

SPECTRA AND STRUCTURE OF PHOSPHORUS-BORON COMPOUNDS

XV:* *Vibrational Studies of Substituted P-Hexamethylcyclotriborophosphanes*

J. R. DURIG, M. A. SENS,[†] V. F. KALASINSKY and J. D. ODOM

Dept. of Chemistry, University of South Carolina, Columbia, S.C. 29208, U.S.A.

(Received 7 July, 1976)

Abstract. The infrared spectra ($3500\text{--}30\text{ cm}^{-1}$) of solid hexa-substituted P-hexamethylcyclotriborophosphanes $[(\text{CH}_3)_2\text{PBX}_2]_3$ where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and CH_3 and some corresponding B-monosubstituted and disubstituted species have been recorded. The Raman spectra ($3500\text{--}10\text{ cm}^{-1}$) of the corresponding solids have also been investigated. The vibrational spectra of the hexa-substituted compounds could best be interpreted on the basis of C_{3v} molecular symmetry. The observed intermolecular vibrations for these solids indicate little factor group effects. The vibrational spectra of the corresponding B-monosubstituted compounds were very similar to those for the parent molecules with the addition of three 'new' B-X motions. The molecular symmetries are discussed in relation to a recent nuclear magnetic resonance study.

1. Introduction

In a recent nmr study of the B-hexamethyl-P-hexamethylcyclotriborophosphane molecule [1], it was concluded from a variable temperature ^1H study that the methyl groups were either undergoing rapid axial-equatorial interchange at -95°C or that the molecule had assumed an essentially planar conformation with complete methyl substitution. The other B-hexasubstituted molecules were not studied because of their low solubility. The corresponding nmr studies of the mono- and di-substituted compounds showed that the molecules were in the 'chair form'. The resonance positions for the axial and equatorial methyl groups could clearly be seen and their interchange followed with a variation in temperature.

Recently we investigated [2] the infrared spectra of solid and gaseous P-hexamethylcyclotriborophosphane, $[(\text{CH}_3)_2\text{PBH}_2]_3$, along with the Raman spectra of the solid, liquid and gas. The vibrational data for this molecule were interpreted in detail on the basis of C_{3v} molecular symmetry (chair form) for all three physical states. As a continuation of this earlier work, we have recorded the vibrational spectra of the corresponding hexa-substituted P-hexamethylcyclotriborophosphanes, $[(\text{CH}_3)_2\text{PBX}_2]_3$, where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and CH_3 , in the solid state in the hopes of determining the effect of the substitution on the molecular symmetry. The infrared spectra of all but the iodine compound have been studied previously in KBr discs [3]. Without complimentary data from Raman experiments, Chapman only attempted to assign the more obvious fundamentals. In addition to the hexa-substituted species, a number of mono- and di-substituted compounds have been studied.

* For Part XIV, see *Spectrochim. Acta*, **33A** (1977), in press.

[†] Taken in part from the Ph.D. Thesis of M. A. Sens.

In this work, the simplest member of this series of rings, P-hexamethylcyclotriborophosphane is for simplicity called the 'trimer'. All derivatives are substituted on the boron atom(s) and are referred to as hexa-'X'-trimer, e.g., hexachlorotrimer for B-hexachloro-P-hexamethylcyclotriborophosphane.

2. Experimental

The compounds used in this study were kindly donated by M. H. Goodrow, Modesto Junior College, Modesto, California.

The mid-infrared spectra were obtained on a Perkin-Elmer model 621 grating spectrophotometer. The spectra of the solids were obtained from KBr pellets of the compounds and are shown in Figure 1.

