A study of the infrared, Raman, and nuclear magnetic resonance spectra of isotopically substituted bisboranohypophosphite anions

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(Received 19 March 1968)

Abstract—The sodium salts of the bisboranohypophosphite anions $H_2P(BH_3)_2^{-}$, $D_2P(BH_3)_2^{-}$, and $H_2P(BD_3)_2^{-}$ have been studied as solids and as aqueous solutions by infrared and Raman spectroscopy. Correlation of these data, including Raman depolarisation ratios, has enabled detailed assignments to be made of most of the vibrational modes. An approximate P—B bond force constant has been calculated. In addition, proton- and ¹¹B-NMR data are presented and assigned for each of the molecules.

INTRODUCTION

Following our previous report [1] of the infrared and Raman spectra of the compound $Na^+(BH_3 \cdot PH_2 \cdot BH_3)^-$, infrared and NMR spectra of some further salts of this interesting bisboranohypophosphite anion have been reported [2]. The vibrational spectra have seemed to be consistent with the assignment of the whole molecule to the C_{2n} symmetry point group, so that the analysis of the spectra has followed that described by HERTZBERG [3] for n-propane. However, with 27 normal modes to be accounted for, and none of these being formally degenerate, the vibrational analysis has necessarily been rather speculative. The steric factors presumed to be preventing free rotation of the CH_3 groups in the propane molecule are absent in the bisboranohypophosphite anion, due to the greater size (covalent radii [4]: C, 0.77 Å; P, 1.10 Å) of the central phosphorus atom, so that retention of the C_{2n} selection rules for the whole molecule must be taken as indicating some form of multiple-bond character in the P-B bonds. Evidence for this seemingly unlikely possibility of P-B π -bonding, arising from hyperconjugative electron transfer from the B-H bonds, has been presented for triphenylphosphineborane [5]. We have prepared and made a study of the spectra of both the phosphorus and the boron deuterium-substituted analogues of the $PH_2(BH_3)_2^-$ anion; viz: $PD_2(BH_3)_2^-$ and $PH_2(BD_3)_2^{-}$. Comparisons of frequencies within this set of anions helps considerably in establishing an unambiguous assignment, and thereby provides some information on the nature of the P---B bonds.

^[1] R. E. HESTER and E. MAYER, Spectrochim. Acta 23A, 2218 (1967).

^[2] J. W. GILJE, K. W. MORSE and R. W. PARRY, Inorg. Chem. 6, 1761 (1967).

^[3] G. HERTZBERG, Infrared and Raman Spectra of Polyatomic Molecules, p. 360. Van Nostrand (1945).

^[4] L. PAULING, Nature of the Chemical Bond, 3rd Edition, p. 224. Cornell University Press (1960).

^[5] M. A. FRISCH, H. G. HEAL, H. MACKLE and I. O. MADDEN, J. Chem. Soc. 899 (1964).

EXPERIMENTAL

Standard vacuum line techniques were used for the preparation of the airsensitive compounds. All reactions and manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen. The fully hydrogenated sodium salt, Na⁺[PH₂(BH₃)₂]⁻, was prepared by reaction of phosphonium iodide with sodium borohydride at -78° C in monoglyme as solvent [1]. The mixture was warmed slowly to room temperature and stirred until evolution of hydrogen had ceased. The partially deuterated salt, Na⁺[PD₂(BH₃)₂]⁻, was prepared by reaction of trideuterophosphineborane, D₃P·BH₃, with sodium borohydride using the same reaction conditions. The salt Na⁺[PH₂(BD₃)₃]⁻ was similarly prepared by reaction of phosphonium iodide with sodium borodeuteride. All reaction products were purified by removal of polymeric material in benzene solution, followed by dissolving the desired products in ether, leaving behind NaI and excess NaBH₄ or NaBD₄.

Proton NMR spectra were obtained for D_2O solutions of the compounds, using a Perkin-Elmer model R10 60 Mc/s spectrometer. ¹¹B NMR spectra were similarly obtained using an A.E.I. spectrometer* at 20 Mc/s. ³¹P NMR spectra also were run on the A.E.I. instrument, but no definite absorption was detectable for any of the samples. In the case of the partially deuterated compounds, the proton NMR spectra showed only very weak features due to the presence of the fully hydrogenated species as an impurity. We estimate from the band intensities an impurity level of ~10% in the PH₂(BD₃)₂⁻ system, and still less than this in the PD₂(BH₃)₂⁻ system.

