Assignment
	254 vw			
	391 ms			
	511 vw			
	581 vw			
692 ms		604 s	498 s	wag. NH_2
	719			sym stretch. ^{10}BN, ^{11}BN
	727			
760 ms		706 ms	737 ms	as. stretch. ^{10}BN, ^{11}BN
925 w				rock. BH_3 (?)
	962			NN stretch
992 s	998 mw		768 ms	wag. NH_2
1 052 w	1 059 s			
1 145 vs			875 ms	bend. BH_3
1 165 sh		893 s	904 s	
1 189 sh	1 190 sh			
1 228 ms	1 200 vs	1 255 ms	970 ms	rock. NH_2
1 310 s		1 305 s	1 025 s	
	1 381 mw			def. NH_2
1 565 ms		1 558 ms	1 166 s	
	1 604 mw			
2 282 vs	2 300 vs	1 668 ms	1 668 vs	stretch. BH_3
2 357 vs	2 369 sh	1 748 sh	1 735 sh	
2 391 vs	2 407 vs	1 794 vs	1 790 vs	
2 570 w				
2 657 w				
2 735 w				
2 813 w				
3 001 ms	3 115 w	2 982 ms	2 252 ms	stretch. NH_2
3 074 vs		3 076 s	2 309 s	
3 161 s	3 172 ms	3 160 ms	2 370 s	
3 214 vs	3 205 ms	3 211 vs	2 415 vs	

vs Very strong, s strong, ms medium strong, w weak, sh shoulder.

N—N *and* B—N *stretching vibrations.* The N—N stretching vibration in *II* belongs to the totally symmetric class A_g, hence it is Raman-active. In agreement with this, we attribute the Raman band at 962 cm^{-1} to that vibration. This assignment is in accordance with the observed increase of the wavenumber of the N—N stretching vibration with the increasing charge at the nitrogen atom. This vibration was found at 885 cm^{-1} for solid NH_2NH_2 (ref.[5]), at 985 – 952 cm^{-1} for complexes of hydrazine with transition metal chlorides, and at 970, 912, and 1027 cm^{-1} for *V*(ref.[9]), *I* (ref.[1]), and $N_2H_6Cl_2$ (ref.[10]), resp. There are two B—N stretching vibrations in the molecule of *II*, *viz.* the totally symmetric vibration, class A_g (Raman-active), and the antisymmetric vibration, class B_u (IR-active). In the case of *I*, the doublet at 745, 752 cm^{-1} is attributed[1] to the symmetric ^{10}BN, ^{11}BN vibration, and the band at 912 cm^{-1} to the antisymmetric vibration. A coupled BNN vibration is assumed in both cases. In the spectrum of H_3NBH_3, the band at 787 cm^{-1}, partly sensitive to deuteration (the perdeuterio derivative 708 cm^{-1}), is attributed to that vibration by Taylor[11], who came to the conclusion – based on the calculation of potential energy distribution – that the B—N and B—F stretching vibrations are coupled in H_3NBF_3, whereas in the complex with BH_3 no coupling occurs between the B—N and B—H stretching vibrations. In our case, we attribute the IR band of *II* at 760 cm^{-1} and that of *IV* at 737 cm^{-1} to the antisymmetric BN stretching vibration, and the doublet at 719, 727 cm^{-1} in the Raman spectrum to the totally symmetric vibration ^{10}BN, ^{11}BN.

A summary of the assignment of the infrared and Raman spectral bands of *II* and that of the infrared bands of *III* and *IV* is given in Table I.

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