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Spectra and Structure of Phosphorus–Boron Compounds. 13.[1]
A Multinuclear Magnetic Resonance Study of Cyclic Boron–Phosphorus Compounds

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A multinuclear investigation of the magnetic resonance parameters of 14 *P*-hexamethylcyclotriboraphosphanes and *P*-octamethylcyclotetraboraphosphane has been carried out. Chemical shifts (^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{31}P) and a variety of coupling constants have been obtained. Results show that NMR (especially ^{11}B NMR) is invaluable for structural assignment. In the unsymmetrically boron-substituted compounds the ring-flipping motion, which equilibrates axial and equatorial sites, can be discerned with variable-temperature studies. In the symmetrical B-substituted compounds, this motion is evidently still rapid and cannot be discerned on the NMR chemical shift time scale.

Introduction

One of the more interesting aspects of boron–phosphorus chemistry is the formation of extremely stable cyclic systems containing alternating boron and phosphorus atoms, with the general formula $(R_2PBX_2)_n$, where $n = 2, 3$, or 4 (R = organic radical; X = H, halogen, organic radical).[3] Commonly, the R groups on phosphorus are the same and most of the compounds reported have been trimeric species ($n = 3$).[3]

The first and the simplest member to date of this series, *P*-hexamethylcyclotriboraphosphane,[4] $[(CH_3)_2PBH_2]_3$ (henceforth referred to as the trimer), was first synthesized by Burg and Wagner[6] in 1953. A single-crystal x-ray study of this molecule[7] reported that it assumed a chair conformation very similar to that of cyclohexane. Solution and vapor-phase infrared and Raman studies[8] have also been reported for this molecule. Numerous boron- and phosphorus-substituted derivatives of the trimer have been prepared and characterized.[3]

Perhaps the most striking characteristic of this group of compounds is their thermal and chemical stability. Despite the presence of B–H bonds, these compounds can be readily stored in air; hydrolysis is slow even in acidic media[6,9] and many are thermally stable[5] to over 240 °C. In view of this unusual stability, the nature of the bonding in these systems has been of interest, especially concerning the presence or absence of $p\pi$–$d\pi$ back-bonding within the boron–phosphorus ring.[6–8]

To date, there have been no detailed NMR studies reported for this class of compounds. However, NMR studies of similar ring systems appeared as part of a synthetic study as this article was in preparation.[10] The utility of the NMR technique in the study of various cyclic compounds is well known. It was our objective in this study to determine whether the NMR parameters of these systems would be of value in conformational studies and whether there was any conformational preference or equilibration between various sites. In addition we sought to ascertain the usefulness of NMR as a characterization tool in various substituted derivatives and to determine which parameters might be sensitive to bonding and substitution of new groups in these molecules. As a part of a larger study on boron–phosphorus systems, we have investigated the nuclear magnetic resonance parameters of a number of *boron-substituted* trimers by ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR. The majority of the compounds are either mono- or hexasubstituted. For simplicity they will be referred to simply as "mono-X trimer" or "hexa-X trimer", e.g., monoiodo trimer for *P*-hexamethyl-*B*-monoiodocyclotriboraphosphane. In addition, we report NMR data for the *B,B'*-dibromo trimer and the parent tetrameric molecule, *P*-octamethylcyclotetraboraphosphane (henceforth referred to as the tetramer), a cyclic molecule with D_{2d} symmetry.[11]

Experimental Section

The compounds used in this study were prepared and purified by previously published[5,6,12–15] methods. Deuterated solvents (Columbia Organics) were stated to be 99.5% D and gave satisfactory ^{1}H and ^{13}C spectra. Nuclear magnetic resonance spectra were obtained on Varian Associates XL-100-15 (^{1}H, 100.1 MHz; ^{11}B, 32.1 MHz; ^{13}C, 25.1 MHz; ^{19}F, 94.1 MHz; ^{31}P, 40.5 MHz), CFT-20 (^{13}C, 20.0 MHz), or A-60 (^{1}H, 60.0 MHz) NMR spectrometers. Standard variable-temperature techniques were employed and all temperatures (accurate to ±0.5 °C) were measured with a copper–constantan thermocouple. With the exception of ^{1}H spectra, all experiments were performed in the FT mode. Boron-11 resolution-enchanced spectra were obtained by employing previously published methods.[16,17]

All ^{1}H chemical shifts are referenced to internal TMS. Boron-11 chemical shifts are referenced to external $BF_3 \cdot O(C_2H_5)_2$ and ^{31}P chemical shifts are referenced to external 85% H_3PO_4. Carbon-13 chemical shifts were referenced to internal C_6D_6 and converted to TMS by using the equation $\delta_{TMS} = 128.1 - \delta_{C_6D_6}$. Spectra were obtained on samples which were approximately 0.5 M in C_6D_6 unless limited by solubility or quantity of compound.

