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Spectra and Structure of Phosphorus–Boron Compounds. IX.[1] Vibrational Analysis and Molecular Symmetry of Solid $B_2Cl_4{\cdot}2PH_3$ and $B_2Cl_4{\cdot}2PD_3$

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The Raman (25–2500 cm^{-1}) and infrared (90–2500 cm^{-1}) spectra of solid $B_2Cl_4{\cdot}2PH_3$ and $B_2Cl_4{\cdot}2PD_3$ have been recorded. The vibrational data have been interpreted on the basis of a trans (C_{2h}) molecular conformation in the solid state. This structure requires that the principle of mutual exclusion holds, and this is seen to be the case since the P–B stretching frequencies observed in the infrared and Raman effect are 651 and 713 cm^{-1}, respectively, in $B_2Cl_4{\cdot}2PH_3$ and 620 and 658 cm^{-1}, respectively, in $B_2Cl_4{\cdot}2PD_3$. Differences in frequencies between the adducts and the parent molecule are attributed to phosphorus–boron coordination. The assignments of torsional fundamentals give 2.92 ± 0.18 kcal/mol for the periodic barriers to internal rotation about the P–B bonds.

Introduction

The symmetries of molecules having the general formula X_2Y_4 have been under investigation in this laboratory over the past few years.[3-15] These investigations have involved compounds which have group Va elements as the central atoms as well as studies on the diboron tetrahalides. More recently, the effects upon symmetry resulting from the coordination of the lone-pair electrons on nitrogen in hydrazine and phosphorus in diphosphines have been investigated.[16-18] The results have been identical in that for the solid phases, the molecules of tetramethyldiphosphine–bis(borane)[16] and hydrazine–bis(borane)[17] have both been found to exist as one conformer, the C_{2h} (trans) form. For these trans molecules, the differences between the infrared and Raman frequencies as required by symmetry were most pronounced for the skeletal and bending motions.

To continue our studies of the effects of adduct formation in relation to structure, we have undertaken the vibrational analysis of diboron tetrachloride–bis(phosphine). This molecule differs from previously examined adducts in that the symmetry must change from D_{2h} (crystalline solid) in the parent B_2Cl_4 molecule to either or both of the likely forms, C_{2h} (trans) and C_2 (gauche). The possible symmetries of the bis(borane) adducts of hydrazine[17] and tetramethyldiphosphine[16] are the same as those possible for the parent molecules. No previous structural work has been reported for $B_2Cl_4{\cdot}2PH_3$ and no vibrational data are available for this molecule.

Experimental Section

With the exception of the phosphine syntheses, all preparative work was carried out in a high-vacuum system employing greaseless stopcocks. All ground-glass apparatus was lubricated with Kel-F 90 grease to prevent decomposition of halogen-containing species. Boron trichloride was obtained commercially (Matheson) and was purified by trap-to-trap fractionation or by distillation on a variable-temperature vacuum fractionation column[19] followed in either case by exposure to mercury until the vapor pressure was 476 Torr at 0°.[20] The diboron tetrachloride was prepared either by a slightly modified method of that reported by Wartik, *et al.*,[21] or by the method of Brennan.[22] Purification was by high-vacuum column distillation.

Phosphine was prepared under a stream of gaseous nitrogen in a well-ventilated fume hood as described in the literature.[23] Phosphine-d_3 was prepared in a similar manner using D_2O and D_2SO_4. All phosphine species were purified by passing them through a trap at −131° (*n*-pentane slush) into a trap at −196°. Purity was monitored by vapor pressure measurements[24] and infrared spectra.[25]

Diboron tetrachloride–bis(phosphine) was prepared by allowing B_2Cl_4 and PH_3 in a 1:2 mole ratio, respectively, to react at −80°.[26] The reaction tube was immersed in a −22° bath (CCl_4 slush) and pumped under dynamic vacuum to remove any $H_3P{\cdot}BCl_3$ which may have been formed or any traces of unreacted B_2Cl_4 or PH_3.

Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer equipped with a Coherent Radiation Model 53

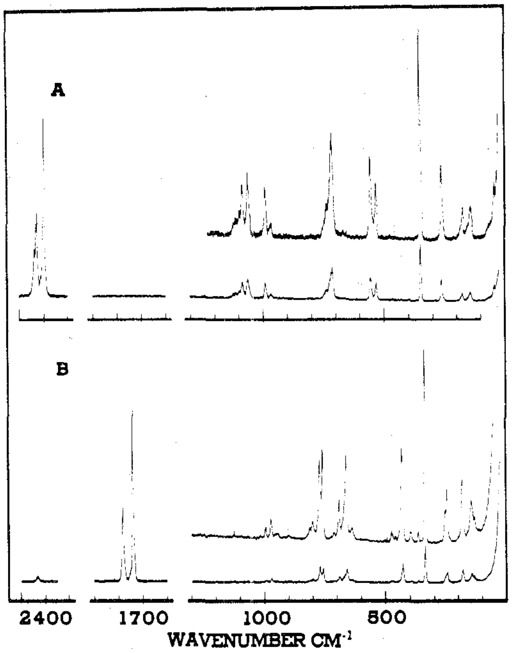

Figure 1. Raman spectra of (A) $B_2Cl_4{\cdot}2PH_3$ and (B) $B_2Cl_4{\cdot}2PD_3$. The ordinate is in arbitrary units.

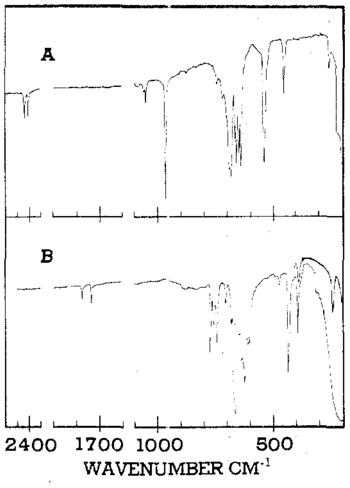

Figure 2. Mid-infrared spectra of (A) $B_2Cl_4{\cdot}2PH_3$ and (B) $B_2Cl_4{\cdot}2PD_3$.

argon ion laser using 5145-Å excitation. Spectra of solid diboron tetrachloride–bis(phosphine) were obtained by using a low-temperature cell similar to one previously described[6] with the sample supported on a solid brass plate at an angle of 15° from the normal. Samples were sublimed onto the brass plate held at ~−196° and then annealed until the spectra showed no change. Typical spectra are shown in Figure 1.

A Perkin-Elmer Model 621 grating spectrophotometer was used to record mid-infrared spectra from 2500 to 200 cm^{-1}. The instrument was purged with dry nitrogen and calibrated as described in the literature.[27] Spectra were obtained using both a cell[6] cooled with liquid nitrogen and a cryostat[28] with temperature regulation down to 14°K. Conventional vacuum sublimation techniques were used to deposit a solid film of sample on the CsI substrate. Annealing was done in the usual manner. Mid-infrared spectra of solid $B_2Cl_4{\cdot}2PH_3(2PD_3)$ are shown in Figure 2.

Far-infrared spectra were recorded from 90 to 350 cm^{-1} using a Beckman Model IR-11 spectrophotometer. Atmospheric water vapor was removed by flushing with dry nitrogen gas at all times except when the instrument was calibrated.[29] The low-temperature cell used is similar to one described previously.[6] Modifications allow liquid nitrogen to flow through a brass cold finger around the wedged silicon window[30] which was used as the support medium. Deposition and annealing procedures were as described above. Far-infrared spectra are shown in Figure 3. All frequencies reported are expected to be accurate to within ±2 cm^{-1}.

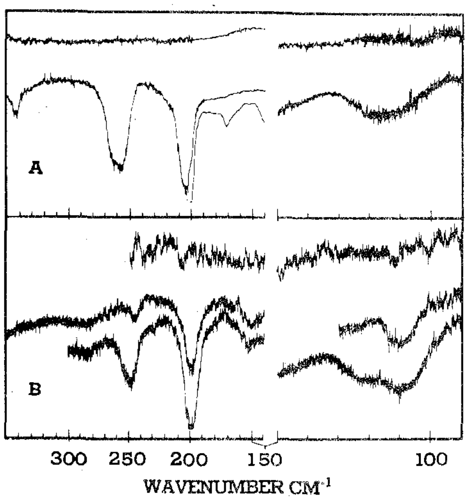

Figure 3. Far-infrared spectra of (A) $B_2Cl_4{\cdot}2PH_3$ and (B) $B_2Cl_4{\cdot}2PD_3$. The uppermost trace in each section is the cell background.

