be similar. Part of the reason for the change in trends may be that the polyether undergoes a second conformational change. There is no kinetic evidence for this, but a third conformer for the metal bound ligand has been reported from x-ray studies.[21] In the case of the polarizable cations Ag^+ and Tl^+ there is the distinct possibility that the removal of primary solvated water other than the first molecule is ligand assisted perhaps through a covalently bonded interaction on first substitution. This effect is analogous to the directional trans effect in substitutions of square-planar complexes.

The kinetic evidence appears to suggest a mechanism more complex than the elementary two-step mechanism used in data interpretation. Presently we cannot distinguish our preference for any one of the proposed modifications. Indeed all might contribute to different degrees. Further insight may be gained from temperature dependent studies and investigations using other crown polyethers. Both studies are in progress.

It is apparent from the variations in k_{23} that the overall stability constants K_T are not solely determined by the changes in the rates of decomplexation. The specificity that the ligand has for a particular metal is for the most part determined by the decomplexation rate, yet release of the ligand on demand is still a very rapid process, and is of great significance to mass transport processes. 18-Crown-6 appears to be a rather flexible molecule capable of rapid conformational changes in both its complexed and uncomplexed state, which makes it suitable as a building block for a catalyst.

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Supplementary Material Available: listing of the α/f^2 data for the various cations complexed by 18-crown-6 (14 pages). Ordering information is given on any current masthead page.

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^{15}N and ^{17}O Nuclear Magnetic Resonance of Organophosphorus Compounds. Experimental and Theoretical Determinations of ^{15}N–^{31}P and ^{17}O–^{31}P Nuclear Spin Coupling Constants

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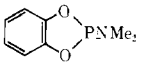
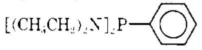
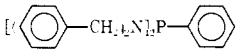
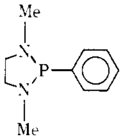
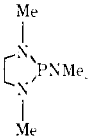
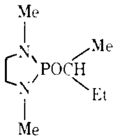
Abstract: Natural abundance ^{15}N and ^{17}O NMR studies have been carried out on a series of organophosphorus compounds for the purpose of determining ^{31}P–^{15}N and ^{31}P–^{17}O nuclear spin couplings. The ^{31}P–^{15}N couplings are sensitive to both electronegativity of substituent and conformation. Finite perturbation coupling calculations within the CNDO/2 approximation were performed to probe the effect of conformation and structure as well as the trigonal-pyramidal geometry balance at the nitrogen. Theoretical ^{31}P–^{17}O couplings were also computed for a wide variety of P–O bonding situations, giving clear evidence for the dominance of the coupling by the Fermi contact mechanism. New experimental ^{31}P–^{17}O couplings include those for $R_3P{=}O$ for R = C, N, F, Cl, and Br.

Pulsed Fourier transform NMR techniques have made the observation of a "weak" nucleus such as ^{13}C routine. While natural abundance ^{15}N and ^{17}O NMR spectra are also possible using the same techniques, their lower natural abundance, long T_1's (for ^{15}N), and quadrupolar broadening associated with ^{17}O resonance have slowed progress in their use. Our previous studies of organophosphorus compounds have relied on ^{13}C NMR[2] and more recently ^{15}N NMR[3] with the goal of a better understanding of the nature of chemical bonding involving phosphorus. Of special concern is the sensitivity of nuclear spin couplings to changes in the electronic structure of organophosphorus compounds as governed by geometrical deformations and electronegativity effects. Our previous work[3] on $^1J_{P-N}$ and that of others[4-8] have concentrated on the signs and magnitudes of this coupling as a function of the oxidation state at phosphorus. There has been some prior study of ^{31}P–^{17}O couplings.[9] A very early report[9a] encountered difficulties in peak assignment, which led to an uncertainty with values reported therein. The present work is directed toward an exploration of electronegativity effects of the magnitudes of these

Table I. Experimental $^{31}P-^{15}N$ and $^{31}P-^{17}O$ Nuclear Spin Coupling Constants in Organophosphorus Compounds