Spectral simulations were achieved using the LAOCN3[18] method. By this method an iterative calculation, based on the least-squares criterion, is used to bring the calculated frequencies of assigned lines as close as possible to the corresponding observed lines. Chemical shifts and coupling constants are then obtained from this best fit.

Results

Boron-11 Spectra. The NMR parameters obtained from ^{11}B spectra are summarized in Table I. With the exception of the hexafluoro trimer all ^{11}B chemical shifts are shielded with respect to $BF_3 \cdot O(C_2H_5)_2$. The ^{1}H-coupled spectrum of the parent trimer consists of a triplet of triplets which closely resembles a quintet ($J_{BH} = 100$ Hz, $J_{BP} = 79.3$ Hz). A resolution-enhanced spectrum confirms this assignment. Noise decoupling at 100 MHz causes this multiplet to collapse to a simple triplet. The appearance of the ^{11}B spectrum of the tetramer is almost identical with that of the trimer, consisting of a triplet of triplets in the ^{1}H-coupled spectrum ($J_{BH} = 98$ Hz, $J_{BP} = 80.1$ Hz) and a triplet in the ^{1}H-decoupled spectrum.

All monosubstituted trimers exhibit two ^{11}B resonances with relative area ratios 2:1. With the exception of the monocyano trimer all resonances representing the unsubstituted boron (BH_2) are shielded with respect to the substituted boron (B(H)X) resonance. In the case of the monocyano trimer, the two boron resonances are nearly coincident (Figure 1) and the ^{1}H-decoupled spectrum appears to be a simple triplet. However the completely coupled spectrum is complex and it is apparent that there are two boron resonances present (Figure 1a). Resolution enchancement allows a complete assignment of the ^{11}B spectrum (Figure 1b) which consists of an overlapping triplet of triplets ($J_{BH} = 102.4$ Hz, $J_{BP} = 79.8$ Hz) and a doublet of triplets ($J_{BH} = 102.4$ Hz, $J_{BP} = 84.9$ Hz). In the monotosylate trimer the substituted boron resonance

Table I. Boron-11 and Phosphorus-31 NMR Data[a]

Compd	$\delta[^{11}$B-(sym)$]^b$	$\delta[^{11}$B-(unsym)$]^b$	$\delta(^{31}P)^c$	J_{BP}(sym)^d	J_{BP}(unsym)^d	J_{BH}(sym)^d	J_{BH}(unsym)^d
Trimer	32.43		48.2	79.3		100	
Hexafluoro	−3.79		71.0				
Hexachloro	0.72		48^e	108			
Hexabromo	14.05		48^e	90^f			
Hexaiodo	44.17		59^e	94			
Hexamethyl	21.79		44.2	65.7^g			
Monobromo	32.43	18.71	48.3^h	78	88	100	100
Monoiodo	32.43	27.04	49.7^h	78	82	100^f	100^f
Monocyano	33.02	33.08	49.7	79.8	84.9	102.4	102.4
Monoisocyanato	32.84	20.45	49.6^h	77	86	96	100
Monomethylthio	31.73	19.64	48.3^h	71.1	83.6	101	102
Monomesylate	31.60	18.98	49.9^h	78.4	86.4	97	97
Monotosylate	32.55	10.73	51.6	75	*i*	98	*i*
Dibromo	33.68	19.66	47.6	75	73	101	96
Tetramer	29.89		51.6	80.1		98	

[a] Positive sign indicates resonances to higher shielding in the chemical shift measurements. [b] ±0.02 ppm. [c] ±0.2 ppm unless stated. [d] In Hz, ±1 in the last figure given. [e] ±2 ppm; see Discussion. [f] Due to the broadness and/or overlap of the lines, this is accurate to ±3 Hz. [g] This resonance did not appear as a pure triplet pattern; the inner line was considerably broader and more intense. Simulations indicate that this arises from either a smaller $^1J_{BP}$ or larger $^2J_{PP}$ than the other molecules studied. The separation is not $^1J_{BP}$ but is within $^1J_{BP}$ ± 5 Hz. [h] Center of broad, single line; see Discussion. [i] Spin–spin coupling wiped out; see Discussion.