Infrared spectra were obtained for Nujol and hexachlorobutadiene mulls of the solids held between CsI plates. All mulls were prepared in a nitrogen-filled dry box, and the CsI plates taped together to exclude air when the samples were removed to the spectrometer. Aqueous solutions ($\sim 30 \%$ w/w) were held between CaF₂ windows. A Perkin-Elmer 621 infrared spectrometer was used throughout. Raman spectra were obtained using a Perkin-Elmer LR-1 spectrometer, modified to include a Spectra-Physics 80 mW He/Ne c.w. laser as the light source. Solid samples were loaded into the standard Perkin-Elmer solid sampler in a nitrogen-filled dry box, and the entrance and exit apertures were sealed with transparent tape before removal to the spectrometer. Interference filters were used to reduce the intensity of the scattered laser light and to prevent spurious He and Ne emission lines from reaching the sample. Solutions for Raman spectroscopy were forced through micropore filters to remove any suspended material, and then contained in small volume glass cells designed to permit multi-passing of the exciting laser beam.

RESULTS AND DISCUSSION

Vibrational spectra

Table 1 contains infrared and Raman data from the Na⁺[PH₂(BH₃)₂]⁻ compound in the solid state and in aqueous solution. Tables 2 and 3 contain the corresponding data from the salts Na⁺[PD₂(BH₃)₂]⁻ and Na⁺[PH₂(BD₃)₂]⁻, respectively, though only solid-state samples were used in this part of the work. For the fully hydrogenated compound, the Raman polarisation data enable a clear assignment of

^{*} We are grateful to J. W. AKITT for the ¹¹B and ⁸¹P spectra, which were obtained at the University of Newcastle-upon-Tyne, Department of Inorganic Chemistry.

I.R.		Raman		Assignments	
Solid	Aq. soln.	Solid	Aq. soln.		
~230 w,b				A ₁ PB ₂ deformation?	
325 w,b	— ·	—			
399 m		386 w	415 w,b	E BH _a rock	
555 m)	_	\sim 560 s	560 s,p	A ₁ PB ₂ stretch	
564 sh}				¹⁰ B-isotope shift	
635 m	—	_	—	B_1 PH ₂ rock	
652 m,sp	_	657 w	643 m,dp	$B_1 PB_2$ stretch	
660 sh 了		—		¹⁰ B-isotope shift	
890 m		942 w	933 w	B ₃ PH ₂ rock	
1060 s,spj	1068 vs	1059 m	ן 1074 m,p	A_1 PH ₂ deformation	
1086 s Š	—	1085 w	1093 m,p	A_1 BH _s deformation	
1148 m	1170 m	1154 w	1175 m,dp	E BH _a deformation	
1216 m	—	1229 w	—	Combination band	
2160 sh			—	Overtone of A_1 BH ₂ deform	
2280 sh				Overtone of E BH, deform	
2312 vs	2280 sh)	2329 m]	2297 sh,p)	A ₁ BH, stretch	
2362 m,sp (2310 sh	L	→ ⁻ }	E BH _s stretch	
2380 s,sp	2365 vs	2385 vs	2364 vs,p)	A_1 PH ₂ stretch	
2400 s.sp		2408 sh j	_	B, PH, stretch	

Table 1. Infrared and Raman spectra of $Na^+[PH_2(BH_3)_2]^-$ in the solid state and in aqueous solution*

* All frequencies in cm⁻¹. w = weak, m = medium, s = strong, v = very, b = broad, sp = sharp, sh = shoulder, p = polarised, dp = depolarised.

I.R.	Raman	Assignments
350 m		B, PD, rock
375 w	384 w	E BH, rock
545 m)	Laser	$A_1 PB_s$ stretch
552 m)	Interference	¹⁰ B isotope shift
645 m	652 w	B ₁ PB, stretch
772 m,sp	770 w	A, PD, deformation
783 m,sp	—	
892 w,sp)		
925 w,sp }	—	
943 m,sp)	946 w	
1082 s	1085 w	A_1 BH, deformation
1152 m	1153 w	E BH, deformation
1220 m	1219 w	•
_	1378 w	
1730 s, sp	1730 vs)	A, PD, stretch
1747 m,sp	1751 s 🖇	$B_1 PD_2$ stretch
1760 w,sp)		
2155 sh		Overtone of A_1 BH ₂ deform?
2285 sh		Overtone of E BH ₃ deform?
2315 vs	2327 m	A ₁ BH ₂ stretch
2367 s,sh J	2377 sh	E BH, stretch
	2385 m {	PH ₂ (BH ₂) ⁻ impurity?
	2402 vwĴ	PH ₂ (BH ₃) ⁻ impurity?