No.	Compd	$^1J_{P-N}$, Hz	No.	Compd	$^1J_{P-O}$
1	$(Me_2N)_2PNMe_2$	59.1[a]	10	$Me_3P{=}O$	120 ± 15
2	Cl_2PNMe_2	89.4	11	$(Me_2N)_3P{=}O$	145 ± 10
3		89.0	12	$(MeO)_3P{=}\mathit{O}$ $(Me\mathit{O})_3P{=}O$	165[c] 90[c]
4	F_2PNH_2	73.0[b]	13	$Cl_3P{=}O$	205 ± 3
5		75.5	14	$Br_3P{=}O$	201 ± 5
6		76.7	15 16 17	$F_3P{=}O$ $PhCl_2P{=}O$ $(MeO)_3P$	184 ± 3[d] 187 ± 7 154[c]
7		49.8			
8		51.8 endo 24.0 exo			
9		57.6			

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couplings in aminophosphines and phosphine oxides by sequential replacement of the groups around phosphorus. We will also provide evidence for a large dependence of $^1J_{P-N}$ on the conformation of nitrogen. The interpretation of the experimentally determined P-N and P-O couplings will be augmented by CNDO/2 calculations of the couplings by use of finite perturbation theory (FPT).[10] This approach has been fruitful when applied to P-C and P-H,[11-14] P-N,[3] and Si-C[15] couplings. The Fermi contact contribution is computed through placing a spin perturbation on atom B, given as

$$h_B = (8\pi/3)\beta\mu_B S_B^2(0) \qquad (1)$$

The Fermi contact contribution to the coupling constant between A and B is then computed as

$$J_{AB} = \frac{4}{3} h\gamma_A\gamma_B\beta^2 S_A^2(0) S_B^2(0) \left\{\frac{\delta}{\delta h_B} P_{S_A}{}^2(h_B)\right\}_{h_B=0} \qquad (2)$$

In this expression $S(0)$ is the density of an s orbital at the nucleus and $P_{S_A}{}^2$ is the diagonal spin density matrix element for the valence s orbital of atom A. The other variables are given their usual designations. There have also been several studies of P-H, P-C, P-F, P-O, P-Se, and P-P couplings[16-21] using molecular orbital calculations within the Pople-Santry formalism.[22] In this case the coupling is given, normally, by

$$J_{A-B} = h(4\beta/3)^2\gamma_A\gamma_B(^3\Delta E)^{-1} S_A^2(0) S_B^2(0) P_{S_AS_B}{}^2 \qquad (3)$$

Here $^3\Delta E$ represents the average excitation energy from the ground to all triplet states and $P_{S_AS_B}$ is the s bond order between A and B. This method requires a judicious assignment of $^3\Delta E$ or a more exacting and tedious sum-over-states method. Notice that it also requires J_{A-B} to be directly proportional to the square of the s bond order, whereas the FPT method does not. It appears that, at the present time, the FPT approach gives nuclear spin couplings to phosphorus which are in better agreement with experimental values than these by the Pople-Santry method.

Experimental Section

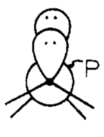
NMR Measurements. ^{15}N NMR spectra were obtained at 10.1 MHz using a Varian XL-100 WG/S-124XL 16K Fourier transform spectrometer. Samples were usually run with ~10% C_6D_6 for internal lock in 10- or 12-mm tubes at ~30 °C, employing 5-s acquisition times resulting in couplings accurate to ±0.2 Hz. Broad-band ^1H decoupling was used, leading to observed inversion of resonances from the negative nuclear Overhauser enhancement expected for ^{15}N.

^{17}O NMR spectra were usually obtained on the neat liquids at 13.5 MHz in 12-mm tubes using external ^{19}F lock. Typically, acquisition times of 0.05-0.10 s were employed. On those compounds exhibiting narrower lines, the experiment was repeated five to ten times varying the position of the rf carrier. The measured couplings were then averaged and the reported errors represent the degree of confidence in the coupling value. **15** was run neat at ca. −40 °C.