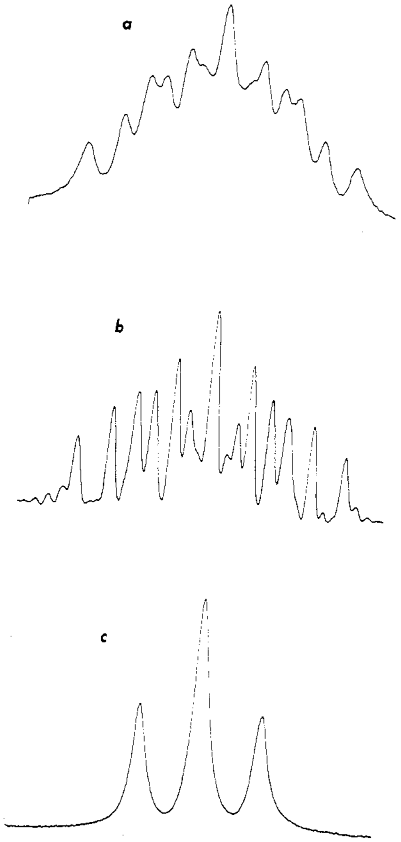


Figure 1. The ^{11}B spectra of the monocyano trimer showing the (a) fully coupled spectrum, (b) line-narrowed spectrum, and (c) ^{1}H-decoupled spectrum; 500 Hz shown.

is a very broad single line in both the completely coupled and the ^{1}H-decoupled spectra making it impossible to extract J_{BH} and/or J_{BP} values from this resonance.

The only disubstituted molecule studied was the *B,B'*-dibromo trimer. The coupled ^{11}B spectrum consists of two resonances: a broad doublet of triplets (B(H)Br) and a more shielded, better resolved triplet of triplets (BH_2). The ^{1}H-decoupled ^{11}B spectrum of this compound also consists of two resonances: a broad triplet and a more shielded, well-resolved triplet with area ratio 2:1, respectively.

The hexachloro, hexabromo, and hexaiodo trimers all exhibit one ^{11}B resonance, a broad triplet. There is no observable change in the appearance of the resonance nor in individual line widths with ^{1}H decoupling. The hexafluoro trimer exhibits a complex, yet symmetrical ^{11}B resonance which could not be analyzed in a first-order manner. The completely coupled and ^{1}H-decoupled spectra of the hexamethyl trimer are almost identical and resemble a triplet although the relative intensities of the individual lines are not those expected for first-order splitting. Elevated temperatures have no effect on this signal.

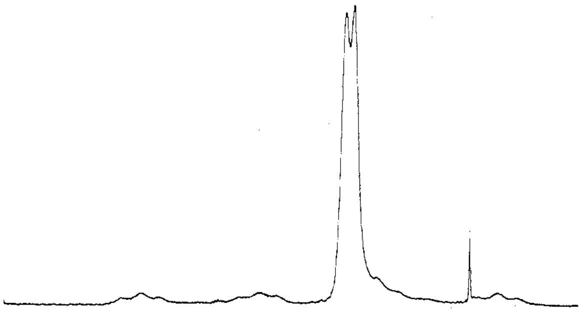


Figure 2. The ^{1}H spectrum of the trimer in toluene-d_8 + TMS; 1 cm = 20 Hz.

Phosphorus-31 Spectra. The ^{31}P chemical shifts are summarized in Table I. In the ^{1}H-decoupled spectra the trimer and the tetramer exhibit one resonance, a broad septet confirming the values of J_{BP} obtained from the ^{11}B spectra. The chemical shifts are in agreement with the values reported previously.[19] With the exception of the monocyano trimer, whose ^{31}P resonance is resolved into a broad septet, all monosubstituted compounds exhibit a broad single line ($W_{1/2} \approx 300$ Hz) in both the ^{1}H-coupled and ^{1}H-decoupled spectra. The hexamethyl and hexafluoro trimers also exhibit a broad, single line. Because of severe solubility problems with the hexachloro, hexabromo, and hexaiodo trimers, their ^{31}P chemical shifts were obtained from resonance frequencies needed to completely decouple ^{31}P in ^{1}H-observe experiments and are only considered accurate to ±2 ppm.

Hydrogen-1 Spectra. The ^{1}H data are summarized in Table II. The spectrum of the trimer consists of an apparent doublet (Figure 2) assigned to the $P(CH_3)_2$ protons and a quartet of triplets, resulting from the BH_2 protons. This pattern is not field dependent, and at low temperature (<−50 °C) the "doublet" resonance collapses to a single line but with no increase in line width. Boron-11 noise irradiation causes the doublet structure to collapse into an AA′A″X pattern[20,21] (sharp outer lines, multitude of inner, lower intensity lines).

Table II. Hydrogen-1 NMR Data[a]

