chloroform, liquid sulfur dioxide, dioxane, dimethyl sulfide, dimethyl sulfoxide, and nitromethane. The titanium compound reacts with HCl gas in dry benzene to form a purple solution from which the expected $(C_5H_5)_2TiCl_2$ could not be isolated.

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Nuclear Magnetic Resonance in Polycyclic Compounds. II. Long-Range H^1–H^1 and H^1–P^{31} Coupling in Some Adamantane and Bicyclo[2.2.2]octane Derivatives[1a,b]

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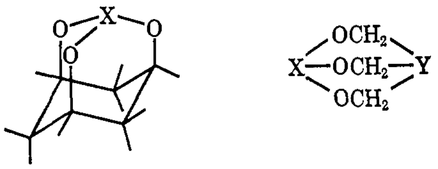
Abstract: The proton nmr spectra of fourteen polycyclic compounds of the types $X(OCH)_3(CH_2)_3$ (where X = HC (I), X = P (II), and X = O=P (III)) and $X(OCH_2)_3Y$ (where X = HC, Y = CCH_3 (IV); X = P, Y = CCH_3 (V); X = O=P, Y = CCH_3 (VI); X = HC, Y = CH (VII); X = P, Y = CH (VIII); X = O=P, Y = CH (IX); X = HC, Y = P (X); X = HC, Y = P=O (XI); X = P, Y = P (XII); and X = O=P, Y = P=O (XIII)) were examined for evidence of long-range spin-spin coupling. Unexpectedly large four-bond POCCH phosphorus-proton couplings were observed for VIII and IX (7.2 and 6.2 cps, respectively) as well as PCOCH phosphorus-proton couplings in X and XI (1.0 and 3.0 cps., respectively). Five-bond HCOCCH proton-proton couplings unprecedented in saturated systems were recorded for I and VII (1.25 and 1.7 cps., respectively). The observed four- and five-bond couplings are discussed in terms of possible through-bond and through-space mechanisms. Syntheses for the new compounds VII, VIII, IX, X, and XI are reported.

The first paper in this series[1a] contained a report of the three-bond POCH coupling constants for various Lewis acid adducts of 2,8,9-trioxa-1-phospha-adamantane (II) and 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (V). Recent reviews of P^{31} nmr spectra[2,3] reported no four-bond phosphorus-proton coupling constants. Values for J_{POCCH} in polycyclic systems reported in this work are up to 15 times larger than values observed in open-chain trialkyl phosphites.[4] Because of the relatively small degree of s character in bonding orbitals of phosphorus, factors other than the Fermi contact interaction may be important in describing phosphorus-hydrogen coupling.[5] In an effort to reveal the effect of molecular geometry on such spin interactions, the proton nmr spectra of the phosphorus compounds II, III, V, VI, and VIII-XIII shown in Figure 1 were studied.

Many four-bond proton-proton coupling constants in saturated systems are known and are the subject of a recent review article.[6] No five-bond proton-proton spin couplings have been reported for saturated systems. In view of a through-space mechanism suggested for four-bonded proton-proton interactions,[7] proton nmr spectra were obtained for I, IV, VII, X, and XI. Although four-bond and six-bond proton-proton couplings were negligible or unobservable in these compounds, appreciable five-bond interactions were observed in I and VII.



	X
I	H-C
II	P
III	O=P

	X	Y
IV	H-C	CCH_3
V	P	CCH_3
VI	O=P	CCH_3
VII	H-C	C-H
VIII	P	C-H
IX	O=P	C-H
X	H-C	P
XI	H-C	P=O
XII	P	P
XIII	O=P	P=O

Figure 1. Structures and formulations of the compounds whose nmr spectra were studied.

Experimental Section[8]

Solvents. All solvents were reagent grade and were dried over Linde 4-A Molecular Sieve. Trimethyl orthoformate was purified by distillation from anhydrous magnesium sulfate and the constant-boiling fraction stored over Linde 4-A Molecular Sieve.

Measurements. Proton nmr spectra were obtained on 5 to 20% by weight solutions on a Varian HR-60 nmr spectrometer operating at 14,100 gauss. The solvent used in all cases was carbon tetrachloride except where indicated. Infrared spectra in the sodium

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(1) (a) For part I see J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, 4, 83 (1965); (b) presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., 1965.