Table 2. Infrared and Raman spectra of solid Na⁺[PD₂(BH₃)₂]^{-*}

* All frequencies in cm^{-1} . w = weak, m = medium, s = strong, v = very, sp = sharp, sh = shoulder.

totally symmetric modes to be made. However, comparison of the highest frequency groups of Raman lines from the aqueous solution and the solid samples shows some effects which are characteristic of hydrogen-bonding shifts. The solid sample line at 2385 cm⁻¹ clearly is shifted down to 2364 cm⁻¹ in the solution spectrum, and the 2329 cm⁻¹ line is shifted down to 2297 cm⁻¹. Comparison of these frequencies with those given by the deuterated compounds in Tables 2 and 3 shows unambiguously that the higher frequency lines arise from PH₂ stretching modes, while the lower ones arise from BH₃ stretching. Their polarised character shows these to be symmetric stretching modes. The drop in frequency indicates that water molecules

I.R.	Raman	Assignments
270 w,b	<u> </u>	E BD, rock
495 m	501 m	A ₁ PB ₂ stretch
540 vw		
602 s	~590 m	B, PB, stretch
647 w	_	· · ·
686 m		B_1 PH ₂ rock
725 w	—	
821 s		A_1 BD _a deformation
852 m,sh	848 w	
885 m	882 w	$E BD_{s}$ deformation
945 w	951 w	
976 m		B ₂ PH, rock
1035 w	<u> </u>	· ·
1073 m	1070 m	A ₁ PH ₂ deformation
1634 m	1650 s	A_1 BD, stretch
1698 m		
1754 w.sh	1734 m)	
1770 vs	1770 m}	$E BD_{a}$ stretch
1790 sh		·
2355 w.sp]		
2362 w,sp		
2380 s,sp (2385 vs)	A ₁ PH ₂ stretch
2400 s,sp	2405 s	$B_1 PH_2$ stretch

Table 3. Infrared and Raman spectra of solid Na⁺[PH₂(BD₃)₂]^{-*}

* All frequencies in cm⁻¹. w = weak, m = medium, s = strong, v = very, b = broad, sp = sharp, sh = shoulder.

hydrogen-bond to both the phosphorus hydrogens and the boron hydrogens in solution. When stretching mode frequencies are lowered by H-bonding in this way, it is usual for the corresponding hydrogen deformation modes to be raised in frequency, due to the effective increase in the rigidity of the interbond angles. This solution hydrogen-bonding proposition is reinforced then by the fact that the next lower frequency polarised Raman lines are a pair at 1093 cm⁻¹ and 1074 cm⁻¹, these corresponding to solid sample lines at 1085 cm⁻¹ and 1059 cm⁻¹, respectively. Comparison of these with the deuterated species confirms that they can satisfactorily be assigned to symmetric deformation modes of the BH₃ and PH₂ groups, respectively. The aqueous solution Raman line at 1175 cm⁻¹ corresponds with a solid sample line at 1154 cm⁻¹. The solution line is depolarised, and comparison again with the deuterated species suggests strongly its assignment as an asymmetric deformation mode of BH₃. The correspondence between the Raman and infrared spectra given in Table 1 and discussed this far is seen to be good, the infrared spectra showing the H-bonding shifts also.

As before [1], we can assign the strong polarised Raman line at $\sim 560 \text{ cm}^{-1}$ to the symmetric PB_2 stretching mode. An unfortunate coincidence with a spurious laser line generated by the Perkin–Elmer monochromator made this line particularly difficult to determine in the Raman spectra of the solid samples, but its presence in the aqueous solution spectrum and in the solid infrared spectrum, where it shows a high-frequency shoulder, is certain. The asymmetric PB_2 stretching mode can be assigned as the depolarised Raman line at 643 cm^{-1} in the solution spectrum. Again the corresponding infrared line at 652 cm^{-1} has a weak high frequency shoulder. These shoulders on the PB₂ stretching lines can satisfactorily be explained as ^{10}B isotope shifted components. It is most common to find the deformation mode of an AB_{2} system at approximately one half the frequency of the symmetric stretching mode. A weak line at 230 cm^{-1} in the infrared spectrum is therefore tentatively assigned to the PB₂ deformation, rather than the $\sim 400 \text{ cm}^{-1}$ line previously thus assigned [1]. Treating the PB_2 skeleton independently of the hydrogens, it is then possible to calculate an approximate force constant for the P-B bonds. Since the B_1 asymmetric stretching mode generates only a 1×1 block in the secular determinant for the $C_{2v}AB_2$ system, this provides the simplest method of obtaining the **P**—B bond stretching force constant. Using the BH_3 group mass of 14 in the ex-

