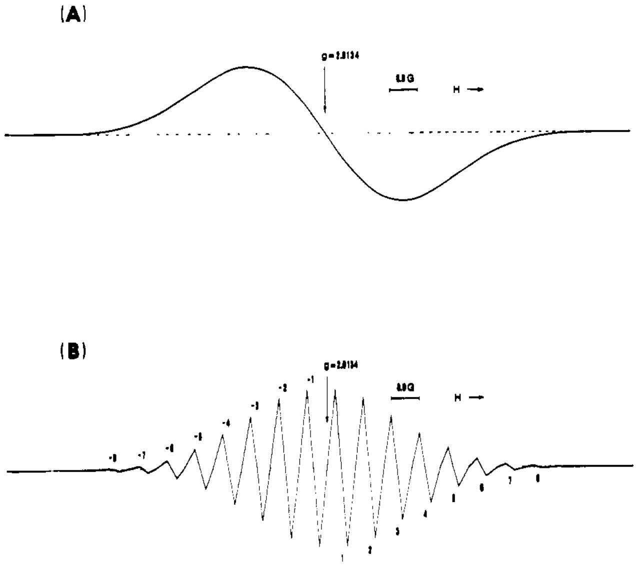

Figure 3. Decomposition of simulated ESR spectrum of S_5^+ into resolved and unresolved portion: (A) Lorentzian shaped background, (B) resolved portion.

S_8^{2+},[10-12] the radical is probably in equilibrium with these diamagnetic species. The reaction which produces S_5^+ would then be more complex than previously expected. The disproportionation of $S_8^{2+} \rightleftarrows S_3^+ + S_5^+$ would also produce an S_3^+ species which is not observed. If the S_3^+ species is somehow rapidly used up, then higher concentrations of S_5^+ should be produced, but no bulk susceptibility was observed.[7] Possibly the S_8^{2+} could react with neutral sulfur: $S_8^{2+} + S_2 \rightleftarrows 2S_5^+$.

Comparison of A_{iso} (8.9 G), with that of the free sulfur nucleus (975 G),[20] suggests that the free electron is in a π orbital. Since the five sulfurs are equivalent, it seems likely that S_5^+ is planar. Simple molecular orbital theory dictates that S_5^+ has an E degenerate ground state and probably an E excited state. Also it should exhibit a Jahn-Teller effect which would lower the D_{5h} symmetry by distortion to a less symmetric planar or nonplanar structure. This distortion may only be small, and the tautomerism between various equivalent forms may be so rapid that the sulfurs appear equivalent in the ESR spectrum.

In addition, the identification of the blue species as S_5^+ is not inconsistent with the MCD.[14] Since the ground state is degenerate, the MCD spectrum should exhibit a derivative line shape. A similar line shape is expected for S_4^+. However, the MCD of S_5^+ should be temperature dependent while that of S_4^+ should be temperature independent.

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An Investigation of the Ring Size of Cyclopolyphosphines[1]

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Abstract: Several alkyl-, aryl-, and perfluoroalkylcyclopolyphosphines have been examined by NMR, ir-Raman, and mass spectroscopy. It is found that three-, four-, and five-membered rings can be distinguished in solution by observing the ^{31}P NMR spectrum while decoupling all other nuclear spins. The decoupled ^{31}P NMR spectrum of a four-membered ring collapses to a sharp singlet, while spectra of the three- and five-membered rings yield second-order AB_2 and AA′BB′C (or ABCDE) spin systems, respectively. The ^{31}P NMR chemical shift is found to be indicative of ring size and linearly dependent upon the average endocyclic P-P-P bond angle. The molecule $(C_2F_5P)_n$ has been shown to exist as a stable three-membered ring. The determining factor in the ring size of alkylcyclopolyphosphines appears to be steric crowding of the pendant organic groups, with four-membered rings being favored when the organic group is bulky. Attempts to prepare mixed cyclopolyphosphines $(RP\text{-}PR')_n$ were unsuccessful. No Lewis basicity was exhibited in solution by either methyl- or ethylcyclopolyphosphine rings towards either trichloroborane or trifluoroborane.

The ring size of cyclopolyphosphines $(RP)_n$ has been determined with certitude only in a very few cases, usually by x-ray crystallography.[2-6] Even when the solid state structure is known, there is some question as to the integrity of the ring in solution.[7] Solution molecular weight determinations, for reasons that are not understood, usually yield anomalously low values. For example, $(C_6H_5P)_5$ and $(C_6H_5P)_6$, for which the solid state structures are known,[5,6] both had isopiestic, cryoscopic, and ebullioscopic molecular weights corresponding to $(C_6H_5P)_4$.[8] As with cyclopolyarsines,[9] the determination of molecular weights of cyclopolyphosphines by mass spectrometry is also of questionable utility. The fragmentation is