Compd	$\delta(^1H)(P(CH_3)_2)$[b,c]	$\delta(^1H)(P(CH_3)_2)$[c,d]	$\delta(^1H)(BH_2)$[e]	$\delta(^1H)(B(H)X)$[e]	$^2J_{HBP}(BH_2)$	$^2J_{HBP}(B(HX))$[e]	Other
Trimer	0.90		1.22		16		
Hexafluoro	−0.57[e]						
Hexachloro	1.10[e]						
Hexabromo	1.25[e]						
Hexaiodo	1.57[e]						
Hexamethyl	0.56						
Monobromo	0.67, 1.06	0.53, 0.95	1.30	2.74	18	9	
Monoiodo	0.66, 1.02	0.52, 0.94	1.34	2.59	*e*	10	
Monocyano	0.68, 0.89	0.50, 0.89	1.22	1.70	17	20	
Monoisocyanato	0.48, 0.86	0.54, 0.90	1.35	3.72	10	17	
Monomethylthio	0.73, 1.13	0.65, 1.02	~1.4[g]	2.35	*g*	15	$\delta(^1H)(SCH_3)$ 2.08[c]
Monomesylate	1.20, 1.24	0.65, 0.85	*g*	2.42	16	*g*	$\delta(^1H)(SO_2CH_3)$ 2.20[c]
Monotosylate	0.76, 0.88	0.63, 0.81	~1.4[g]	3.50	*g*	*f*	$\delta(^1H)(OTs)$ 1.70, 6.50, 7.88;[c] $J_{HH} = 7$
Dibromo	0.67, 1.08	0.49, 0.92	1.48	2.72	18	10	
Tetramer	0.99		1.57		15		

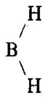
[a] Positive sign indicates resonances toward a more deshielded position in chemical shift measurements; δ in ppm; *J* in Hz. [b] The resonances for the axial and equatorial sites of the $P(CH_3)_2$ groups nearest to the X group are given. No assignment for the axial and equatorial groups is made. [c] Unless noted, these resonances are taken in toluene d_8 at −94.5 °C. [d] The resonances for the axial and equatorial sites of the $P(CH_3)_2$ groups farthest from the X groups are given. No assignment for axial and equatorial sites is made. [e] Taken in benzene-d_6 at +28 °C. [f] Couplings are not observed; see Discussion. [g] Due to partial overlap and/or broadness of lines, these resonances were not clearly seen. Where possible, approximate positions are given.

Irradiation at the ^{31}P frequency causes the resonance to collapse to a single line and lowering the temperature (−94.5 °C) decreased $W_{1/2}$ to ~6 Hz.

The hexahalo-substituted trimers all display a single, broad ^1H resonance assigned to the $P(CH_3)_2$ protons. Boron-11 noise decoupling produces an AA′A″X pattern very similar to the one displayed by the trimer. With ^{31}P noise irradiation all resonances sharpen to a single line. Solubility problems with these compounds precluded work at lower temperatures.

The spectrum of the hexamethyl trimer exhibits two resonances, one resembling the doublet-like pattern of the trimer, another, more shielded resonance is a 1:3:3:1 quartet. The spectrum is field independent. The area ratio between the two resonances is 1:1 and the more shielded resonance is assigned to the $B(CH_3)_2$ protons (the "coupling" seen is not $^2J_{BCH}$ since a 1:3:3:1 rather than a 1:1:1:1 quartet is observed). Boron-11 noise decoupling causes the resonance attributed to the $P(CH_3)_2$ protons to appear as a AA′A″X pattern similar to that of the trimer, while the $B(CH_3)_2$ region displays increased fine structure. In $^1H\{^{31}P\}$ experiments each multiplet collapses to a single line. Lowering the temperature while decoupling phosphorus brought about no additional change except a sharpening of the two lines.

With the mono- and disubstituted trimers, the fully coupled ^1H spectra at 60 and 100 MHz are very complex and unsymmetrical. When the group on boron contains hydrogen atoms (e.g., SCH_3) their proton resonances are easily observed. In some cases broad BH_2 signals appear just above the baseline. Boron-11 decoupling permits the clear observation of the BH_2 and B(H)X resonances (except where accidental overlap occurs with other ^1H resonances). With the exception of the resonance of the B(H)OTs group, which appears as a single, broad line; all $^1H\{^{11}B\}$ resonances are triplets from coupling to phosphorus ($^2J_{HBP}$). No geminal coupling



is observed.

In the $^1H\{^{31}P\}$ experiments on the mono- and disubstituted compounds, the $P(CH_3)_2$ multiplets collapse into two, three, or four resonances. Where four resonance lines are displayed in the $^1H\{^{31}P\}$ spectra, e.g., in the $^1H\{^{31}P\}$ spectrum of the dibromo trimer (Figure 3), the area ratios are correct for separate axial and equatorial positions associated with the two different $P(CH_3)_2$ groups. When less than four resonances occur, area ratios indicate that accidental overlap of these separate sites is occurring. Investigation over a temperature range of +108.5 to −94.5 °C shows a separation of resonances at lower temperatures and coalescence at higher temperatures.

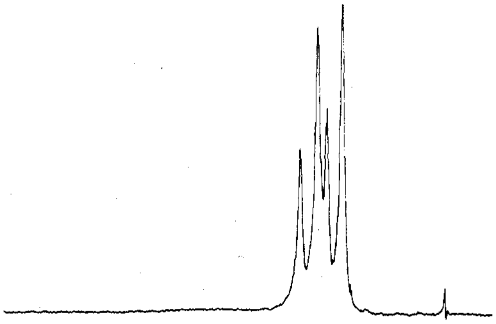


Figure 3. The $^1H\{^{31}P\}$ spectrum of the *B,B′*-dibromo trimer at 29 °C; 1 cm = 20 Hz.