Results

The infrared or Raman activity of the 36 fundamentals will be determined by the molecular symmetry. For a C_{2h} structure we expect, from group theory, 11 A_g, 8 A_u, 7 B_g, and 10 B_u fundamentals, with mutual exclusion where the gerade modes are Raman active and the ungerade modes are infrared active. For the other possible structure, the C_2 (gauche) conformer, the irreducible representation is 19 A + 17 B with all modes being allowed in the infrared and Raman effect. No previous work has been reported on the structure of $B_2Cl_4{\cdot}2PH_3$, but by considering the reaction involved in adduct formation and the fact that previous coordination compounds have shown this trend, we felt that the trans structure was the more likely of the two.

Comparison of the infrared and Raman spectra of solid $B_2Cl_4{\cdot}2PH_3$ immediately leads one to believe that a center of symmetry causes mutual exclusion. Table I lists the frequencies observed and their assignments. In addition to differences in bending and skeletal vibrations there seem to be differences in the PH_3 stretching frequencies that are beyond the limits of experimental error. The symmetric PH_3 stretch is at 2395 cm^{-1} in the Raman spectrum (in-phase motion) and at 2413 cm^{-1} in the infrared spectrum (out-of-phase motion) in $B_2Cl_4{\cdot}2PH_3$. In the deuterated analog these respective motions shift to 1739 and 1738 cm^{-1}, which are within experimental error of one another. Assignments of fundamentals associated with the PH_3 moiety were facilitated by deuteration and analogy with previous work.[31-33] These are likewise listed in Table I and need little further comment, although the torsions will be dealt with later.

The B–B stretching motion is an A_g mode and is allowed only in the Raman effect for C_{2h} symmetry. This would provide the means of determining the symmetry were it not for the fact that it is expected to be weak in the Raman spectrum as observed for B_2Cl_4[3] and B_2Br_4.[4] We assign this fundamental to a Raman line of medium intensity at 1061 cm^{-1} in $B_2Cl_4{\cdot}2PH_3$, which shifts to 969 cm^{-1} in $B_2Cl_4{\cdot}2PD_3$ for the ^{11}B–^{11}B isotope. With naturally occurring ^{10}B and ^{11}B in a ratio of 20:80 we expect the intensity of the ^{10}B–^{11}B motion to be half that of the ^{11}B–^{11}B mode. This is the ratio observed for the lines at 990 and 969 cm^{-1} in $B_2Cl_4{\cdot}2PD_3$. In $B_2Cl_4{\cdot}2PH_3$, however, the line at 1081 cm^{-1} is more than half as intense as the one at 1061 cm^{-1}. Since we expect an antisymmetric PH_3 deformation in the region near 1100 cm^{-1} we attribute the enhanced intensity at 1081 cm^{-1} to the overlapping of the ^{10}B–^{11}B stretch with this deformation.

Table I. Observed Fundamentals (cm^{-1}) of *trans*-$B_2Cl_4 \cdot 2PH_3$ and *trans*-$B_2Cl_4 \cdot 2PD_3$