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(6) S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964).

(7) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).

(8) All reactions were carried out under nitrogen flush.

chloride region were obtained on potassium bromide pellets or carbon tetrachloride solutions on a Perkin-Elmer Model 21 spectrometer. Melting points were taken in closed capillary tubes and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., and are listed in Table I.

Table I. Melting Points and Analyses of New Compounds

Compound	Mp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
VII	90–92	51.70	6.89	50.30	6.87
VIII	126–127	35.79	5.23	35.98	5.40
IX	245–247	32.00	4.66	31.82	4.74
X	88–89	35.79	5.23	35.73	5.28
XI	152–155	32.00	4.66	32.94	5.12

2,8,9-Trioxaadamantane (I). The method used for preparing this orthoformate ester was previously described by Stetter.[9]

2,8,9-Trioxa-1-phosphaadamantane (II). This tricyclic phosphite and its 1-oxo derivative (III) were prepared as described previously.[1a,10]

4-Methyl-2,6,7-trioxabicyclo[2.2.2]octane (IV). This orthoformate ester was prepared according to a method originally described by Doering and Levy.[11]

4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (V). The preparation of this bicyclic phosphite and its 1-oxo derivative (VI) have been described elsewhere.[1a,12]

2-Hydroxymethyl-1,3-propanediol. This triol was obtained by modification of a procedure previously reported.[13] To 40 g (1.1 moles) of lithium aluminum hydride in 300 ml of diethyl ether was added dropwise 40 g (170 mmoles) of triethyl methanetricarboxylate in 200 ml of diethyl ether while cooling with ice. The resulting solution was refluxed for 72 hr, after which it was decomposed by dropwise addition of water and partially neutralized by saturating with carbon dioxide. After siphoning off the ether phase, the bulky white precipitate was filtered and the filtrate neutralized with sulfuric acid. The water was then removed by vacuum distillation and the residue dried azeotropically with benzene. Distillation of the dried residue after extraction into absolute ethanol yielded 2.5 g (18% yield) of a low-melting solid (bp 140–144° at 0.3 mm) compared to a yield of 5% reported in the literature.[13]

2,6,7-Trioxabicyclo[2.2.2]octane (VII). A mixture of 1.0 g (9.4 mmoles) of 2-hydroxymethyl-1,3-propanediol, 1.1 g (10 mmoles) of trimethyl orthoformate, and 2 drops of triethylamine was refluxed for 3 hr, followed by removal of methanol at 90° over a 20-hr period at atmospheric pressure. Sublimation of the oily residue at room temperature and 0.01 mm into a liquid nitrogen trap produced 0.06 g (5% yield) of the orthoformate which collected at the top of the trap. This material was resublimed for purification.

2,6,7-Trioxa-1-phosphabicyclo[2.2.2]octane (VIII). A mixture of 0.4 g (4 mmoles) of 2-hydroxymethyl-1,3-propanediol, 0.5 g (4 mmoles) of trimethyl phosphite, and 2 drops of triethylamine was refluxed at 100° for 30 min. After methyl alcohol was removed from the reaction mixture by atmospheric distillation, the residue was solidified by cooling to 0°. Sublimation of this mixture at room temperature and 0.01 mm produced 0.25 g (30% yield) of colorless crystals which were purified by resublimation.

1-Oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (IX). A solution of 0.1 g (0.8 mmoles) of the above phosphite (VIII) in 10 ml of ethanol was oxidized by the dropwise addition of 0.1 g (0.9 mmoles) of 30% hydrogen peroxide. Colorless crystals formed when this solution was cooled, which on sublimation at 100° and 0.01 mm gave 0.07 g (70% yield) of the phosphate.

Trishydroxymethylphosphine. A procedure described previously[14] was followed which involved the use of 9 g (47 mmoles) of tetrakishydroxymethylphosphonium chloride.

3,5,8-Trioxa-1-phosphabicyclo[2.2.2]octane (X). To the triol synthesized in the preceding preparation was added 5.0 g (47 mmoles) of trimethyl orthoformate and 2 drops of triethylamine. The procedure was the same as that used for VII, giving 1.6 g (25% yield) of the orthoformate ester.