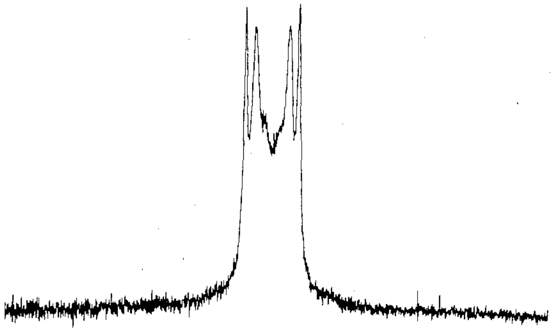


Figure 4. The $^{13}C\{^1H\}$ spectrum of the trimer; the full 500-Hz window is shown.

The spectrum of the tetramer is very similar to that of the trimer in the fully coupled pattern (apparent doublet for the $P(CH_3)_2$ region, quartet of triplets for the BH_2 region), in the ^{11}B-decoupled spectrum (AA′A″X second-order pattern), and in the ^{31}P-decoupled spectrum (single line down to −94.5 °C).

Carbon-13 Spectra. The fully coupled, NOE-enchanced ^{13}C spectrum of the trimer is a 1:3:3:1 quartet (J_{CH} = 124 Hz) of multiplets due to C–P, P–P, and long-range C–H interactions. Proton irradiation collapses the quartet into a single, complex, second-order, symmetrical resonance (Figure 4).

Table III. Carbon-13 NMR Data[a]

Compd	$\delta(^{13}C)$, ppm	$^1J_{CP}$, Hz	$^3J_{CP}$, Hz	Other
Trimer	14.25	31.5	8.6	$^1J_{CH} = 124$ Hz
Hexachloro	55.8	25	9	
Hexamethyl	4.2	14	11	$\delta(B(CH_3)_2)$ 4.0 ppm; $^1J_{CB} = 42$ Hz
Tetramer	14.38	35.4	7.7	$^1J_{CH} = 132$ Hz

[a] Positive sign denotes resonances toward a more deshielded position in the chemical shift measurements.

The hexachloro and hexamethyl trimers as well as the tetramer exhibit $^{13}C\{^1H\}$ spectra very similar to that of the trimer and their NMR parameters are summarized in Table III. The monosubstituted trimers all exhibit complex, unsymmetrical spectra in the methyl region (3–21 ppm deshielded from the TMS resonance) and were examined only with ^1H decoupling. In the parent trimer the $^{13}C\{^{31}P\}$ spectrum consisted of a 1:3:3:1 quartet (from J_{CH}) with no experimentally observable second-order perturbations. Due to lower solubility and/or limited quantities of other compounds, ^{31}P decoupling was not feasible from time considerations.

Fluorine-19 Spectra. The fully coupled ^{19}F NMR spectrum of the hexafluoro trimer consisted of a symmetrical multiplet. The pattern was second-order and was not assigned. The chemical shift was 4.9 ppm deshielded from an external sample of 20% C_6F_6 in C_6D_6. Phosphorus-31 decoupling caused the multiplet to collapse to a 1:1:1:1 quartet (J_{BF} = 96 Hz).

Discussion

If these molecules assume the same conformation in solution as in the solid state, the symmetry allows separate axial and equatorial positions for the species attached to the ring. If interchange of these positions is rapid on the NMR time scale, averaging of the chemical shifts and coupling associated with each position will occur. On the other hand, if a rigid conformation exists separate parameters for each position will result. It is paramount for the study of the NMR parameters of these molecules to have an understanding of whether the potential exchange is averaging the positions or not before an interpretation is attempted.

In addition to the potential exchange between sites, consideration of the magnetically active nuclei in these boron–phosphorus ring systems immediately leads to the realization that they are extremely complex spin systems. Although a wealth of NMR information is potentially available, the spectra must be analyzed with this complexity in mind. With the exception of carbon, all nuclei are magnetically active in nearly 100% natural abundance and all nuclei (except the hydrogens on any given methyl group) are also magnetically nonequivalent. Furthermore, the boron atoms introduce two additional complications: (1) boron occurs as two isotopes ^{10}B (20%, I = 3) and ^{11}B (80%, $I = {}^3/_2$) causing isotope shifts and spin–spin splitting effects resulting from the statistical distribution of these isotopes and (2) both boron isotopes possess nuclear quadrupoles and their relaxation effects can lead to significant line broadening which could, in principle, mask fine spectral details.

Although computer programs to handle the larger number of nuclei, potential exchange between sites, and the quadrupolar nature of the boron atoms with their inherent relaxation terms are not available, judicious use of the simulation technique for select portions of the molecule along with appropriate double-resonance and line-narrowing experiments have enabled us to directly obtain a large amount of information. In addition we have, in many cases, placed reasonable limits on other nonobservable NMR parameters.