P-B bond stretching force constant. Using the BH₃ group mass of 14 in the expression $\lambda = 4\pi^2 v^2 = f_{P-B}/m_{BH_3}$ produces the force constant $f_{P-B} = 3.5 \text{ mdyn/Å}$. The same calculation for the BD₃ substituted molecule gives $f_{P-B} = 3.6 \text{ mdyn/Å}$, suggesting that the assumption of only small coupling between P-B and B-H modes is reasonable. The PD₂ substituted compound also is in good agreement, since the B_1 PB₂ mode has approximately the same frequency here as in the PH₂(BH₃)₂⁻ system (Tables 1 and 2). We can compare these P-B force constants with that derived from the P-B stretching mode of the simple phosphine borane H₃P-BH₃. The frequency of this mode has been reported as 564 cm⁻¹ in the infrared spectrum [6]. Treating the H₃P and BH₃ as point masses of 34 and 14, respectively, the force constant is obtained from the relation $f_{P-B} = 4\pi^2 v^2 \mu$, where μ , the reduced mass, has the value 9.92. This gives $f_{P-B} = 1.9 \text{ mdyn/Å}$, a value which is only about half that of the bisboranohypophosphite force constant. These values are in keeping with the relative chemical reactivities of the species: the phosphine borane, H₃P·BH₃, has a dissociation pressure of 200 mm at 0°C and slowly evolves hydrogen [7], while the salt Na⁺[PH₂(BH₃)₂]⁻ is stable at room temperature.

Further detailed assignment of lines to particular symmetry species depends on how much coupling there is between the internal vibrations of the two BH₃ groups in the anion, and on whether or not the BH₃ groups can rotate freely about the P—B bonds. If the C_{2v} model is used, with non-rotating BH₃ groups in a symmetrical configuration with respect to the σ_v planes, a simple vibrational mode analysis predicts $2A_1 + A_2 + 2B_1 + B_2$ BH₃ stretching modes, $2A_1 + A_2 + 2B_1 + B_2$ BH₃ angle deformation modes, $A_1 + A_2 + B_1 + B_2$ BH₃ rocking modes, and $A_2 + B_2$ —BH₃ twisting modes. Only the A_2 modes are infrared inactive. However, if the BH₃ groups are not in a fixed configuration, but undergo free rotation, the twisting modes disappear. Further, if the coupling between the two BH₃ groups is

^[6] R. W. RUDOLPH, R. W. PARRY and C. F. FARRAN, Inorg. Chem. 5, 723 (1966).

^[7] E. L. GAMBLE and P. GILMONT, J. Am. Chem. Soc. 62, 717 (1940).

very small, so that they can be treated independently according to their local C_{3v} symmetry, then the BH₃ stretching modes are reduced to $A_1 + E$, the BH₃ angle deformations to $A_1 + E$, and a single *E*-type rocking mode remains. Examination of the P—H and B—H stretching region of the spectra given in Table 1 shows that the free-rotation, no BH₃—BH₃ coupling, model is completely adequate to explain all but the solid state infrared spectrum. For this, the 2380 cm⁻¹ and 2400 cm⁻¹ lines can be assigned as the A_1 and B_1 PH₂ group bond stretching modes, and the 2312 cm⁻¹ and 2362 cm⁻¹ lines as the BH₃ A_1 and *E* stretching modes, but

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	$\tau(\mathrm{BH_3'})$	$\tau(\mathrm{PH_2})$	$J(\mathrm{B-H'})$	J(P-H)	$J(\mathbf{P}-\mathbf{H'})$	$J(\mathbf{H}-\mathbf{H'})$
$^{\dagger}\mathrm{H_{2}P(BH_{3}')_{2}^{-}}$	9.57	6.90	93	320		7
$D_2P(BH_3')_2$	9.52		91		12	
$H_2^{-}P(BD_3)_2^{-}$		6.92		321		

Table 4. 60 Mc proton NMR spectra of isotopically substituted bisboranohypophosphite anions*

* Coupling constants, J, all in c/s units.