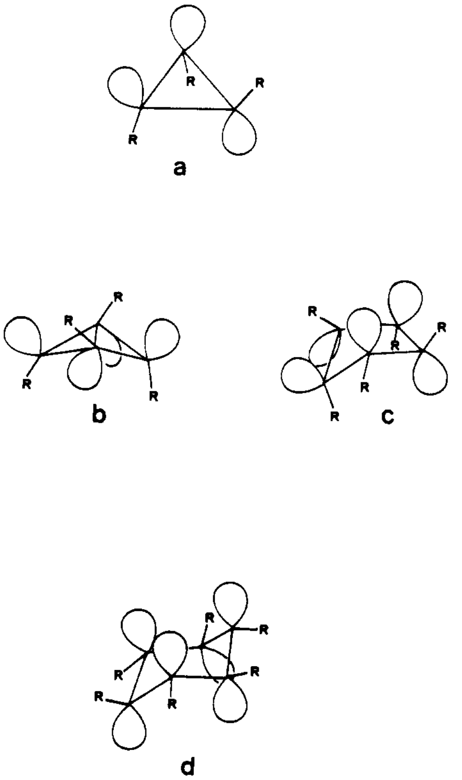

Figure 1. Structure, indicating phosphorus lone pairs, for a, cyclotriphosphines; b, cyclotetraphosphines; c, cyclopentaphosphines; and d, cyclohexaphosphines.

very sensitive to such variables as compound purity, as well as inlet temperature and ionizing voltage of the spectrometer. The parent peak is usually very weak, and often collision species corresponding to n values for $(RP)_n$ greater than the parent species are present.[10] Vibrational spectroscopy has also failed to provide a means of determining ring sizes in cyclopolyphosphines.[11,12] Amster, Henderson, and Colthup concluded from ir-Raman studies that the compounds now known to be $(C_6H_5P)_5$ and $(C_6H_5P)_6$ were both tetrameric in the solid state.[11] The ^{31}P NMR chemical shifts for a number of the cyclopolyphosphines have been reported,[8,13] but, using the accepted values for the ring size, no correlation could be found between the chemical shift and either the organic substituent or the ring size.

In addition to the problems involved with the actual determination of the ring size of cyclopolyphosphines, the factors controlling the size of the ring are obscure.[7a] For example, where the organic moiety is methyl, the ring size has been reported to be five;[8] for ethyl, four;[8] for perfluoromethyl, four and five;[14] for perfluoroethyl, three and four[15] or four and five.[16] From electrochemical[17] and photoelectron studies[18] it has been concluded that phosphorus $p\pi$ → phosphorus $d\pi$ bonding is not involved, irrespective of the ring size.

We herein report a simple NMR method of determining the ring size of cyclopolyphosphines in solution. We find that the ring size of several cyclopolyphosphines has been previously misassigned. A correlation between the ring size and ^{31}P NMR chemical shift is presented, and the factors controlling the ring size for hydrocarbon substituents are discussed. The controversy over the first reported three-membered ring $(C_2F_5P)_3$ has been resolved.[15,16] A preliminary report of some of this material has previously appeared.[19]

Results and Discussion

We have found that three-, four-, and five-membered cyclopolyphosphine rings, which constitute all known cyclopolyphosphines except for hexaphenylcyclohexaphosphine, can be distinguished in solution simply by recording the ^{31}P NMR spectrum of the sample while decoupling all other nuclei in the molecule with spin.[19] The phosphorus atoms in four-membered rings have lone pairs which alternate in a trans manner around the ring (Figure 1b). This is to be expected in order to minimize lone-pair–lone-pair and R-group–R-group interactions, and it is also the case for all known crystal structures.[2-6] Assuming only that the pendant R groups are symmetry equivalent on the NMR time scale, then the four phosphorus atoms all belong to a single set of magnetically equivalent nuclei. (Rapid puckering of the four-membered ring is not requisite for chemical shift equivalence; only D_{2d} symmetry is necessary.) While the undecoupled ^{31}P NMR spectrum will be complex with the phosphorus nuclei constituting an $AA'A''A'''$ spin system, the decoupled ^{31}P NMR spectrum should collapse to a singlet because the magnetically equivalent set of phosphorus atoms are coupled to no other nuclei, i.e., an A_4 spin system. The six-membered hexaphenylcyclohexaphosphine ring,[6] like the four-membered rings, has lone pairs which alternate around the ring in a trans manner (Figure 1d). The proton decoupled ^{31}P NMR spectrum of hexaphenylcyclohexaphosphine should collapse to a sharp singlet, as do those of the four-membered rings. Indeed, this has recently been reported.[7c]

Table I. Decoupled ^{31}P NMR Spectra of Several Cyclopolyphosphines[a]

R	Ring size	Solvent	Chemical shift (ppm)	Multiplicity[d]
C_6H_5	6	THF	+22.0	S
CH_3	5	C_6D_6	−17.3	CM
CH_3	5	Neat	−18.8	CM
C_2H_5	5	Neat	−16.0	CM
n-C_3H_7	5	Neat	−13.1	CM
n-C_3H_7	5	C_6D_6	−11.6	CM
n-C_4H_9	5	Neat	−13.4	CM
C_6H_5	5	THF	+ 4.7	CM
i-C_3H_7	5[b]	$(i\text{-}C_3H_7P)_4$	−13.5	CM
t-C_4H_9	4	C_6D_6	+57.3	S
c-C_6H_{11}	4	C_6D_6	+68.9	S
sec-C_4H_9	4	Neat	+65.5	CM[c]
i-C_3H_7	4	C_6D_6	+61.8	S
i-C_3H_7	4	Neat	+62.2	S
n-C_3F_7	4	C_6D_6	+62.6	S
C_2F_5	4	Neat	+72.9	S
C_2F_5	3	$(C_2F_5P)_4$	+145.1	M J_{AB} = 168 ± 10 Hz

[a] Spectra were recorded at ambient temperature. [b] Decomposition of $(i\text{-}C_3H_7P)_4$, not isolated. [c] Mixture of isomers, see text. [d] Key: S = singlet, CM = complex multiplet, M = multiplet.