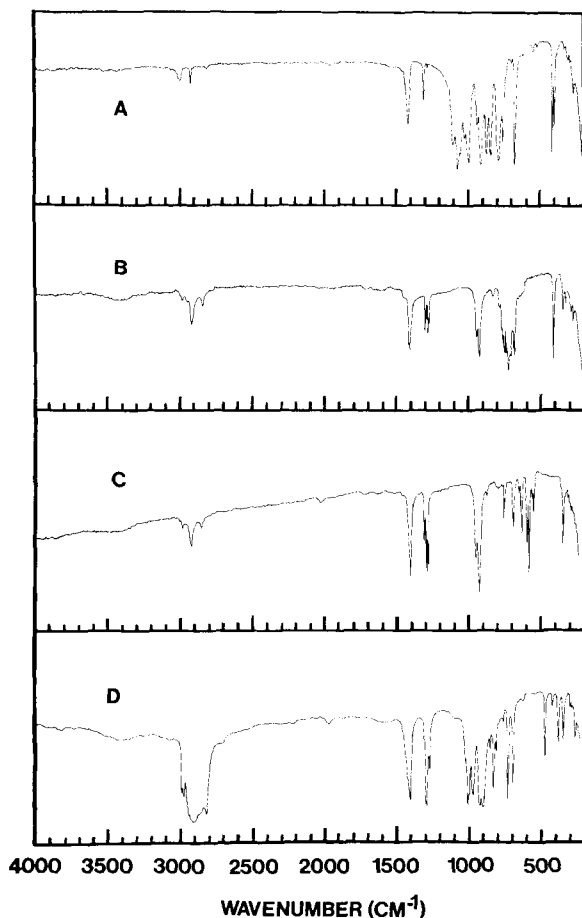


Fig. 1. The mid-infrared spectra of the hexasubstituted trimers, (A) hexafluorotrimer, (B) hexachlorotrimer, (C) hexaiodotrimer, (D) hexamethyltrimer.

The far infrared spectra ($700\text{--}40\text{ cm}^{-1}$) shown in Figure 2 were obtained on a Digilab FTS-15B interferometer with a 12.5 micron Mylar beamsplitter and purged with dry nitrogen during use. The solid samples were ground to a fine powder and pressed between polyethylene plates to obtain the spectra. A similar polyethylene holder, without the sample, was used as a reference. Due to the beamsplitter utilized, the regions $230\text{--}260\text{ cm}^{-1}$ and $490\text{--}530\text{ cm}^{-1}$ were not of value.

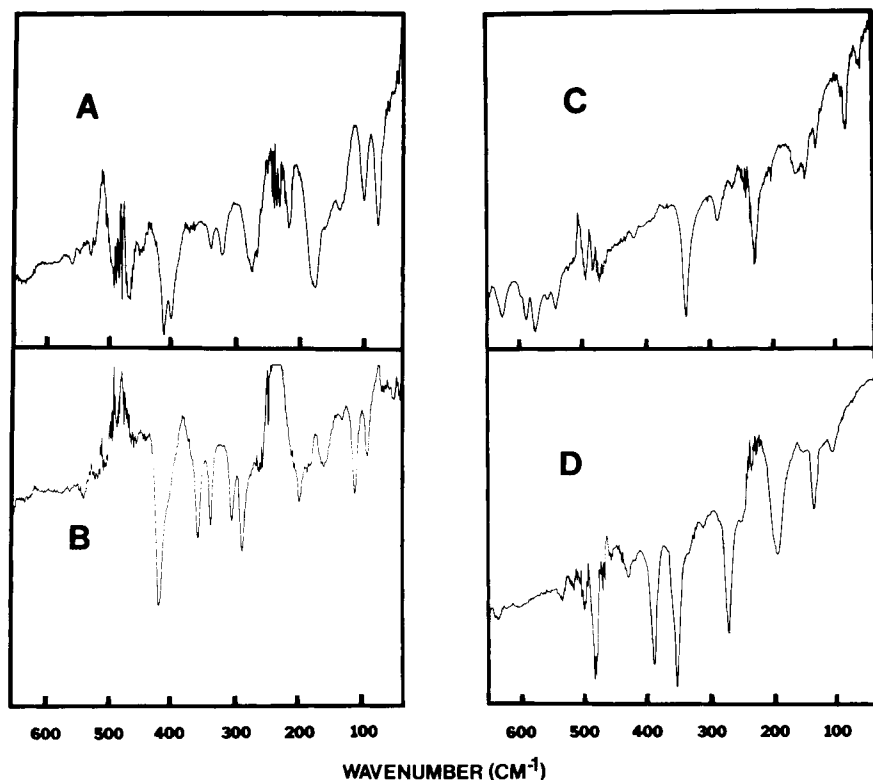


Fig. 2. The far infrared spectra of the hexasubstituted trimers, (A) hexafluorotrimer, (B) hexachlorotrimer, (C) hexaiodotrimer, (D) hexamethyltrimer.