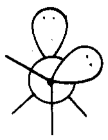
Results and Discussion

$^{15}N-^{31}P$ Couplings. Table I lists the experimentally determined $^{15}N-^{31}P$ couplings for a variety of aminophosphines. Although the low natural abundance and long T_1's for these *nonprotonated* nitrogens necessitate very concentrated samples, the narrow line widths allow reasonably accurate measurements of $^1J_{P-N}$ as evidenced by Figure 1.

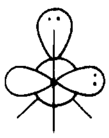
Before launching into a discussion of the magnitudes of the P-N couplings in Table I, a review of the stereochemistry available to these compounds needs to be mentioned briefly. One can envision the following conformations for aminophosphines (see **18-21** below). Structural determinations in



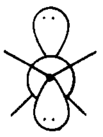
18
cis



19
gauche



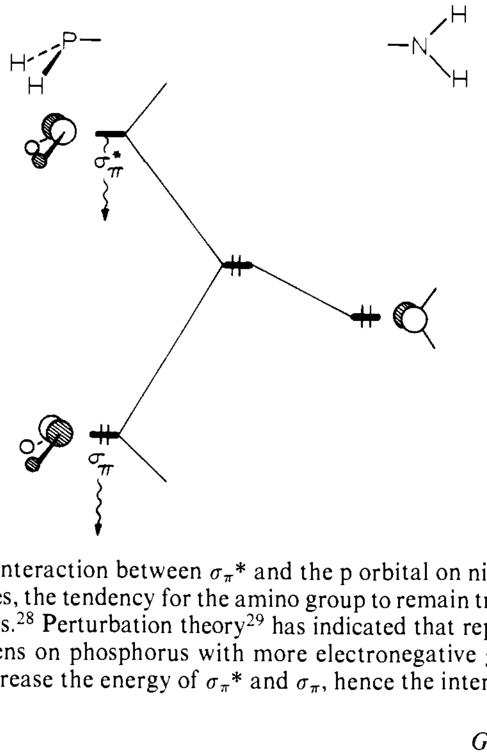
20
planar gauche



21
trans

the gaseous and solid state have shown conformations analogous to **20** to be present. Molecular orbital calculations of aminophosphine[24] at the ab initio level have also predicted **20** with a 90° dihedral angle, ϕ, between the adjacent lone pairs to be more stable than that with a geometry possessing a pyramidal nitrogen and $\phi = 90°$.[24a] However, the energy differences with excursions away from **20** are computed to be quite small. In our previous work[3] we suggested that the population of vibrational states analogous to **19** (with $\phi = 60$-$90°$ exhibiting the normal gauche effect[25]) would also be large in the liquid state at room temperature. Therefore, an average of the computed P-N couplings for **19** and **20** were considered to be representative of the experimental situation. The interconversion between various conformers in substituted, acyclic aminophosphines as studied mainly by NMR techniques[26] appears to be a complex situation. The predominant attitude is that there is a subtle interplay between electronic and steric effects on nitrogen and phosphorus which interconverts various conformers of **20** by a coupled rotational-inversion process.

In discussing the magnitudes of $^1J_{P-N}$ for the aminophosphines it is important to consider not only how a given substituent on phosphorus or nitrogen affects $^1J_{P-N}$ independent of the conformation, but also on how the substituent affects the relative stabilities of **18-21**. In Table I the 30.5- and 29.9-Hz increase in going from **1** to **2** and **3**, respectively, may be due in part to an electronegativity increase. Or in terms of the popular Bent-Walsh[27] arguments, substitution of more electronegative groups at phosphorus in an aminophosphine will concentrate greater atomic p character toward the electronegative substituent, leaving more s character directed toward the nitrogen. The CNDO/2 FPT calculations[3] show this trend. For example, the calculated $^1J_{P-N}$ in going from aminophosphine to triaminophosphine increases by 7.2 Hz and $P_{S_PS_N}{}^2$ increases from 0.0142 to 0.0154. However, the increase in $^1J_{P-N}$ upon substitution of more electronegative groups on phosphorus need not only be due to this factor. The calculated FPT values are also very sensitive to the geometry at nitrogen. For example, trigonal aminophosphine in the conformation given by **20** has a calculated $^1J_{P-N} = 75.6$ Hz, while that for the pyramidal conformer, **19**, gives a $^1J_{P-N} = 57.7$ Hz. A rationale for why **20** is preferred over **19** lies in the ability of a low-lying $\sigma_\pi{}^*$ orbital centered primarily on phosphorus to interact with the lone pair orbital on nitrogen as indicated below.