1-Oxo-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane (XI). According to a procedure reported by Baltz and Fischer[15] for the oxidation of phosphorus compounds, molecular oxygen was bubbled into a solution of 0.31 g (2.1 mmoles) of the phosphine orthoformate (X) in 50 ml of diethyl ether. The mixture was irradiated in a quartz tube with an ultraviolet lamp (Hanovia lamp No. 658A) at room temperature for 30 min during the bubbling. Evaporation of the ether gave a white solid which sublimed at 50° and 0.01 mm pressure, forming 0.034 g (10% yield) of colorless crystals. If the ether and oxygen were rigorously dried, only a semisolid which resisted characterization was formed from the reaction.

Other Derivatives of Trishydroxymethylphosphine. The preparations of XII and XIII are reported elsewhere.[16]

Discussion

Supporting evidence for the structures assigned to compounds I–XI stems from the volatility of the compounds, their melting points and analyses, and the proton nmr data summarized in Table II. The infrared spectra obtained for these compounds are consonant with the proposed structures. Complete assignments of the bands in these and other polycyclic systems will be included in another paper.[17] Easily assignable significant modes were the P=O stretching frequencies which occurred at 1308 cm^{-1} in the spectrum of III, 1307 cm^{-1} in the spectrum of IX, and 1198 cm^{-1} in that of XI. Similar modes for III, VI, and XIII are discussed elsewhere.[12,16]

The trends in the chemical shifts reported in Table II for the groups of similar compounds—I–III; IV–VI; VII–IX; VII, X, XI; and VII, XII, XIII—generally seem to be dominated by an electron-withdrawing effect of the bridgehead group of the molecule which appears to increase from HC to P to P=O.[18] Hence the downfield trend of the methylene protons on the β position[20] from VII to X to XI is expected as the group Y changes from HC to P to P=O. Although a downfield trend in the shift of the methine proton on the β position is not observed from I to II as it is in III, a distinct trend is observed for the methylene protons on this position in the compound groups IV, V, VI; VII, VIII, IX; and VII, XII, XIII. In the last group, the enhancement of the chemical shift differences can be ascribed to the presence of two similar bridgehead groups in each molecule. In spite of the absence of any trend in the equatorial protons on the γ positions, downfield trends are observed for the axial protons from I to II to III as well as for the methine protons on this position from VII to VIII to IX. The methyl protons in the δ position of IV, V, and VI are not sensitive to the HC and P bridgehead groups. As in the case of the methine β protons in I and II, the inductive effect of the X group does not become dominant until

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(18) Some of the spectra in Table II were obtained using more polar solvents because of solubility considerations. The significant trends discussed in this section involve increments of chemical shift larger than those expected from solvent effects on the proton in question.[19]

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(20) Greek letters used herein designate the position of the atoms with respect to the bridgehead group X in Figure 1.

Table II. Proton Chemical Shifts (ppm *vs.* $Si(CH_3)_4$) and Coupling Constants (cps)[a]

Compound	CH_3	CH_2	HCO-$(CH_2)_2$	HCO_3	$HC(CH_2)_3$	J_{PCH}	J_{POCH}	J_{POCCH}	J_{PCOCH}	J_{HCCH}	J_{HCOCH}	J_{HCOCCH}
$HC(OCH)_3(CH_2)_3$ (I)[b]		2.65[g]								2.7[g]		
		1.65[h]	4.24	5.38						<1[h]	~0.2	1.25
$P(OCH)_3(CH_2)_3$ (II)[b]		2.99[g]										
		1.82[h]	4.20				6.0	~0.5[h]		*b*		
$OP(OCH)_3(CH_2)_3$ (III)[b,c]		2.73[g]										
		1.85[h]	4.97				18.0	2[h]		*b*		
$HC(OCH_2)_3CCH_3$ (IV)	0.79	3.79		5.31							~0.2	
$P(OCH_2)_3CCH_3$ (V)[b]	0.72	3.86					1.8					
$OP(OCH_2)_3CCH_3$ (VI)[b,c]	0.90	4.48					7.0					
$HC(OCH_2)_3CH$ (VII)		4.04		5.25	1.94					2.3	~0.2	1.7
$P(OCH_2)_3CH$ (VIII)[c]		4.12			2.03		1.6	7.2		2.3		
$OP(OCH_2)_3CH$ (IX)[d]		4.72			2.53		6.5	6.2		1.9		
$HC(OCH_2)_3P$ (X)		4.33		5.32		8.53			1.0		~0.2	
$HC(OCH_2)_3PO$ (XI)[c]		4.42		5.54		7.4			3.0		~0.2	
$P(OCH_2)_3P$ (XII)[e]		4.45				9.3	2.7					
$OP(OCH_2)_3PO$ (XIII)[e,f]		5.28				7.8	8.7					