 \dagger Chemical shifts, τ , relative to 3-trimethylsilylpropanesulphonic acid (Na salt), used as an internal standard.

‡ Chemical shifts, τ , relative to (CH₃)₄Si, TMS, used as an external standard.

 Table 5. 20 Mc ¹¹B NMR spectra of isotopically substituted bisboranohypophosphite anions*

		•	
	δ (ppm)	J(B—H')	J(P—B)
$H_2P(BH_3')_2^{}$	57.4	94	64
$D_{2}P(BH_{3}')_{2}$	57.4	93	64
$H_2P(BD_3)_2^-$	~58†		~64†

* Coupling constants, J, all in c/s units. Chemical shifts, δ , all measured relative to $B(OCH_3)_3$, used as an external standard.

[†] These values obtained from a very broad band with two indistinctly resolved maxima.

this still leaves two lines (shoulders on the intense 2312 cm^{-1} line) at 2160 cm^{-1} and 2280 cm⁻¹ unaccounted for. However, these lines occur at close to twice the frequencies of the 1086 cm⁻¹ and 1148 cm⁻¹ BH_3 deformation modes, and can easily be accounted for as overtones. For the alternative rigid C_{2r} model, there is a missing line in the infrared spectrum and five missing Raman lines for the B-H, **P**—H stretching region. The lower frequency lines also appear to be satisfactorily accounted for without the need to postulate hindered rotation about the P-B bonds. The assignments made in Tables 1, 2, and 3 are therefore based upon this simple free rotation model, treating the BH₃ and BD₃ group vibrations according to their local C_{3v} symmetry. Although this procedure appears to be satisfactory for the $PH_2(BH_3)_2^-$ spectra, there are problems with it when applied to the deuterated analogues, as shown by the several unassigned (though weak) lines given in Tables 2 and 3. Two possible explanations suggest themselves: either there is significant coupling between the two BH_3 group vibrations, or the local site-symmetry of the BH_3 groups in the solid is lower than C_{3v} . Either, or indeed both of these explanations can apply, and it is not possible to distinguish between them on the basis of the

available data. For simplicity, assignments are made in the Tables on the basis of local C_{3v} symmetry for the BH₃ groups.

Nuclear magnetic resonance spectra

Tables 4 and 5 summarise the proton and ¹¹B NMR spectra obtained for the three anions PH₂(BH₃)₂⁻, PD₂(BH₃)₂⁻, and PH₂(BD₃)₂⁻. No ³¹P spectra are given, since these contained only weak, and very broad, featureless bands, which were of no help in the analysis. The first important point to be made about the ¹H and ¹¹B spectra is that they were fully compatible with the structures used as a basis for assigning the vibrational bands. In $PH_2(BH_3)_2^{-}$, two distinct types of proton signal were observed. The structures of these showed that the protons within the BH_{a} groups were all equivalent, but that coupling with the ¹¹B nucleus (I = 3/2) gave a widely spaced equal intensity quadruplet, each component of which was broad but unresolved. The PH₂ proton signal was a widely spaced equal intensity doublet, due to the ³¹P coupling $(I = \frac{1}{2})$, each component of this showing a clearly resolved 1:6:15: 20:15:6:1 septet structure due to coupling with the six equivalent BH₃ protons. The chemical shifts and coupling constants are listed in Table 4. It is of interest that no coupling was observed between the ¹¹B and the phosphorus-protons, even when clear proton-proton coupling was evident. The deuterated anion proton spectra confirmed the analysis of the fully hydrogenated anion spectrum, and the PD₂- $(BH_3)_2^{-}$ spectrum further showed clearly resolved structure due to coupling between the ³¹P and the boron-protons. This coupling constant, of 12 c/s, can be compared with that of 16 c/s reported for the analogous phosphine borane, $H_3P \cdot BH_3$ [6].

¹¹B NMR spectra showed the structures expected. Both ³¹P and boron-proton coupling were observed, and coupling constants are given in Table 5. The P—B constant of 64 c/s is similar to that reported for the substituted phosphine-borane, $(CH_3)_2PH\cdot BH_3$, (50 c/s) [8], but, surprisingly, is quite different from that reported for phosphine borane itself (27 c/s) [6].

[8] J. N. SCHOOLERY, Discussions Faraday Soc. 19, 215 (1955).