The Raman spectra were obtained on a Cary model 82 Raman spectrophotometer equipped with a Spectra Physics model 171 argon ion laser. The 5145 \AA exciting line was used for all work. The samples of the hexafluoro-, hexachloro-, hexaiodo-, and hexamethyltrimers were finely ground and packed into a standard Cary solid sample holder, which consists of a conical cavity in the end of a stainless steel rod. Spectra were recorded with the surface of the samples held at an angle of 30° to the laser beam. The spectrum of the hexabromotrimer was obtained with the powdered sample held in a Pyrex capillary. All spectra were obtained at room temperature and are shown in Figures 3 and 4.

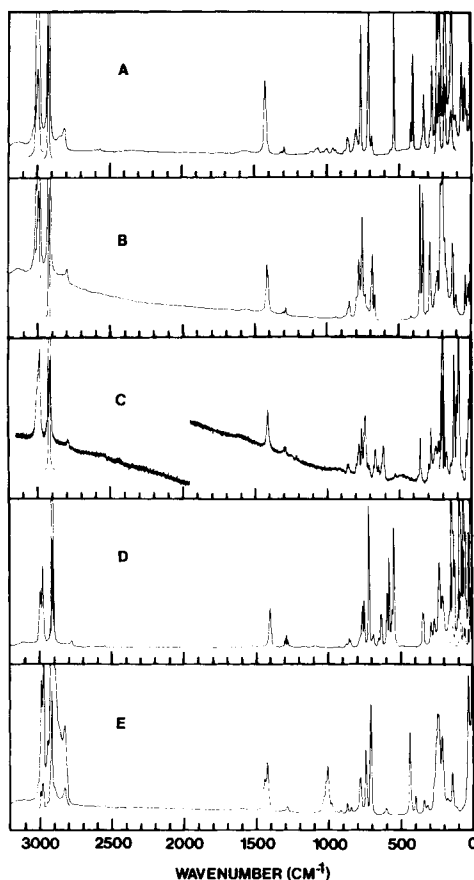


Fig. 3. The Raman spectra of the hexasubstituted trimers, (A) hexafluorotrimer, (B) hexachlorotrimer, (C) hexabromotrimer, (D) hexaiodotrimer, (E) hexamethyltrimer.

Due to the extreme insolubility of these compounds, solution work was precluded. Studies of the neat liquids or gas phases of these compounds was also prohibited due to their decomposition above 300° without melting and to their very low vapor pressures.

3. Vibrational Assignments

Since an X-ray crystal structure determination has not appeared for any of the hexasubstituted trimers, the conformation of these rings was not known. Two conformations seemed possible, the C_{3v} 'chair' conformation that the trimer assumes or a structure where the ring is planar, D_{3h} . Vibrational studies can distinguish between these two choices. The 'chair' conformation, C_{3v} , has the following irreducible representations, $21A_1 + 13A_2 + 34E$. The A_1 and E vibrations are allowed in both the infrared and Raman effects, while the A_2 modes are forbidden. In the D_{3h} conformation however, the normal vibrations span the

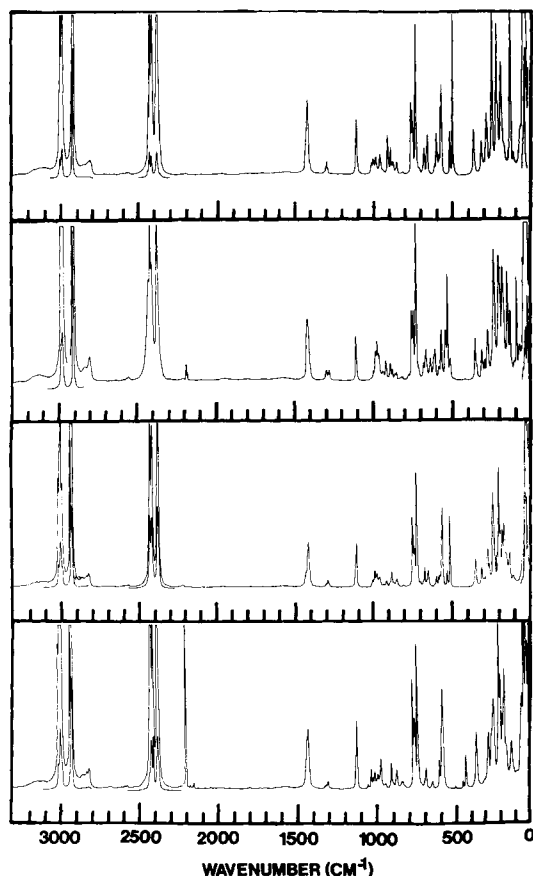


Fig. 4. The Raman spectra of the (A) monoiodotrimer, (B) dibromotrimer, (C) monoiodotrimer, (D) monocyanotrimer.