[a] The spectra were obtained on CCl_4 solutions except where indicated to the contrary. [b] See ref 19. [c] In $CDCl_3$. [d] In $(CD_3)_2S{=}O$. [e] See ref 15. [f] In D_2O. [g] Equatorial. [h] Axial.

the third member of the compound group is reached (III and VI, respectively). No ready explanation for this insensitivity to HC and P groups is apparent. The orthoformyl protons in VII, X, and XI are deshielded as the bridgehead group changes from HC to P to P=O in agreement with the trends previously discussed. Although the commonly accepted electronegativity scales contain higher values of electronegativity for carbon than for phosphorus,[21] it might be cautiously inferred from our results that the electronegativity of carbon in the polycyclic orthoformates is less than that of phosphorus in either the polycyclic phosphite or phosphate compounds. Comparing the chemical shifts of the methylene protons in the series IV, V, VI and VII, VIII, IX, the inductive effect of the methyl group is apparent. These shifts are much larger than those observed in methyl substitution of simple acyclic systems.[22]

It was found that J_{PCH} decreases upon oxidation of XII to XIII[16] but in both cases was larger than the value for trishydroxymethylphosphine (2.3 cps). Cyclization of trishydroxymethylphosphine to X results in a similar increase in J_{PCH} and a similar decrease in this coupling upon oxidation of X to XI. Previously it was not possible to assign the coupling constants J_{PCH} and J_{POCH} in XIII.[16] Since the smaller of the two values (7.8 and 8.7 cps) found for XIII is more consistent with the J_{PCH} value found in XI (7.4 cps), the larger value is tentatively assigned to J_{POCH}. The three-bond phosphorus–phosphorus coupling constants found in the P^{31} spectra of XII and its derivatives will be the subject of a future publication.

Four-bond coupling constants of the type POCCH in acyclic systems have been found to be rather small (0.4 cps).[4] In II and III, the coupling constant J_{POCCH} was shown to involve the axial protons[19] and rises from 0.5 to 2 cps upon oxidation of II to III. In striking contrast, J_{POCCH} in the bicyclo[2.2.2]octane compounds VIII and IX is 7.2 and 6.2 cps, respectively, and is seen to decrease upon oxidation of VIII to IX. Increasing the coupling path by one bond by replacement of the apical proton by a methyl group (V) reduces the coupling so far as to be undetectable.[19] The difference in magnitude of J_{POCCH} and the reversal in trend of its value upon oxidation in these pairs of analogous compounds seem to be highly dependent upon the geometry of the coupling nuclei and the bond system connecting them. In compounds VIII and IX, the C–H group is collinear with a threefold axis through the phosphorus. Also the three connecting POCC bond systems have dihedral angles of 0°. In compounds II and III the C–H groups are parallel with a threefold axis through phosphorus, and the two connecting POCC bond systems for each axial hydrogen have dihedral angles of 60°. The rise of J_{POCCH} upon oxidation of II to III is consistent with a through-bond coupling mechanism similar to that involved for three-bond POCH coupling. That is, the rise in s character in the P–O bonds associated with oxidation increases the Fermi contact interaction. It is significant that in compounds X and XI, where the bridging groups are reversed, the four-bond phosphorus–proton coupling drops to values comparable with those for II and III and shows a similar upward change on oxidation of the phosphorus. Such a σ-bond mechanism will not account for the POCCH couplings observed in VIII and IX because of their large values and their decrease on oxidation of the phosphorus. It is possible to speculate that a through-space mechanism may also be operating, involving interaction of the nonbonding lobe on the carbon associated with the hydrogen–carbon bond and that on phosphorus associated with the lone-pair orbital. In VIII and IX, these nonbonding lobes would be directed toward one another along the threefold molecular axis. The decrease in coupling upon oxidation can then be explained in terms of a decrease in s character of the nonbonding lobe of phosphorus resulting in a smaller interaction. The unusually large magnitude of this long-range coupling in VIII and IX can then be ascribed to the shorter path between the phosphorus and the CH group. Conditions disfavoring a through-space mechanism for POCCH (axial proton) coupling in I and II may be the non-