In this survey of the NMR parameters all nuclei were examined in an effort to determine the best routes to obtain specific information (synthetic characterization, exchange dynamics, conformational preference, etc). We found ^{11}B NMR is excellently suited for determining the extent and position of substitution within the ring while ^1H NMR provided the most information concerning the ring dynamics. The ^{31}C and ^{31}P spectra do not contain as much readily extractable information and proved to be merely complementary to the spectra of the other nuclei.

The ^{31}P chemical shifts remain fairly constant throughout, a result not surprising for substitution occurring two bonds away. The septets obtained for the trimer and tetramer confirm the J_{PB} values obtained from ^{11}B spectra. The broad single line obtained for the remaining mono- and disubstituted trimers are presumably due to noncoincident but overlapping septets arising from chemically different P atoms. In the hexafluoro trimer, long-range phosphorus–fluorine spin coupling which gives rise to a multitude of lines could satisfactorily explain the broad resonance obtained. The hexamethyl trimer appears to have either a smaller J_{BP} or larger $^2J_{PP}$ so the resulting septet of triplets resembles a broad single line.

The ^{13}C spectra are very complex and information was obtained on few compounds. Computer simulation[22] proved useful in interpreting some symmetrical compounds and the results are given in Table III. In the mono- and disubstituted compounds the complexity and severe overlap of resonances (in addition to potential exchange dynamics and conformational preference at ambient temperatures) prevented assignment. Experiments at higher fields and/or triple-resonance studies (decoupling ^1H and ^{31}P) are needed for these compounds.

Boron-11 NMR chemical shifts can be obtained and assigned without difficulty by a comparison of the fully coupled and ^1H-decoupled spectra. Only in the case of the monocyano trimer are the two ^{11}B resonances overlapping severely, yet with line-narrowing techniques the assignments can readily be made.

When a bulky group such as tosylate or a quadrupolar nucleus is attached to boron, the ^{11}B resonances are considerably broadened and in the case of the B(H)OTs resonance all spin–spin coupling is removed. This is undoubtedly due to a shortening of the spin–lattice relaxation time (T_1) for this substituted boron atom.[24]

The spin–spin coupling of boron and phosphorus is readily measured[25] and is relatively invariant with monosubstitution. Other studies[26,27] have dealt with the magnitude of J_{BP} in the phosphinoborane systems but structural differences between the phosphinoborane systems and these cyclic molecules preclude any extrapolation of experimental results.

Undoubtedly the most useful aspect of ^{11}B NMR is in the unequivocal determination of the position and extent of substitution on the ring. For example, although nongeminal substitution was suspected[13–15] in the dibromo trimer (from steric arguments and infrared measurements), ^{11}B NMR readily confirms that this is the case. The coupled spectrum consists of a doublet of triplets (B(H)Br) and a triplet of triplets (BH_2) with relative intensities 2:1. The multiplet with relative intensity 2 is also deshielded with respect to the other resonance which is in accord with other substituted boron resonances in these systems. Also, the lines are significantly broader in the deshielded multiplet which, as stated previously, is consistent with the substitution of a quadrupolar nucleus on boron.

The ^1H spectra of these compounds are most informative concerning the dynamics of the ring systems. However, the fully coupled spectra are complex and the most useful data are obtained with heteronuclear decoupling and variable-temperature studies. For example, while it is tempting to attribute the "doublet-like" appearance of the resonance in the $P(CH_3)_2$ region in the trimer and tetramer to separate axial and equatorial sites within the molecules, the lack of field strength dependence, the collapse of the resonance to a single line at low temperatures, the appearance of an AA′A″X pattern with ^{11}B noise decoupling, and the appearance of a single resonance with ^{31}P decoupling all demonstrate that this is not the case. Rather, this "doublet" results from complex coupling of several nuclei yielding the deceptively simple yet definitely second-order pattern. The single line that appears in the $^1H\{^{31}P\}$ spectra of the trimer and the tetramer and remains unchanged to −94.5 °C is consistent with rapid exchange of axial and equatorial sites or with the chemical shift equivalence of these two sites at the field strength employed. Based on our work with mono- and disubstituted derivatives (vide infra) the former explanation is the preferred one.