irreducible representation $11A'_1 + 6A''_1 + 7A'_2 + 10A''_2 + 18E' + 16E''$. Of these the A''_1 and the A'_2 modes are symmetry-forbidden in both the infrared and Raman, the A'_1 and E'' modes are allowed only in the Raman, the A''_2 modes are allowed only in the infrared, and the E' modes are allowed in both the infrared and Raman effects. Thus, in both the conformations the same number of fundamentals are seen; however, in the C_{3v} conformation all normal vibrations are coincident between the infrared and Raman, while in the D_{3h} geometry only 18 coincidences occur. Based on the number of coincidences between the infrared and Raman spectra, it appears that these substituted derivatives maintain the C_{3v} symmetry exhibited by the trimer.

Unfortunately, the complete vibrational assignment of these compounds was precluded. Depolarization ratios could not be obtained on these compounds since most are extremely insoluble and decompose without melting at over 300° [4, 5]. The one compound potentially amenable to obtaining depolarization ratios is the hexafluorotrimer. However, since this spectrum is remarkably similar to that of the trimer

764 m	765 sh 762 s	760 s 755 s sh	759 s sh 754 s	731 s	717 s	740 s 738 sh	740 m 738 m	PC ₂ symmetric stretch
683 s	683 w	699 vw 689 m	689 sh	669 w 638 w	599 sh 593 m	~640 vw		Ring deformation (E)
559 vw	558 w	667 w	667 w	660 m	579 s		599 w	Ring deformation (A ₁)
531 vw	531 s	685 sh, m	684 m	607 m	545 w	703 s	703 s	Ring breathing
425 m	425 m			98 m				BX ₂ scissors (E)
404 m	402 s	207 sh	206 s	117 s	85 w	390 s	392 w	BX ₂ scissors (A ₁)
340 w	339 w, sh			121 s, sh	94 w	312 vw	312 w	BX ₂ twist (E)
322 w		304 m	305 vw	138 w	134 w	355 s		BX ₂ wag
218 m	218 vs	130 w, m	132, 129 s	85 s	64 vw	196 m	241 s	BX ₂ rock (A ₁ , E)
						62 w		
							336 w	PC ₂ scissors
	332 m	287, 282 m	289 m	350 m	338 m			
						347 m		
						341 m		
268 vw	270 s		246 m, sh	291 w	289 w	273 m	272 m	PC ₂ wag
			238 m	275 m	289 mw		265 w	PC ₂ twist
			235 m		278		241 s	PC ₂ scissors
						234 m	234 s	PC ₂ rock
177	234 s		214 s	244 w, m	264 w	267 m, w	211 s	(A ₁)
138 m	178 vs	197 m	198 s	225 w, m	230 m	230 m	157 w	Ring bending (E)
	137 s	181 w	186 sh	169 w		194 ms	138 m	
	109 w, g	159 w		74 w	126 w			
100 m		110 m	107 w	60 vw	52 s	176 vw	172 w	
78 s		90 m		33 m	47 w	109 vw		
	66 ms, b	64 vw		29 m	30 s		40 vs	
60 vw	62 sh	50 vw		18 m	20 s		18 s	Lattice Modes
52 vw			40 m		18 s			
45 vw	44 m, s		27 w		13 s			
	39 w, sh		20 w, m					
	31 w							

^a Abbreviations used are as follows: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad.

^b Designations of A₁ or E next to the approximate descriptions refer to the probable symmetry block and analogy to the corresponding modes in the unsubstituted trimer [2].

^c Overtones and combinations of these modes are not listed although they are apparent in the spectra.

(where depolarization ratios are known) and the B—F motions are distinct and not overlapping other motions, the added value of such solution work is dubious. Furthermore, the solutions of the hexafluorotrimer decompose slowly, depositing a nonvolatile solid on container walls. The lack of data from the gas phase, where depolarization ratios and band contours can be obtained from the Raman and infrared spectra, respectively, also make it difficult to make a totally unambiguous assignment. Table I lists the observed frequencies and the approximate descriptions of molecular motions. The assignments were made by comparison with the unsubstituted trimer [2], the H_3PBX_3 adducts [6], and the mono- and disubstituted trimers (*vide infra*). Where possible, the symmetry of these motions is given.