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collinearity of the nonbonding lobes of the C–H axial bond and of the phosphorus lone pair as well as the increased distance from phosphorus to the methylene carbon (2.2 A in VIII and IX *vs.* 2.6 A in II and III as revealed by Dreiding models). The presence of oxygen substitution on the phosphorus atom appears to be necessary for large four-bond phosphorus–proton coupling since coupling can be drastically reduced by transposing oxygen and carbon substituents, without significantly changing the geometry of the system in VIII and X and IX and XI.

The five-bond HCOCCH couplings in I and VII are unexpectedly large for saturated systems. In I the coupling was found by spin decoupling to be specifically between the apical proton and the three axial methylene protons, assigned in previous work.[19] Coupling between the two apical protons in VII was similarly verified. The ratio of the five-bond couplings in I and VII is approximately 2:3, inconsistent with the advent of a new coupling mechanism in VII as was proposed for its phosphorus analogs VIII and IX but consistent with possible equal through-bond contributions *via* two paths in I and three in VII. In both cases the C–H groups involved in coupling are parallel and opposed, but collinear only in VII. The COCC dihedral angle is zero in VII and 60° in I, making it unlikely that this has any great bearing on the mechanism of coupling. A similar opposed and approximately parallel orientation of C–H bonds has been noted in many four-bond couplings in saturated systems[6] and five-bond couplings in some norbornenes having sp^2-hybridized carbon atoms.[23]

Sheppard has observed[24] that five-bond coupling in certain unsaturated systems follows a "straight zigzag" path and suggests a stereospecific σ-bond contribution to coupling. Similar specific coupling has been found in a number of aromatic aldehydes.[25] The coupling systems in I and VII differ from these in that rotation of 180 and 120° about the central bond has taken place. If one mechanism is responsible for all the five-bond couplings cited, it must be independent of the geometry of the central bond. The relative signs of these long-range couplings are being investigated.

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Isotopically Labeled Tetraborane(10) and Pentaborane(11)[1]

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Contribution No. 1326 from the Department of Chemistry, Indiana University, Bloomington, Indiana. Received June 23, 1965

Abstract: Reactions of tetraborane(8) carbonyl provide convenient routes to two new isotopically labeled boron hydrides. Reaction of tetraborane(8) carbonyl and deuterium yields a dideuterium-labeled tetraborane(10), μ,1-dideuteriotetraborane(10). Also, B_4H_8CO (enriched in either the ^{10}B or ^{11}B isotope) and B_2H_6 (enriched in the other isotope) react to form pentaborane(11) labeled in basal (2–5) positions. Mass, infrared, and ^{11}B nuclear magnetic resonance spectral evidence establish the position and degree of labeling of these compounds. The ^{11}B nmr spectra also support the previously suggested structures for B_4H_8CO and $B_4H_8PF_3$.

Relatively few reactions have been found which can be used for the preparation of specifically isotopically labeled tetraborane(10)'s. Evidence for tetraborane labeled with an ^{11}B atom in the 2-position[2,3] and with a single deuterium atom in a bridging (μ) position has been reported.[4] Also, kinetic evidence has been cited for the formation of 1,3-dideuteriotetraborane from exchange reactions between tetraborane and deuterated diborane.[5,6] No example of a specifically labeled pentaborane(11) has yet been reported. Recently, we have found that by substituting deuterium or isotopically enriched diborane for hydrogen or normal diborane in the reaction of the latter two with tetraborane(8) carbonyl,[7] a new specifically labeled dideuteriotetraborane(10) and a basal boron labeled pentaborane(11) can be prepared.

Experimental Section

Spectroscopic Techniques. The ^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates Model 4300B spectrometer operating at 19.3 Mc/sec equipped with standard

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[1] Studies of Boranes. XXI. For paper XX of this series, see J. Dobson and R. Schaeffer, in press.

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