Symmetry	$B_2Cl_4 \cdot 2PH_3$		$B_2Cl_4 \cdot 2PD_3$		Description
	Ir	Raman	Ir	Raman	
A_g ν_1		2426		1780	PH_3 (PD_3) antisym str
ν_2		2395		1739	PH_3 (PD_3) sym str
ν_3		1085		803^a	PH_3 (PD_3) antisym def
ν_4		1061		969	B–B str
ν_5		990		762^a	PH_3(PD_3) sym def
ν_6		713		658	P–B str
ν_7		533		427	PH_3(PD_3) rock
ν_8		350		335	BCl sym str
ν_9		262		251	BCl_2 wag
ν_{10}		257		251	B–B–P bend
ν_{11}		177		181	BCl_2 scissors
A_u ν_{12}	2443		1782		PH_3(PD_3) antisym str
ν_{13}	1053		775		PH_3 (PD_3) antisym def
ν_{14}	736^a		713		BCl_2 antisym str
ν_{15}	547		429		PH_3 (PD_3) rock
ν_{16}	207		199		BCl_2 twist
ν_{17}	171		123		PH_3 (PD_3) torsion
ν_{18}	115		111		BCl_2 rock
ν_{19}					B–B torsion
B_g ν_{20}		2434		1784	PH_3 (PD_3) antisym str
ν_{21}		1085		803^a	PH_3 (PD_3) antisym def
ν_{22}		739		689	BCl_2 antisym str
ν_{23}		556		427	PH_3 (PD_3) rock
ν_{24}		257		244	BCl_2 twist
ν_{25}		177		128	PH_3 (PD_3) torsion
ν_{26}		144		145	BCl_2 rock
B_u ν_{27}	2443		1778		PH_3 (PD_3) antisym str
ν_{28}	2413		1738		PH_3 (PD_3) sym str
ν_{29}	1053		761		PH_3 (PD_3) antisym def
ν_{30}	964		748		PH_3 (PD_3) sym def
ν_{31}	689^a		666		BCl_2 sym str
ν_{32}	651^a		620		P–B str
ν_{33}	542		392		PH_3 (PD_3) rock
ν_{34}	261		249		BCl_2 wag
ν_{35}	255		249		B–B–P bend
ν_{36}	201		199		BCl_2 scissors

^{a} Average of a pair of frequencies.

Next we shall consider the P–B stretches. The Raman-active motion is the A_g in-phase P–B stretch while the B_u out-of-phase motion is infrared active for the trans conformer. From other studies[33,34] we expect these to be in the region between 600 and 700 cm^{-1}. In the Raman spectra there are reasonably intense lines at 713 and 658 cm^{-1} for $B_2Cl_4 \cdot 2PH_3$ and $B_2Cl_4 \cdot 2PD_3$, respectively. The infrared spectra show lines at 661 and 642 cm^{-1} in the d_0 species and at 620 cm^{-1} in the d_6. These lines have been assigned to the P–^{11}B motions because of intensity considerations and shoulders attributable to P–^{10}B species. The reason for the doubling of the infrared band in $B_2Cl_4 \cdot 2PH_3$ will be discussed in a subsequent section.

The totally symmetric BCl_2 stretch is assigned to the strong Raman bands at 350 and 335 cm^{-1} in the d_0 and d_6 species, respectively. The out-of-phase symmetric BCl_2 stretch should be infrared active only and is thus assigned at 689 and 666 cm^{-1} in these molecules. These assignments are consistent with those in B_2Cl_4.[3] The frequencies of the antisymmetric motions do not seem to be as easily transferred. In B_2Cl_4[3] the in-phase motion is assigned at 920 cm^{-1} with the out-of-phase at 947 cm^{-1}. These regions of both the infrared and Raman spectra are relatively clean. We must postulate then that the dative bond formation has affected these motions, as might be expected. By comparison with $H_3P \cdot BCl_3$,[34] in which the antisymmetric BCl_3 stretch is at 730 cm^{-1} in the Raman spectrum, we assign the out-of-phase BCl_2 antisymmetric stretch to infrared bands at 736 and 713 cm^{-1} and the in-phase motion to weak Raman lines at 739 and 689 cm^{-1} in $B_2Cl_4 \cdot 2PH_3$ and $B_2Cl_4 \cdot 2PD_3$, respectively.

Yet to be assigned are motions which give rise to normal modes below 300 cm^{-1}. Most of these are associated with BCl_2 bending motions. These are assigned in the order $\nu_{\text{wag}} > \nu_{\text{twist}} > \nu_{\text{scissors}} > \nu_{\text{rock}}$ on the basis[35] of the relative frequencies for the BCl_3 symmetric and antisymmetric deformations. The frequencies are listed in Table I and require no further discussion. The B–B–P bend is assigned at 257 and 251 cm^{-1} in the d_0 and d_6 species while the corresponding out-of-phase motion is observed in the infrared spectra at 255 and 249 cm^{-1} for these same molecules.