The strongest line in the Raman spectrum is assigned to the CH_3 symmetric stretch. Since only one line appears in this region, the A_1 and E modes must be accidentally coincident. In the hexamethyltrimer, a strong infrared counterpart is seen, but in the hexahalotrimers, the infrared bands are quite weak. This is consistent with the spectra of the substituted adducts [6–9], $\text{H}_{3-x}(\text{CH}_3)_x\text{PBH}_3$ where weak CH_3 stretches were observed in the infrared spectra. The two antisymmetric CH_3 stretches are also strong in the Raman and occur between $2992 \rightarrow 3005 \text{ cm}^{-1}$ in all compounds. The additional lines occurring at $2976, 2979 \text{ cm}^{-1}$ in the hexamethyltrimer are probably due to the $\text{B}(\text{CH}_3)_2$ antisymmetric stretches.

The CH_3 antisymmetric deformations occur in the $1400\text{--}1430 \text{ cm}^{-1}$ region for all compounds. The additional features at 1441 and 1452 cm^{-1} in the hexamethyltrimer are assigned to the $\text{B}(\text{CH}_3)_2$ antisymmetric deformations. The CH_3 symmetric deformations in all compounds appear in the 1275 to 1320 cm^{-1} region. These are typically strong in the infrared and weak in the Raman spectra [6–9].

The last methyl motions are the rocks which are seen in the $850\text{--}1000 \text{ cm}^{-1}$ region. In all compounds these are again strong in the infrared while weak and often quite broad in the Raman spectra.

Two PC_2 antisymmetric stretches are noted in each compound. The highest set occur at 805 and 794 cm^{-1} in the Raman spectrum of the hexafluorotrimer; the lowest set occur at $764, 752,$ and 747 cm^{-1} in the Raman spectrum of the hexaiodotrimer. All have infrared counterparts.

The two PC_2 symmetric stretches occur approximately 50 cm^{-1} below the PC_2 antisymmetric stretches in each compound. Most have infrared counterparts and all are typically very strong in the Raman spectra. These motions belong to the A_1 and E modes so this intensity is expected.

The PC_2 A_1 scissoring motion occurs [2] very near 340 cm^{-1} in all compounds except the hexachlorotrimer where a somewhat lower frequency is seen. This motion is generally of medium intensity in both the infrared and Raman spectra and is removed enough from other motions so that its identification is straightforward.

The remaining PC_2 motions occur in the $280\text{--}230 \text{ cm}^{-1}$ region in all the compounds. They are assigned in the order wag > twist > scissors > rock and are presented in Table I.

The BX_2 motions in the hexasubstituted compounds are very similar to those in simple adducts, H_3PBX_3 [6]. Often the frequencies were within 5 cm^{-1} ; larger deviations ($>50\text{ cm}^{-1}$) were rare. The BF_2 antisymmetric stretches for the hexafluorotrimer were in the region $1060\text{ cm}^{-1} \rightarrow 1108\text{ cm}^{-1}$ compared to 1120 cm^{-1} for the H_3PBF_3 adduct. For the hexachlorotrimer, these stretches occurred between 712 cm^{-1} and 742 cm^{-1} in the Raman spectra compared to 730 cm^{-1} in the corresponding adduct. These vibrations in the hexabromotrimer, appearing at 712 cm^{-1} and 701 cm^{-1} , again very closely correspond to the antisymmetric stretch observed at 699 cm^{-1} in the phosphine-tribromoborane adduct. In the hexaiodotrimer the frequencies occur between 612 cm^{-1} and 692 cm^{-1} , again most favorably comparing with a 660 cm^{-1} line for the H_3PBI_3 adduct. The BC_2 antisymmetric stretches were assigned by comparison with the gem-dimethyltrimer.

The BX_2 symmetric stretches were assigned by comparison with the H_3PBX_3 adducts as above. The results are presented in Table I and require no further comment.