The three- and five-membered cyclopolyphosphine rings cannot have symmetric trans alternation of phosphorus lone pairs around the ring (Figure 1a,c). The phosphorus nuclei belong, then, to an ABB' spin system for a three-membered ring, and to an $AA'BB'C$ or $ABCDE$ spin system for a five-membered ring,[20] and decoupling of the pendant R groups will not yield a singlet, but rather a second-order spectrum corresponding to the respective spin systems. The five-membered methyl-[21] and perfluoromethylcyclopolyphosphine[22] rings have recently been analyzed, and the phosphorus atoms were found to constitute $AA'BB'C$ spin systems.

We have examined a number of cyclopolyphosphines $(RP)_n$, including those where R = methyl, ethyl, n-propyl, isopropyl, n-butyl, *tert*-butyl, cyclohexyl, and phenyl (see Table I). For isopropyl, *tert*-butyl, and cyclohexyl, the ^{31}P [^{1}H] NMR spectra appear as sharp singlets (width at half-height from 0.3 to 2.0 Hz), indicating that these exist as tetracyclopolyphosphines $(RP)_4$ in solution.[20] An x-ray crystal structure determination has shown the solid cyclohexylcyclopolyphosphine to be a four-membered ring,[3] with the cyclohexyl groups alternating in a trans manner around the ring; thus, the ring size integrity is maintained in solution. The methyl substituted ring yields a ^{31}P [^1H] NMR spectrum which is an AA′BB′C spin system,[21] and $(C_6H_5P)_5$ yields a complex multiplet which does not exactly fit either an AA′BB′C or an ABCDE system.[7c] Ethylcyclopolyphosphine was originally believed to be tetrameric[8] and more recent investigations concluded possibly that both four- and five-membered rings existed.[15] We find evidence only for the existence of pentaethylcyclopentaphosphine. Upon ^1H decoupling, only a complex ^{31}P NMR multiplet is apparent. If any tetramer exists, it is less than ca. 5%. In addition, we have found that *n*-propyl-[8] and *n*-butylcyclopolyphosphines[8,34] are pentamers and not tetramers as previously reported. Both exhibit only ^{31}P NMR multiplets upon proton decoupling.

The pentafluoroethylcyclopolyphosphines were first reported by Cowley, Furtsch, and Dierdorf[15] as a mixture of a trimer and a tetramer. The assignment of a trimer to the more volatile compound was based on gas-phase molecular weight determinations. Elmes, Redwood, and West[16] reported the pentafluoroethylcyclopolyphosphine system, based on mass spectral data, to be composed of a tetramer and a pentamer. The pentamer was reported to have a boiling point which corresponded to that of the trimer prepared by Cowley, et al.[15] West et al. reported a ^{31}P NMR chemical shift of +144.2 ppm for the pentamer and +71.9 ppm for the tetramer.[16] West noted that after several weeks at room temperature, there was a 100% conversion of pentamer to tetramer.[16] Laurent'ev et al.[24] found the opposite, that is, conversion of the tetramer to the pentamer, when the cyclopolyphosphines were heated to 145–183°. However, the boiling point of Laurent'ev's pentamer corresponds to Cowley's and West's tetramer and the boiling point of Laurent'ev's tetramer corresponds to West's pentamer and Cowley's trimer. Laurent'ev's only characterization of the compounds was by molecular weight determinations. In a sample provided to us by Cowley, which had previously contained both the trimer and tetramer, we found that the $^{31}P[^{19}F]$ NMR spectrum showed only a singlet at +72.9 ppm thus confirming the assignment of a tetramer. The $^{31}P[^{19}F]$ NMR spectrum of a freshly prepared sample of the pentafluoroethylcyclopolyphosphines gave a singlet at +72.9 ppm and a multiplet at +145.1 ppm. The multiplet at +145.1 ppm can be precisely duplicated by a calculated spectrum for an AB_2 spin system, with J_{P-P} = 168 Hz. This indicates that the ^{31}P NMR chemical shift of +144.2 ppm, which West[16] recorded for the pentamer, was actually an AB_2 spin system of a trimer, thus substantiating the claim of Cowley, Furtsch, and Dierdorff[15] to having synthesized the first cyclotriphosphine. The tetramer is apparently the thermodynamically favored ring size, as claimed by West et al.[16]

The perfluoro-*n*-propyl system was also examined; however, only a sharp singlet at +62.6 ppm was observed for the $^{31}P[^{19}F]$ NMR spectrum. This singlet is attributed to the four-membered ring. The resonance that had previously been reported at +141.4 ppm for the five-membered ring was not observed.[16,36] However, due to the fact that the ^{31}P NMR shift at +141.4 ppm is similar to that of the three-membered perfluoroethylcyclopolyphosphine ring, it is probable that this ^{31}P NMR shift is also due to a three-membered ring and not a five-membered ring (vide infra). As pointed out by Hoffman and Caulton,[7c] the recently claimed $(C_6H_5P)_3$[25] is in all probability actually the pentamer.