Torsional motions include one about the B–B bond, which should be infrared active, and two about the P–B bonds, one infrared and one Raman active. In B_2Cl_4 the torsional frequency was observed[36] at 23 cm^{-1}. In $B_2Cl_4 \cdot 2PH_3$ we expect this frequency to be even lower and it remains unobserved. In assigning the torsion of the phosphine moiety we look first to the deuterated species. In the Raman spectrum there appears to be a shoulder at 128 cm^{-1} on the low-frequency side of the line assigned to the BCl_2 in-phase rock. If this is assigned as the PD_3 torsion, we calculate that the corresponding motion for the PH_3 in-phase torsion is buried under the 177-cm^{-1} line which was assigned to the BCl_2 scissors. In the infrared spectrum there seems to be a shoulder at 123 cm^{-1} on the high-frequency side of the 111-cm^{-1} band which has been attributed to the BCl_2 out-of-phase rock. From this frequency for the PD_3 torsion one would predict a frequency of 173 cm^{-1} for the d_0 species. The far-infrared spectrum shows a weak band at 171 cm^{-1}.

Considering the distances involved, we assume negligible interaction between the two phosphine tops and attribute the differences in frequency to experimental error. Thus, we report the periodic barrier[37] to internal rotation of the PH_3 group around a P–B bond to be 2.92 ± 0.18 kcal/mol.

The assignments detailed herein and summarized in Table I are supported by the Teller–Redlich product rule. In calculating the moments of inertia which were used, we assumed the following structural parameters: r(B–B), 1.702 Å; r(P–B), 1.935 Å; r(P–H), 1.40 Å; r(B–Cl), 1.75 Å; ∠H–P–H, 101°, ∠P–B–Cl, 114°; ∠Cl–B–Cl, 114°. The theoretical τ values expected for the A_g, A_u, B_g, and B_u symmetry blocks are 5.45, 3.94, 3.81, and 5.50, respectively. The corresponding observed values based on the assignments given above are 5.40, 3.72, 3.75, and 5.47. All of them compare favorably, with the A_u block having the greatest error, but it must be remembered that the frequencies for the B–B torsion have been neglected and the shift for the PH_3 torsion has been assumed to be 1.4.

Discussion

Assignments for $B_2Cl_4 \cdot 2PH_3$ and $B_2Cl_4 \cdot 2PD_3$ have been made on the basis of C_{2h} symmetry with no coincidences between the infrared and Raman frequencies except for the P–D stretching motions. It is apparent from the Raman spectra at first glance that there are not enough lines to assign to 36 fundamentals. The alternatives are either to consider mutual exclusion or to attribute the spectra to a simpler molecule which could be a decomposition product. The likely decomposition products are B_2Cl_4 and phosphine or possibly $H_3P \cdot BCl_3$. The spectra of these compounds are well known,[3,31,32] and by comparison with those obtained in this study, we have ruled out this possibility.

In obtaining spectra of the solid, annealing was done slowly. It was evident that, after allowing the sample of $B_2Cl_4 \cdot 2PH_3$ to warm to ambient temperatures a number of times, decomposition was taking place. Bands grew into the O–H stretching and bending regions presumably from a hydrolysis product of the sample with water residue adhering to the inside walls of the cold cell.

In the bis(phosphine) adducts, the frequencies of the P–H stretching motions are higher than these found in the uncomplexed PH_3 molecule (ν_1 2327 cm^{-1}, ν_3 2421 cm^{-1}).[31] This is consistent with the expected shortening of the P–H bond length upon coordination, and this effect has been found in previous work.[32,33,34]