The hexasubstituted trimers all display a single resonance in the $P(CH_3)_2$ region which upon ^{11}B or ^{31}P decoupling yields patterns similar to the parent trimer. Although low-temperature work was precluded in the hexahalo compounds due to the low solubility of these compounds, temperature variation was feasible with the hexamethyl trimer. The $^1H\{^{31}P\}$ spectrum displayed a single line down to −94.5 °C in the $P(CH_3)_2$ region (also in the $B(CH_3)_2$ region) indicating either rapid axial–equatorial exchange of groups or chemical shift equivalence of the methyl groups. Although steric interactions are probably fairly severe in the hexamethyl trimer (and some hexahalo compounds), this could actually lower the energy to interconversion.[28] Work with dodecamethylcyclohexasilane[29] shows the equivalence of methyl groups at −94.0 °C and 1,1,3,3-tetramethylcyclohexane has a lower barrier than cyclohexane.[30] Alternately, these sterically hindered derivatives may undergo a geometry change which renders the methyl groups equivalent. Vibrational studies are under way in our laboratory in order to further clarify the behavior of the hexasubstituted compounds.

The $^1H\{^{31}P\}$ spectra of the mono- and disubstituted compounds strongly suggest that separate axial and equatorial sites exist with respect to the NMR time scale. In most cases in the monosubstituted compounds, the methyl region can be resolved into four resonances (singlets), two lines of relative area 2 assigned to the axial and equatorial methyl protons on the phosphorus atoms adjacent to the substituted boron atom and two lines of relative area 1 assigned to the two methyl groups on the phosphorus atom between the two unsubstituted boron atoms. Variable-temperature experiments show that at high temperatures the two singlets of area 2 coalesce into a single line at the same rate as the two singlets of area 1 coalesce into a single line. At low temperatures the four lines are completely separated from one another. All changes in the spectra are reversible and studies are currently under way to further elucidate this behavior.

The existence of four lines (which are relatively broad, $W_{1/2} \approx 10$ Hz) in the $^1H\{^{31}P\}$ spectra can be attributed either to an overwhelming amount of one conformation being present or to the fact that if two conformations are present, their chemical shifts are so similar that we are not able to resolve the separate lines experimentally. NMR studies of these monosubstituted molecules at higher fields or ^{13}C-enriched $^{13}C\{^1H\}\{^{31}P\}$ experiments would help to resolve this problem.

Conclusions

Although they are very complex spin systems, the boron–phosphorus ring systems which have been studied have been quite amenable to a multinuclear NMR study. Because of the thermal and oxidative stability as well as the extensive chemistry which has yet to be fully explored for the ring systems, NMR techniques will be an invaluable tool for assignments of structure in substituted compounds and for characterization of products of chemical reactions. In addition, ^1H NMR has provided some insight into the conformational dynamics of the systems. Further work is now required to obtain quantitative data and to correlate these data with various substituents on the rings. An investigation of this type is currently under way in our laboratory.

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Registry No. $((CH_3)_2PBH_2)_3$, 46131-73-1; $((CH_3)_2PBF_2)_3$, 2285-71-4; $((CH_3)_2PBCl_2)_3$, 59830-74-9; $((CH_3)_2PBBr_2)_3$, 59831-54-8; $((CH_3)_2PBI_2)_3$, 59831-55-9; $((CH_3)_2PB(CH_3)_2)_3$, 59831-56-0; $[((CH_3)_2PBHBr)((CH_3)_2PBH_2)_2]$, 59830-75-0; $[((CH_3)_2PBHI)((CH_3)_2PBH_2)_2]$, 59830-80-7; $[((CH_3)_2PBH(CN))((CH_3)_2PBH_2)_2]$, 59859-52-8; $[((CH_3)_2PBH(NCS))((CH_3)_2PBH_2)_2]$, 59831-57-1; $[((CH_3)_2PBH(SCH_3))((CH_3)_2PBH_2)_2]$, 59831-58-2; $[((CH_3)_2PBH(SO_3CH_3))((CH_3)_2PBH_2)_2]$, 59859-50-6; $[((CH_3)_2PBH(SO_3Ph))((CH_3)_2PBH_2)_2]$, 59831-59-3; $[((CH_3)_2PBHBr)_2((CH_3)_2PBH_2)]$, 59831-60-6; $((CH_3)_2PBH_2)_4$, 58298-94-5; ^{11}B, 14798-13-1; ^{31}P, 7723-14-0; ^{13}C, 14762-74-4.

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extreme narrowing region ($T_1 = T_2$), the effects are seen in the line width as well. The presence of a quadrupolar nucleus (e.g., Br) bound to boron is known to broaden the ^{11}B resonance lines.

(25) In view of the complexity of the spin systems, calculations were performed to determine if nonzero $^2J_{PP}$ or $^3J_{BP}$ would introduce enough second-order character into the patterns so that J_{PB} could not be straightforwardly measured. Values of $|^2J_{PP}|$ and $|^3J_{BP}|$ were allowed to vary from 10 to 20 Hz and the simulations indicated that as long as a triplet pattern appeared J_{BP} could be measured directly from the spectrum. When $^1J_{BP}$ could not be measured directly, the pattern had deviated enough from a triplet pattern so that at least partial resolution of a nontriplet pattern would be experimentally feasible.