After correcting the reported ring size of ethyl-, *n*-propyl-, and *n*-butylcyclopolyphosphines and clarifying the ring sizes in the perfluoroethylcyclopolyphosphine, we find the ^{31}P NMR chemical shift of cyclopolyphosphines to be indicative of ring size. Five-membered rings all resonate approximately between −20 and +10 ppm relative to 85% H_3PO_4, four-membered rings between +50 and +75 ppm, and three-membered rings between +140 and +145 ppm. As can be seen in Figure 2, an essentially linear relationship exists between the ^{31}P NMR chemical shift and the average P–P–P bond angle reported for the solid state structures.[2-6] The greater the ring strain, as measured by the endocyclic phosphorus bond angle, the more upfield the chemical shift,[26] in qualitative accord with the extremely high chemical shift of +488 ppm for the strained P_4 tetrahedron. The recently reported value[7c] for the chemical shift of the only known cyclohexaphosphine $(C_6H_5P)_6$ of +22.6 fits the linear relationship extremely well, as does our value of +22.0 ppm. The J_{P-P} for the cyclotriphosphine $(C_2F_5P)_3$ of 168 Hz is relatively small, possibly indicating a direct relationship between ring size and J_{P-P} in cyclic systems.[7c,21,22]

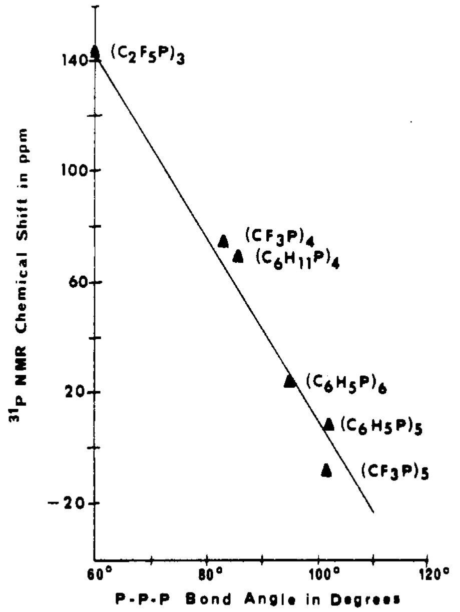

Figure 2. ^{31}P NMR chemical shift dependence of cyclopolyphosphines on average endocyclic P–P–P bond angle. See text for x-ray structure references. Bond angle in $(C_2F_5P)_3$ is assumed to be 60°.

If one uses this relationship between the ring size and chemical shift, then the previously reported ^{31}P NMR chemical shifts may be used to assign or reassign ring size to cyclopolyphosphines which were not included in the present work. The already confirmed solid state structures of $(CF_3P)_4$[2] and $(CF_3P)_5$[4] have chemical shifts of +74.8[36] and −2.2,[27,36] respectively, that fall within the expected ranges. As previously mentioned, the compound reported[16] as $(n\text{-}C_3F_7P)_5$ is in all probability a three-membered ring. From the ^{31}P NMR chemical shifts of $(NCCH_2CH_2P)_4$, −2 ppm,[8] and $(n\text{-}C_8H_{17}P)_4$, −13 ppm,[8] the reassignment of ring size from four to five can be made. The cyclopolyphosphines $[(C_2H_5)_2CHP]_4$, +70,[8] and $(C_6F_5P)_4$, +67,[25] have chemical shifts that fall within the appropriate area for four-membered rings. The chemical shift of +48.3 ppm, which has been reported from the heating of $(C_6H_5P)_5$ above its melting point,[7c,28] may be due to rearrangement of the pentamer to a tetramer. The chemical shift falls very near the region designated for four-membered rings, i.e. +50 to +75 ppm, and the $^{31}P[^1H]$ spectrum was reported to be a sharp singlet.[7c]

Based on the fact that the *sec*-butyl group is an α-branched substituent, the prediction of ring size for $(sec\text{-}C_4H_9P)_n$ is for that of a tetramer. The chemical shift of +65.5 ppm is in total accord with this prediction. The chirality of the P-bonded carbon atom considerably complicates the $^{31}P[^1H]$ NMR spectrum, however. By denoting the chirality of the *sec*-butyl group as *d* or *l* in the cyclotetraphosphine, the following phosphorus spin systems are possible: *dddd* or *llll*, A_4; *dddl* or *llld*, A_2BC; *cis-lldd*, $AA'BB'$; *trans-ldld*, A_2B_2. Statistically, the A_4 spin system should constitute 12.5% of the isomers; A_2BC, 50%; $AA'BB'C$, 25%; and A_2B_2, 12.5%. The simplest spin systems are therefore present in the smallest quantities. Indeed, the $^{31}P[^1H]$ NMR spectrum is extremely complex due to the overlap of the resonances of the four diastereomers. No attempt was made to further analyze the spectrum.

The determining factor in the ring size of the alkylcyclopolyphosphine appears to be steric crowding of the pendant organic groups, with four-membered rings being favored when the organic group is bulky, e.g., cyclohexyl, *tert*-butyl, or isopropyl. The five-membered rings all contain substituents with unbranched carbon atoms bonded directly to the phosphorus. The isopropyl group is a borderline case in size, as a sample of tetraisopropylcyclotetraphosphine was found to contain approximately 30% pentaisopropylcyclopentaphosphine (complex second-order spectrum centered at −13.5 ppm) after being stored in an NMR tube for over a year. No other samples of alkylcyclopolyphosphines were found to contain mixtures of different ring sizes even after a year's time. In the aryl- and perfluoroalkylcyclopolyphosphine rings, steric crowding is not the dominant factor as it is with the alkylcyclopolyphosphines. The phenylcyclopolyphosphines exist as five- and six-membered rings (at ambient temperature), while the perfluoroalkylcyclopolyphosphines can be either mixtures of three- and four- or four- and five-membered rings. The high group electronegativities[29] of both the phenyl and the perfluoroalkyl groups relative to alkyl groups are undoubtedly important. The steric factors that govern the ring sizes in the cyclopolyphosphines also appear to govern the ring sizes in cyclopolyarsines.[30] All known cyclopolyphosphines and cyclopolyarsines with the same substituent consist of the same ring size, with the single exception being the lack of evidence for the existence of a five-membered phenyl-substituted arsenic ring.