Phosphorus–boron coordination also effects other motions, as has been stated previously (*e.g.*, BCl_2 antisymmetric stretch). In addition, we see that the ^{10}B–^{11}B isotopic splitting is not as pronounced for the BCl_2 stretching motions in the bis(phosphine) adduct as was observed in B_2Cl_4.[3] In B_2Cl_4 the splittings between the $^{11}BCl_2$ and $^{10}BCl_2$ counterparts of the ν_9 and ν_{11} stretching motions were 15 and 27 cm^{-1}, respectively. These isotopic effects manifested themselves as unresolved shoulders on the high-frequency side of the $^{11}BCl_2$ stretch in $B_2Cl_4 \cdot 2PH_3$. The mixing of other vibrational modes appears to be extensive in the bis(phosphine) adduct. The shift of the B–B stretch from 1061 cm^{-1} in $B_2Cl_4 \cdot 2PH_3$ to 969 cm^{-1} in $B_2Cl_4 \cdot 2PD_3$ is much larger than the shift attributable solely to the mass effect on deuteration. This is likewise true of the shift from 350 to 335 cm^{-1} of the A_g BCl_2 stretch in these two molecules. In H_3PBCl_3,[34] the A_1 BCl_3 stretching motion was seen to be relatively pure with similar mixing in the d_0 and d_3 species with frequencies of 401 and 397 cm^{-1}, respectively. The P–B stretching frequency does not shift as much upon deuteration as has been observed previously,[33] and this undershift implies that appreciable mixing occurs among the B–B stretch, the in-phase BCl_2 symmetric stretch, and the in-phase P–B stretch. The complex mixing of these motions is likely to be a result of the similarity in the masses of the chlorine atoms and phosphine moiety.

The torsional barrier of 2.92 ± 0.18 kcal/mol is one of the few reported for a PH_3 (PD_3) group. The tentative assignment of vibrational bands in the spectra of $H_3P \cdot BBr_3$ and $D_3P \cdot BBr_3$[33] gave values of 2.92 and 3.28 kcal/mol for the barriers in these molecules. The error limits in these cases are too large to allow any meaningful evaluation of trends, but it looks as though barriers in phosphine–haloboranes tend to be larger than the 2.47 kcal/mol value found in $H_3P \cdot BH_3$.[38]

The crystal structure of diboron tetrachloride–bis(phosphine) is not known so solid effects could not be predicted *a priori*. Within the assignment of C_{2h} symmetry we expect at least 1 A_g and 2 B_g librations (Raman active) and 1 A_u and 2 B_u acoustical translations (inactive). In the Raman spectrum, there seems to be only one line below 100 cm^{-1} in the d_0 species. In the spectrum of the d_6 species there seems to be a doubling of the PH_3 symmetric and antisymmetric deformations at 756 and 769 cm^{-1} and 798 and 809 cm^{-1}, respectively. The infrared spectrum of $B_2Cl_4 \cdot 2PH_3$ shows doubling of all the lines between 600 and 760 cm^{-1} in the annealed solid. The ^{11}B components of the P–B stretch appear at 642 and 661 cm^{-1} while the ^{10}B counterparts are at 650 and 669 cm^{-1}. The BCl_2 symmetric stretch (out of phase) has components at 684 and 693 cm^{-1} while the antisymmetric stretch appears at 724 and 748 cm^{-1}. This frequent doubling is indicative of there being two molecules per unit cell. The lack of observed lattice modes does not rule out this possibility, and the question can only be further resolved by a crystal structure determination.

The physical characteristics of $B_2Cl_4 \cdot 2PH_3$ prevented experimental examination of any phase other than the solid. It is unfortunate that no polarization data were available to aid in the assignment of some fundamentals. The reported[26] decomposition temperature of 60° is well below the melting point.

The C_{2h} molecular symmetry found thus far for coordination compounds whose parents are X_2Y_4 molecules may be a result of the fact that these determinations have been done in the solid state only. For a number of X_2Y_4 molecules, if two conformers exist in the fluid phases, only the trans exists in the solid phase.[11-13] We should emphasize here that this is not true for all molecules of this type.[6-10] In B_2Cl_4, the configuration changes from D_{2d} (twisted) in the liquid to D_{2h} (planar) in the crystalline solid.[3] The reasons for this are thought to result from crystal effects rather than thermodynamic stabilities. This leaves open the question as to what the structure of $B_2Cl_4 \cdot 2PH_3$ might be in the fluid phases. The far-infrared spectra of the d_0 and d_6 species showed very weak bands that disappeared upon annealing which may or may not have been due to molecules of some other conformation trapped within the cold film. The low vapor pressure of the molecule (~0.7 mm[26]) restricts the amount of data that can be gathered with regard to this question.

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Registry No. $B_2Cl_4 \cdot 2PH_3$, 53320-31-3; $B_2Cl_4 \cdot 2PD_3$, 53320-32-4.

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