The remaining BX_2 motions (wag, twist, scissors, rock) are similarly assigned. The agreement between frequencies for vibrations in the simple adducts and substituted trimers is remarkably close. For instance, in the H_3PBI_3 adduct the A_1 symmetric deformation occurs at 135 cm^{-1} while the corresponding BI_2 wag in the hexaiodotrimer is at 132 cm^{-1} . The assignment of the BX_2 motions is also given in Table I.

Stretching motions of P—B bonds are generally found between $550\text{--}650\text{ cm}^{-1}$ [6–11]. When dealing with ring molecules, the internal angle bendings couple with ring stretching vibrations so descriptions of the resulting motions become complicated. Ordinarily the in-phase, totally symmetric stretching vibration of a ring molecule is called the ring breathing mode, and these are typically intense in the Raman spectra [12]. This motion appeared at 556 cm^{-1} in the trimer [2], but shifts to higher frequency in the hexasubstituted trimers, most notably with the hexachloro- and hexamethyltrimers (685 cm^{-1} and 703 cm^{-1} , respectively). This is most probably due to coupling with BX_2 motions, especially the scissoring motion. A similar shift of the P—B stretch is noted for the simple adducts [6, 11]. Other stretching vibrations of the ring, referred to as simply ring deformations, are also affected by substitution. The frequencies associated with such motions are presented in Table I.

In order to aid with the assignment of the hexasubstituted trimers, the Raman spectra (Figure 4) and far infrared spectra of the monoiodo-, monobromo-, monocyano-, B,B'-dibromo-, and B,B'-dimethyltrimers were examined. All these compounds were known from nmr studies [1] to be in the 'chair' conformation, with axial-equatorial exchange occurring that could be monitored with temperature variation in the nmr experiment. This study confirms the 'chair' structure of these compounds and their spectra bear a striking resemblance to the spectra of the parent trimer. Most frequencies were only slightly changed, and the addition of the 'new' B—X or BX_2 motions were clear. The frequencies, assignments and approximate descriptions for the vibrations are given in Table II and require no additional comment here.

TABLE II
Observed infrared and Raman frequencies (cm^{-1}) and proposed assignments for some B-mono- and di-substituted p-hexamethylcyclotriborophosphanes.^a

-I	Br ₂ (non-geminal)		-Br		-C—N		(CH ₃) ₂ (geminal)		Assignment
	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	
	2997 sh 2991 m 2978 s	2988 s 2982 s		2998 ms 2988 sh 2982 s 2974 ms		2999 m 2990 sh 2984 vs		2985 s 2982 s 2973 ms	CH ₃ antisymmetric stretch
						2977 m			
	2911 vvs	2918 sh 2914 sh 2912 vvs		2915 vvs 2902 vs		2917 vvs 2912 vvs		2937 w 2925 w, sh 2917 vs 2904 vvs	CH ₃ symmetric stretch
	2428 wm 2405 s	2430 mw, vb 2409 mw		2422 m sh, b 2400 s		2417 wm, sh 2391 s		2404 m, sh 2380 vs	BH ₂ (BH) antisymmetric stretch
	2418 s 2370 s	2417 m 2374 m		2412 s 2360 s		2404 s 2362 s		2394 vs 2362 vs 2353 sh	BH ₂ (BH) symmetric stretch
						2185 vs			C≡N stretch
								1437 1427	B(CH ₃) ₂ antisymmetric deformation
	1420 sh 1410 m	1424 sh 1418 m		1426 sh 1415 sh 1410 m		1427 1417 m 1411 m		1419 ms, b 1414 sh	CH ₃ antisymmetric deformation
	1304 vvw 1296 vw 1289 w 1283 vw	1302 w 1299 w 1290 w 1283 w		1297 vw 1287 w 1282 vw		1309 vw 1299 vw 1291 vw 1287 vw		1307 vvw 1301 vvw 1293 vw 1288 vw 1284 w 1277 vvw	CH ₃ symmetric deformation
	1102 sh 1098 mw	1115 sh 1111 mw		1111 sh 1106 m		1112 sh 1106 m		1109 m 1101	BH ₂ scissors