The attempts to prepare mixed cyclopolyphosphine rings $(R'P\text{-}RP)_n$, by the reaction of an alkylphosphine with an alkyldichlorophosphine gave only unmixed rings, $(RP)_n$, and $(R'P)_n$. The formation of these unmixed rings would have to involve several bond rearrangements. In each of these reactions immediate release of HCl was observed; however, no product formation was noted for several minutes. The unmixed rings were also obtained in the absence of solvents. The attempts to prepare mixed rings by the reduction of two different alkyldichlorophosphines with an active metal were also unsuccessful. These reductions gave the metal chloride, a black tar, and white phosphorus. In all probability, mixed rings are initially formed in some reactions, but during attempted purification procedures (which involve heating), rearrangements occur yielding only what are apparently the more thermodynamically stable unmixed rings.

In order to try to reproduce the reported adduct formation noted in the reaction of several cyclopolyphosphines with boron trihalides in benzene,[23] tensimetric titrations of pentamethylcyclopentaphosphine and pentaethylcyclopentaphosphine were carried out with boron trifluoride and boron trichloride. No association was noted for either cyclopolyphosphine. This leads us to believe that the adduct formation in benzene was probably due to bond breaking in the cyclopolyphosphines, as is noted for some of the cyclopolyphosphine–metal carbonyl adducts.[9] We found that this is the case for pentamethylcyclopentaarsine. Tensimetric titrations of pentamethylcyclopentaarsine with boron trifluoride and trichloride gave, in both cases, a black polymer.

Experimental Section

All manipulations of air-sensitive compounds were carried out under a nitrogen atmosphere or were performed on a high-vacuum system using standard techniques.[31] The high-vacuum system was equipped with ground glass stopcocks greased with Apiezon M. Working vacuums were maintained between 10^{-3} and 10^{-6} Torr. Tensimetric titrations were performed with a tensimeter[32] constructed of Pyrex glass, using greaseless Teflon stopcocks and couplings. Pressures inside the tensimeter were monitored via a capillary tube mercury manometer in conjunction with a cathetometer.

Instrumental. Raman spectra were recorded on a Jarrell-Ash Model 25-500 laser Raman, and ir spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. The mass spectra were obtained using a Varian MAT-311 mass spectrometer operating at 70 eV. ^{31}P and ^{13}C NMR spectra were recorded on a Varian Associates NMR spectrometer Model XL-100-15. All ^{31}P NMR shifts are reported relative to external 85% H_3PO_4 with upfield shifts (shielded) assigned a positive value. Proton NMR were recorded either on a Varian Associates A-60 or XL-100-15.

Preparations. (a) Pentamethylcyclopentaphosphine, $(CH_3P)_5$, was prepared by the general method of Henderson, Epstein, and Seichter.[8] At −40°, 19.5 g (167 mmol) of dichloromethylphosphine in 25 ml of tetrahydrofuran (THF) was added dropwise with vigorous magnetic stirring to 2.50 g (375 mmol) of Li wire in 100 ml of THF. The mixture was allowed to gradually warm to room temperature and stirred for 48 h. Distillation gave 5.2 g (67% yield) of pentamethylcyclopentaphosphine, bp 135–136° (3 Torr). Pentamethylcyclopentaphosphine was identified by its ^{31}P NMR,[7] ir,[33] and Raman[33] spectra. The ^1H NMR spectrum in C_6D_6 gave a broad complex set of peaks at δ 1.50 (ppm) relative to Me_4Si. The $^{13}C[^1H]$ NMR spectrum in $CDCl_3$ gave three broad peaks in a ratio of 1:2:2 at 11.9, 9.52, and 5.55 ppm, respectively, downfield from Me_4Si.

(b) Pentaethylcyclopentaphosphine, $(C_2H_5P)_5$, (c) penta-*n*-propylcyclopentaphosphine, $(n\text{-}C_3H_7P)_5$, (d) penta-*n*-butylcyclopentaphosphine, $(n\text{-}C_4H_9P)_5$, and (e) tetraisopropylcyclotetraphosphine, $(i\text{-}C_3H_7P)_4$, were prepared by the method of Rauhut and Semsel.[34] The reactions are typified by the following sequence. White phosphorus, 31 g (1.0 mol), was cut under water into 0.3-g pieces and washed with acetone and then benzene. The phosphorus was then added to 0.55 mol of freshly prepared alkylmagnesium bromide and 0.55 mol of alkyl bromide in 300 ml of THF under nitrogen. The reaction was stirred at reflux temperature for 1 h, cooled to room temperature, and diluted by the dropwise addition of 200 ml of water. The mixture was then filtered, and the phases were separated. The organic layer was dried over anhydrous magnesium sulfate and distilled at reduced pressure. The yields of cyclopolyphosphines varied from 5 to 20%. In each reaction there was a considerable amount of higher polymers formed. The cyclopolyphosphines were identified by their ^{31}P NMR spectra.[8] Pentaethylcyclopentaphosphine was also identified by its Raman and ir spectra.[33] The boiling points of the cyclopolyphosphines were in close agreement with the literature values:[8] pentaethylcyclopentaphosphine, 125° (0.05 Torr); penta-*n*-propylcyclopentaphosphine, 142° (0.03 Torr); penta-*n*-butylcyclopentaphosphine, 170° (0.05 Torr); and tetraisopropylcyclotetraphosphine, 95° (0.05 Torr).