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Synthesis and Characterization of Some Partially B-Halogenated 1,2,3,4,5,6-Hexahydrocyclotriboraphosphanes[2,3]

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Using stoichiometrically controlled halogenation of $[(CH_3)_2PBH_2]_3$ (I) with a variety of reagents, a series of partially B-halogen-substituted derivatives of I was prepared. *N*-Halosuccinimides proved to be the most selective of the halogenating agents studied particularly for preparation of individual lower *B*-halo-substituted I with selectivity increasing with increasing atomic number of the halogen. Two isomers each were isolated for the dibromo-, diiodo-, trichloro-, and tetrachloro-cyclotriboraphosphane derivatives. From infrared and NMR spectra, the di- and trihalogenated compounds were assigned structures with nongeminal halogens and the tetrahalogenated I was assigned a structure having one geminal and two nongeminal halogen-substituted borons. Halogenation apparently is sterically controlled and proceeds in a stepwise manner whereby nongeminal substitution occurs preferentially.

Introduction

Over the last 20 years, a considerable amount of research has been directed toward the synthesis of novel inorganic polymers with the objective of discovering systems having extreme chemical and thermal stability. One such metalloid system attaining limited sucess is the polyboraphosphanes containing a P–B backbone structure. The lower member, cyclic polymers show unusual resistance to thermal decomposition and to oxidative and hydrolytic attack.[5]

Attempts to synthesize high molecular weight polymers having desirable physical and chemical properties produced instead only new four-, six-, or eight-membered cyclic structures[5b,6,7,8] when substituents on the monomer unit R_2PBR_2 were altered. Excess Lewis base as end blocking groups aided synthesis of moderate molecular weight linear polymers[5c,9,10] which depolymerized thermally to the cyclic structures. Clearly another approach to stable high molecular weight polymers was required. Condensation polymerization of the stable cyclic structures appeared to be a promising approach to stable high polymers. To this end it was necessary to develop a method for selective placement of two (or more) reactive substituents on a preformed cyclic unit.

Of the many reactions attempted[5] on cyclotriboraphosphanes, only halogen substitution of the hydrogens on boron has proved consistently successful.[5c–e,11,12] 1,1,3,3,5,5-Hexahydrocyclotriboraphosphanes, $(R_2PBH_2)_3$ (where R = methyl, ethyl, or phenyl), have been halogenated with a variety of reagents, namely, haloalkanes, aluminum halide catalyzed haloalkanes, halogens, mixed halogens, hydrogen halides, or *N*-halosuccinimides using a variety of techniques and reaction conditions. In most cases the completely B-hexahalogenated compounds, $(R_2PBX_2)_3$, were explicitly sought. The halogens in these geminally substituted derivatives of I, however, proved to be inert in attempted substitution reactions. It was anticipated that in cyclotriboraphosphane compounds containing three, or fewer, nongeminal >BHX functions the halogens would be more reactive. Indeed, these partially halogenated compounds subsequently proved to possess readily replaceable halogens.[13]

Initially, partially halogenated trimeric species were found as products of ring halogenation with mole ratios of Br_2:I ≤ 3[12] and subsequently as inadvertant by-products of incomplete halogenation of $[(C_6H_5)_2PBH_2]_3$.[11] In the presence of excess chlorinating agent, the latter was reported to produce in addition to the expected *B*-hexachloro derivative some tetra- and pentachlorinated trimers as well. Slow reaction of $[(C_6H_5)_2PBH_2]_3$ with excess iodine in boiling carbon tetrachloride or 1-iodobutane (conditions comparable to total hexahalogenation when chlorine or bromine were used) gave only the triiodide $(C_6H_5)_6P_3B_3H_3I_3$; further substitution did not occur, even on prolonged heating.[5f] Likewise, we have previously observed[5e] a similar reluctance of $[(CH_3)_2PBH_2]_3$ (I) to undergo complete iodination. Whereas chlorination and bromination of I proceeded rapidly at room temperature to give $[(CH_3)_2PBX_2]_3$, iodination required an extensive time at a higher temperature (50 °C). Furthermore, I was readily hexahalogenated with *N*-chloro- or *N*-bromosuccinimides while only partially B-iodinated species were isolable when *N*-iodosuccinimide was used. In sum, one observes that partially substituted species are favored by an increase in steric requirements of the halogen and/or the substituents on phosphorus.

Results

Our initial attempts to obtain specific partially B-halogenated cyclotriboraphosphanes utilized stoichiometric quantities of bromine and I in dibromomethane.[12] A 1:1 ratio of reactants produced a multicomponent mixture of partially B-brominated species. After tedious fractional crystallizations and sublimations, only a small yield of the *B,B'*-dibromo isomer Xa, mp 129–130 °C, was isolated and characterized. Employing a 3:1 bromine:I ratio in glacial acetic acid, a 75% yield of a mixture of tribrominated isomers of I was obtained.