1006 w	1000 vw	1002 w	1017 w	1112 w 1105 w, sh	CH ₃ rock
993 w	985 w	990 mw	995 w	992 w, sh	BH ₂ wag
980 sh	975 wm	978 w	979 sh	987 wm	
975 w	964 w	967 sh	977 vw	945 vvw, b, sh	
	940 vw, b	964 sh	967 vw	939 vvw, vb	
	936 vw, b	960 w	958 w	928 vvw, vb	
949 w	920 w	917 w	925 vw	894 vw, vb, sh	CH ₃ rocks, BH ₂ twist
900 mw	891 w	894 vw, b	897 vw	888 w	
882 w	978 w	885 w	890 w	877 vw	
867 vw	862 vw	882 sh	880 vw	867 vw	
	853 vw	870 vw, b		859 vw	
844 vw		857 vw, b	857 w	842 w	
801 vvw	814, 823 vw, b	850 w	823, 810 w	822 vvw, b	
		806 vw, vb		806 w, b	BH ₂ rocks
				799 vw, b	
751 m	756 m	753 ms	755 s	779 sh	
744 m	750 m	746 m	747 m	772 wm	PC ₂ antisymmetric stretch
739 m	744 m	735 m	740 m	746 s	
724 s	727 s	726 vs	731 vs	741 ms	
720 sh		721 sh			PC ₂ symmetric stretch
				715 vs	
677, 672 sh		702 vw	684 vw	684 vvw, vb	
668 mw	680 w	682 vw	675 w	675 vw	
		674 mw	639 vw	667 w	
645 mw	664 mw	652 vw	634 vw	649 w, b	
		606 s	648 w	638 w	Ring deformation
		610 vw	638 m	634 w	
		608 m	632 m		
640 m	636 w	599 w	590 w	599 vw, vb	
589 mw	607 mw	598 s	582 w	593 bw, vb	
	584 m	585 w	582 w		
572 m	382 w	574 m	575 m	579 w	
		577 w			
668 m					
652 w					
599 m					
588 s					

The lattice motions were evident in the low frequency region of both the hexasubstituted compounds and the partially substituted derivatives. These are not assigned because of the lack of X-ray data to establish the site symmetry. Furthermore, the BX_2 and ring vibrations in this region of the spectrum would hinder an unambiguous assignment of the lattice modes.

4. Discussion

This study has shown that the 'chair' conformation is assumed by both the mono- and disubstituted trimers (which was known from nmr studies [1]) and also in hexasubstituted compounds (where nmr results were ambiguous). In the nmr work, the distinct axial and equatorial positions that were seen in the ^1H experiments (^{31}P decoupled) confirmed the presence of the 'chair' ring conformation in solution. Variable temperature experiments permitted the observation of interchange of these positions on the nmr time scale, similar to the interchanges observed in partially substituted cyclohexanes [13]. The nmr spectra of the hexasubstituted trimers, however, were not entirely conclusive. The hexahalosubstituted compounds could not be studied below room temperature because of solubility problems; the hexamethyl compound showed the equivalence of the methyl groups down to -95° (lowest temperature feasible). The equivalence could be due to rapid axial-equatorial exchange but could also indicate a conformational change.

Vibrational studies presented herein favor the retention of the 'chair' form with hexasubstitution. If the ring flattened to a planar (D_{3h}) conformation, a maximum of 18 coincidences should occur between the infrared and Raman spectra. In contrast, all symmetry allowed vibrations are active in both the infrared and Raman with a C_{3v} conformation. Based on the number of coincidences, it appears that the 'chair' form is retained with hexasubstitution. Additionally, the number of fundamentals observed in the infrared spectra seem to be greater than the number allowed for a D_{3h} molecular symmetry.

Further evidence is seen in the similarity of the $\text{P}(\text{CH}_3)_2$ vibrations with the corresponding vibrations in the parent trimer. A change in conformation might be expected to significantly alter the position of vibrations associated with these motions. Such does not appear to be the case. In fact, the frequencies for the PC_2 vibrations are quite consistent from one compound to another. It appears that the group frequencies for the $\text{P}(\text{CH}_3)_2$ moiety in these ring systems are established in this work. These could be used qualitatively in future work for identification of these ring systems.

The parallel between these rings and the corresponding monomer adducts, H_3PBX_3 is indeed striking. As outlined in the vibrational assignment section, there is a close analogy between the frequencies of BX_3 motions and the BX_2 motions in the rings. This not only makes the assignment of the B—X motions easier but indicates that these, too, are valuable group frequencies that are associated with phosphorous-boron adducts.