(f) Tetracyclohexylcyclotetraphosphine, $(c\text{-}C_6H_{11}P)_4$, was prepared by adding 4.1 g (22 mmol) of cyclohexyldichlorophosphine all at once to 0.55 g (22 mmol) of Mg in 50 ml of THF. The mixture was refluxed and stirred for 2 h. The solution was then filtered, and the precipitate was extracted with 70 ml of THF. The filtrate and washings were combined, and the volume was reduced to 10 ml. Filtration yielded the crystalline tetracyclohexylcyclotetraphosphine which, dried in vacuo, gave a melting point of 214–216° (reported 218–220°).[8] Tetracyclohexylcyclotetraphosphine was also prepared by the method of Rauhut and Semsel.[34] However, since large quantities of higher polymers were also formed, it proved impossible to purify the solid tetracyclohexylcyclotetraphosphine. ^{31}P NMR was used to identify the product.[8] The mass spectrum of tetracyclohexylcyclotetraphosphine gave a characteristic pattern with the most abundant peaks attributed to $(C_6H_{11}P)_4^+$, *m/e* 456; $(C_6H_{11})_3P_4^+$, 373; $(C_6H_{11})_2P_4^+$, 290; $C_6H_{11}P_4^+$, 207; P_4^+, 124; and $C_6H_{11}^+$, 83. The previously unreported Raman spectrum gave the following peaks (cm^{-1}): 152 (vw), 166 (s), 185 (vw), 252 (w), 300 (vw), 322 (vw), 434 (vs), 479 (s), 494 (s), 520 (vw), 794 (vw), 823 (m), 856 (vw), 886 (vw), 1002 (w), 1027 (vs), 1081 (vw), 1104 (vw), 1184 (m), 1266 (w), 1298 (w), 1335 (vw), 1346 (vw), 1442 (w), 2843 (w), 2851 (w), 2882 (w), 2917 (w), 2935 (w), and 2945 (m). The ir spectrum (Nujol mull, KBr plates) gave the following peaks (cm^{-1}): 421 (vw), 487 (vw), 511 (w), 549 (vw), 730 (vw), 811 (vw), 844 (vs), 876 (s), 879 (s), 909 (vw), 993 (s), 1018 (w), 1091 (vw), 1163 (s), 1177 (m), 1179 (w), 1251 (s), 1260 (m), 1287 (m), 1335 (w), and 1330 (w).

(g) **Tetra-*tert*-butylcyclotetraphosphine, (t-$C_4H_9P)_4$,** was prepared in an analogous manner to (c-$C_6H_{11}P)_4$, using dropwise addition of 10.0 g (63.0 mmol) of dichloro-*tert*-butyldichlorophosphine in 40 ml of THF to 1.53 g (63.0 mmol) of Mg in 30 ml of THF. The mixture was stirred and refluxed for 8 h and then filtered to remove $MgCl_2$ and unreacted Mg. The solvent was removed and the resultant solid was sublimed in vacuo to give white crystals, mp 161–162° (reported 167–169°).[13] Tetra-*tert*-butylcyclotetraphosphine was identified by its ^{31}P NMR spectrum.[13] The ^1H NMR spectrum in C_6D_6 consisted of a broad complex set of peaks centered at δ 1.06 relative to Me_4Si. The mass spectrum of tetra-*tert*-butylcyclotetraphosphine with the most abundant peaks attributed to (t-$C_4H_9P)_4{}^+$, m/e 352; (t-$C_4H_9)_3P_4{}^+$, 295; (t-$C_4H_9)_2P_4{}^+$, 238; t-$C_4H_9P_4$, 181; $P_4{}^+$, 124; and t-$C_4H_9{}^+$, 57. The Raman spectrum gave the following peaks (cm^{-1}): 171 (vs), 208 (vs), 290 (vw), 311 (vw), 399 (vw), 421 (w), 492 (m), 497 (w), 587 (s), 814 (m), 943 (w), 1018 (vw), 1178 (w), 1206 (vw), 1328 (vw), 1395 (vw), 1446 (vw), 1463 (vw), 2860 (vw), 2894 (vw), 2920 (vw), and 2961 (vw). The ir spectrum (Nujol mull, KBr plates) gave the following peaks (cm^{-1}): 433 (vw), 499 (vw), 528 (vw), 578 (w), 610 (w), 721 (w), 802 (vs), 880 (vw), 900 (vw), 935 (m), 968 (m), 1010 (m), 1150 (s) broad, and 1310 (vw).

(h) **Tetra-*sec*-butylcyclotetraphosphine, (*sec*-$C_4H_9P)_4$,** was prepared by the addition of 2.4 g (15 mmol) of dichloro-*sec*-butylphosphine in 5 ml of THF to 0.36 g (15 mmol) of Mg in 15 ml of THF. The mixture was refluxed and stirred for 2 h and then filtered to remove $MgCl_2$ and unreacted Mg. The resultant solution was distilled to give tetra-*sec*-butylcyclotetraphosphine (150° (0.05 Torr)). The $^{31}P[^1H]$ NMR spectrum gave a complex set of peaks centered at +65.5 ppm. Anal. Calcd for $(C_4H_9P)_4$: C, 54.54; H, 10.30; P, 35.16. Found: C, 55.14; H, 10.20; P, 35.17.

(i) **Pentaphenylcyclopentaphosphine, $(C_6H_5P)_5$, and (j) hexaphenylcyclohexaphosphine, $(C_6H_5P)_6$,** were prepared according to literature methods.[8] The pentaphenylcyclopentaphosphine, when crystallized from THF melted at 149–150° (reported 148–152°).[8] Raman,[11] ir,[8] ^1H NMR,[8] and ^{31}P NMR spectroscopy[8] were used to identify pentaphenylcyclopentaphosphine. Hexaphenylcyclohexaphosphine remaining from previous work[7b] was used.

(k) **Tetrakis(pentafluoroethyl)cyclotetraphosphine), $(C_2F_5P)_4$, and (l) tris(pentafluoroethyl)cyclotrisphosphine, $(C_2F_5P)_3$,** were prepared by shaking an excess of mercury with $C_2F_5PI_2$[35] overnight in a sealed ampule.[15] The cyclopolyphosphines were pumped from the ampule into a high vacuum system, purified, and transferred to an NMR tube. Tetrakis(pentafluoroethyl)cyclotetraphosphine and tris(pentafluoroethyl)cyclotriphosphine were identified by their ^{31}P NMR spectra[36] and vapor pressures.[15]

(m) **Tetrakis(heptafluoro-*n*-propyl)cyclotetraphosphine, (n-$C_3F_7P)_4$,** was prepared similarly by shaking an excess of mercury with n-$C_3F_7I_2$[35] in a closed ampule overnight.[16] Tetrakis(heptafluoropropyl)cyclotetraphosphine was identified by its ^{31}P NMR spectrum.[36] No tris(heptafluoro-*n*-propyl)cyclotrisphosphine was detected in the reaction ampule.

(n) **Cyclohexyldichlorophosphine, c-$C_6H_{11}PCl_2$, (o) dichloro-*sec*-butylphosphine, *sec*-$C_4H_9PCl_2$, and (p) dichloroisopropylphosphine, i-$C_3H_7PCl_2$,** were prepared by the Grignard reaction of the appropriate alkylmagnesium bromide with bis(dimethylamino)chlorophosphine.[37] The resultant phosphine, $[N(CH_3)_2]_2PR$, was chlorinated with HCl to give the appropriate alkyldichlorophosphine.[38]

(q) **Pentamethylcyclopentaarsine, $(CH_3As)_5$,** was prepared by the method described by Palmer and Scott,[39] and was identified by its ^1H NMR spectrum.[40]

The following compounds which were reaction intermediates were prepared and purified according to literature procedures: phenylphosphine, $(C_6H_5)PH_2$,[41] dichlorodimethylaminophosphine, $(CH_3)_2NPCl_2$,[38] and bis(dimethylaminochlorophosphine, $[(CH_3)_2N]_2PCl$.[38] The following compounds were obtained from commercial sources and used without further purification: dichloro-*tert*-butylphosphine, t-$C_4H_9PCl_2$ (Strem Chemical); cyclohexylphosphine, c-$C_6H_{11}PH_2$ (Strem Chemicals); heptafluoro-*n*-propyl iodide, n-C_3F_7I (PCR, Incorporated); pentafluoroethyl iodide, C_2F_5I (Chemical Procurement Laboratories); dichlorophenylphosphine, $C_6H_5PCl_2$ (Aldrich); dichloromethylphosphine, CH_3PCl_2 (Ethyl Corporation and U.S. Army); and sodium methylarsonate, $CH_3AsO(ONa)_2 \cdot 6H_2O$ (Alfa Inorganics).

Mixed Cyclopolyphosphine Rings. Attempted Preparations. (a) Dichloromethylphosphine (167 mmol) and dichlorophenylphosphine (169 mmol) in 50 ml of THF were added with vigorous magnetic stirring to 4.17 g (600 mmol) of Li wire in 75 ml of THF. The reaction was kept at −40° while the addition took place and then allowed to warm to room temperature. The only products recovered were LiCl, white phosphorus, and a black tar.

(b) Phenylphosphine (45 mmol) in 30 ml of THF was added to dichloromethylphosphine (45 mmol) in 40 ml of THF at −40°. The mixture was warmed to room temperature and the THF was removed. ^{31}P NMR indicated that only pentamethylcyclopentaphosphine and pentaphenylcyclopentaphosphine were present.

(c) Dichloromethylphosphine (7.5 mmol) was added to cyclohexylphosphine (7.5 mmol) in 5 ml of diethyl ether. ^{31}P NMR indicated only pentamethylcyclopentaphosphine and tetracyclohexylcyclotetraphosphine. The solid tetracyclohexylcyclotetraphosphine was removed from the mixture and further identified by its mass spectrum.