The ring breathing motion, a totally symmetric stretch of the ring atoms, is quite strong in the Raman spectrum and of interest in this study. It shifts considerably in the hexasubstituted compounds as shown in Table I. This is probably due to coupling of this motion with BX_2 motions such as the scissoring. Although a normal coordinate analysis of these rings was not attempted, comparison of the ring breathing motion to the P—B stretch in H_3PBX_3 , where such an analysis had been made [6] is fruitful. The P—B stretch in the adducts is not a 'pure' motion but is strongly coupled with the B—X motions. Therefore, the P—B stretching frequency varies considerably throughout the series H_3PBX_3 , X = H, F, Cl, Br, I. A comparison of the P—B stretch in the adducts and in the totally symmetric ring breathing motion in the hexasubstituted compounds shows the frequencies of these vibrations to be quite similar. It is therefore believed that the variance between the ring motions in the hexasubstituted trimers is due to coupling with the BX_2 motions, rather than any alternative explanation such as conformational change.

Several mono- and disubstituted molecules were studied in this work. Although partial substitution reduces the symmetry to, at best, C_s , the marked similarity of the spectra of these compounds to that of the trimer suggests that the chair conformation is maintained. Additional vibrations are seen, since symmetry restrictions on the vibrations are reduced. These occur, however, very near the vibrations seen in the parent trimer with C_{3v} symmetry. Additionally, the 'new' B—X motions are observed. Examination of the frequencies for the $P(CH_3)_2$ motions show that they are very similar to those in both the trimer and in the hexasubstituted derivatives. This gives support to the establishment of these 'group frequencies' in this basic ring system.

The totally symmetric ring breathing motion is of interest in these compounds. The changes in frequency between compounds of this motion is not nearly as dramatic as with the hexasubstituted derivatives but, as can be seen in Tables I and II, changes do occur in the same direction (compared to the unsubstituted trimer) as the change of frequency in the hexasubstituted-trimers.

5. Conclusions

This work has shown the C_{3v} symmetry of the parent trimer is maintained in the solid state of numerous derivatives. Group frequencies for this ring system can be identified. The P—B ring motions appear to be strongly coupled with the BX_2 motions. Lattice modes are not assigned but group factor effects appear to be minimal.

Acknowledgements

The authors gratefully acknowledge the financial support given this study by the National Science Foundation by Grant MPS-74-12231-AO. They also wish to acknowledge the National Science Foundation for funds to purchase the Digilab

FTS-15B interferometer by grant MPS-75-06926. The donation of the compounds used in this study by M. H. Goodrow is also gratefully acknowledged.

References

1. Sens, M. A., Odom, J. D., and Goodrow, M. H.: *Inorg. Chem.* **15**, 2827 (1976).
2. Odom, J. D., Sens, M. A., Kalasinsky, V. F., and Durig, J. R.: *Spectrochim. Acta* **33A** (1977) in press.
3. Chapman, A. C.: *Trans. Faraday Soc.* **59**, 806 (1963).
4. Goodrow, M. H., Wagner, R. I., and Stewart, R. D.: *Inorg. Chem.* **3**, 1212 (1964).
5. Wagner, R. I. and Burg, A. B.: WADC Technical Report, 57-126, part VI (1962).
6. Kalasinsky, V. F.: Ph.D. Thesis, University of South Carolina, 1975.
7. Durig, J. R., Hudgens, B. A., and Odom, J. D.: *J. Phys. Chem.* **77**, 1972 (1973).
8. Durig, J. R., Hudgens, B. A., and Odom, J. D.: *J. Chem. Phys.* **61**, 4890 (1974).
9. Durig, J. R., Kalasinsky, V. F., Li, Y. S., and Odom, J. D.: *J. Phys. Chem.* **79**, 468 (1975).
10. Odom, J. D., Kalasinsky, V. F., and Durig, J. R.: *J. Mol. Struct.* **24**, 139 (1975).
11. Durig, J. R., Riethmiller, S., Kalasinsky, V. F., and Odom, J. D.: *Inorg. Chem.* **13**, 2729 (1974).
12. Durig, J. R., Willis, J. N., Jr., and Green, W. H.: *J. Chem. Phys.* **54**, 1547 (1971).
13. Anet, F. A. L., and Anet, R.: in L. M. Jackson and F. A. Cotton (eds.), *Dynamic Nuclear Magnetic Resonance Spectroscopy*, p. 543, Academic Press, New York, N. Y. (1975).