(d) Cyclohexyldichlorophosphine (8.6 mmol) and dichloro-*tert*-butylphosphine (8.6 mmol) were added to Mg turnings (17.3 mmol) in 10 ml of THF. The only products recovered were $MgCl_2$, white phosphorus, and a black tar.

Tensimetric Titrations. (a) Pentamethylcyclopentaphosphine (0.1 mmol) and 0.8 ml of *n*-nonane were placed in a tensimeter. Boron trichloride was condensed into the tensimeter in 0.1 mmol amounts and allowed to warm to 0°. No adduct formation was noted. The titrations were repeated with boron trifluoride, and again no adduct formation was noted.

(b) The titrations were repeated using pentaethylcyclopentaphosphine with BCl_3 and BF_3. No adduct formation was noted.

(c) Pentamethylcyclopentaarsine (0.1 mmol) and 0.8 ml of *n*-nonane were placed in a tensimeter. Boron trichloride was condensed into the tensimeter, as with the cyclopolyphosphines, and allowed to warm to 0°. A purple-black polymer was formed in the tensimeter well below 0°. The titration was repeated with boron trifluoride. A yellow 1:1 adduct was formed at temperatures below 0°; however, at temperatures above 0° the adduct decomposed to a purple-black polymer.

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(1) The work reported herein fulfilled in part the requirements for the degree of Doctor of Philosophy for L. R. Smith, Aug 1975.

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^{15}N Nuclear Magnetic Resonance of Organophosphorus Compounds. Experimental Determination and SCF–MO Finite Perturbation Calculation of ^{15}N–^{31}P Nuclear Spin Coupling Constants in $(Me_2N)_3P$, $(Me_2N)_3PS$, and $(Me_2N)_3PO$

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Abstract: Natural abundance ^{15}N NMR at 10.1 MHz has been used to determine the ^{15}N–^{31}P nuclear spin coupling constants in $(Me_2N)_3P$, $(Me_2N)_3PS$, and $(Me_2N)_3PO$ as +59.1, $\mp$6.0 and −26.9 Hz, respectively. Two-bond ^{13}C–^{31}P couplings were also determined from the 25.16 MHz ^{13}C spectra as +19.15, +3.3 and +3.4 Hz. The one-bond ^{31}P–^{17}O coupling was obtained from the natural abundance ^{17}O spectrum and has a value of 145 Hz. SCF-MO finite perturbation calculations in the CNDO/2 approximation were carried out on a series of model compounds giving good agreement with experiment for ^{15}N–^{31}P couplings and the ^{31}P–^{17}O coupling using only the Fermi contact mechanism. There is a linear dependence of the calculated ^{15}N–^{31}P coupling with the bond order between the coupled atoms.

Organophosphorus compounds have long been subjects of nuclear magnetic resonance investigations. In particular, structure and bonding have been primary areas of concern. In recent years ^{13}C NMR has added yet another NMR technique toward elucidation of the above, contributing two new sensitive parameters, the ^{13}C chemical shift and the ^{13}C–^{31}P nuclear spin coupling constant. We have carried out extended programs using ^{13}C NMR in this area and now report on studies employing the ^{15}N nuclear resonance in organophosphorus compounds containing nitrogen. From the chemical point of view, phosphorus–nitrogen compounds are rich in synthetic and structural information.[2] Spectroscopically, the group 5 and 6 elements have nuclear spin couplings which exhibit dramatic sign changes and wide ranges of magnitudes. Since it has long been the hope and expectation that molecular properties such as spin couplings could provide sensitive insights into chemical bonding and molecular electronic structure, it is imperative that their behavior, mechanisms, and mechanistic contributions be known and usable. The Fermi contact mechanism for spin coupling has repeatedly been shown to be dominant for homonuclear and heteronuclear coupling involving ^{1}H and ^{13}C, leading to, at times, unfortunate over-extension through literal "s-character" calculations based on models derived for couplings in assumed "model" systems. This is more a reflection of sought-for simplicity than actual rigor since now quite powerful theoretical methods have become available which have been successful in predicting couplings, particularly one-bond couplings involving ^{13}C. Small magnitudes and uncertain signs of ^{13}C–^{15}N couplings have retarded progress in their use, although their accurate prediction should reflect well on any theoretical wave functions and spin coupling theory. Still within group 5, phosphorus produces, in many cases, much larger couplings to nitrogen, a fact which should make theoretical methods much easier to employ in a first effort at reproducing magnitudes and signs.

The use of pulsed Fourier transform NMR has now made ^{13}C NMR widespread. The same techniques have also been applied to natural abundance ^{15}N NMR. In order to attain an overview of what to expect in this class of compounds we have chosen to determine experimentally the ^{15}N–^{31}P couplings and their signs, where possible, in several bonding situations and phosphorus oxidation states. As a guide to the interpretation of the observed couplings and as a further test of theoretical models we then attempt to reproduce them theoretically.

In the early stages of this work there existed only one reported value of a ^{31}P–^{15}N coupling.[3] Subsequently, a few other values in highly fluorinated,[4] dialkylamino,[5] and organometallic[6] phosphorus compounds have been documented. Our studies have restricted substituent changes to those occurring at the phosphorus within the highly symmetric tris(dimethylamino) substituent framework. The large range of substituent effects generated by the several phosphorus oxidation states are then examined through changes in the observed ^{15}N–^{31}P couplings. Subsequently, finite perturbation SCF