As the interaction between $\sigma_\pi{}^*$ and the p orbital on nitrogen increases, the tendency for the amino group to remain trigonal increases.[28] Perturbation theory[29] has indicated that replacing hydrogens on phosphorus with more electronegative groups will decrease the energy of $\sigma_\pi{}^*$ and σ_π, hence the interaction between $\sigma_\pi{}^*$ and the p orbital on nitrogen will increase, stabilizing **20** over **19**. Likewise, as the overlap between phosphorus and its substituents decreases, the energy of $\sigma_\pi{}^*$ will also decrease. A similar argument could be developed using d orbitals on phosphorus. The net result of this analysis is that we, also, expect $^1J_{P-N}$ to increase with the substitution of more electronegative groups on phosphorus because the relative population of conformer **20** will increase. It is therefore somewhat surprising that difluoroaminophosphine, **4**, shows a smaller $^1J_{P-N}$ than that for **2** or **3**. However, the replacement of hydrogens for methyl groups on nitrogen is likely to obscure any comparisons of **1-3** to **4**. We can offer four reasons why alkyl substitution on nitrogen may increase $^1J_{P-N}$. As methyl groups are more sterically demanding than hydrogen a trigonal geometry at nitrogen for an *N,N*-dimethylaminophosphine should be more strongly favored over the pyramidal conformation than for aminophosphine itself. Additional evidence for this effect will be given below. The σ_π orbitals of the methyl groups will raise the energy of the p orbital on nitrogen, bringing it closer to the $\sigma_\pi{}^*$ level on phosphorus and stabilize the trigonal geometry. One could maintain that since the $\sigma_\pi{}^*$-p interaction is a bonding one, the P-N distance should decrease, therefore increasing the P-N coupling. However, the P-N bond length in difluoroaminophosphine was reported to be 1.65 Å,[23d] while that for *N,N*-dimethylaminodifluorophosphine has been given as 1.628,[23e] 1.648,[23a] and 1.66 Å[23c] depending upon whether one takes the x-ray, electron diffraction, or microwave results. The shortening of the P-N bond upon methyl substitution is therefore somewhat ambiguous. Finally, if the trends in $^1J_{P-N}$ for aminophosphines follow those observed in $^1J_{P-C}$ for alkylidenephosphoranes, there is ample precedent for this increase. For example, in going from methylidene- to ethylidene- to isopropylidenetriphenylphosphorane $^1J_{P-C}$ for the alkylidene carbon increases from 100 to 110.7 to 121.5 Hz, respectively.[30]

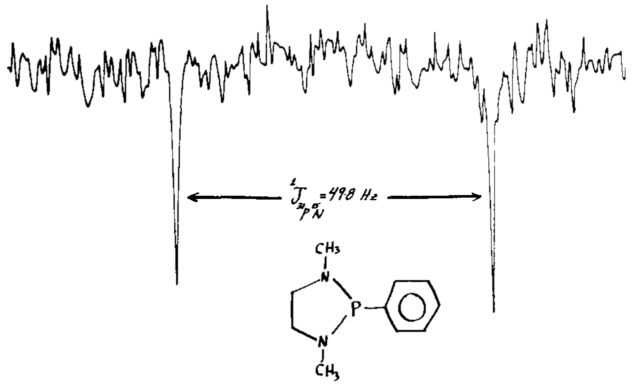


Figure 1. Natural abundance ^{15}N spectrum in 10% C_6D_6 solution. This is a 100-Hz display of the results of 35 533 transients, acquisition time 3.276 s, pulse delay 3.476 s, tip angle 40°, exponential weighting −1.2 s, 2500-Hz spectral width.

In going from **1** to **5** and **6** (Table I) the replacement of a dimethylamino group with a less electronegative phenyl group should cause $^1J_{P-N}$ to decrease. However, this is clearly not the case. Certainly in **6** steric congestion will destabilize the pyramidal conformation at nitrogen.[31] It is the increased preference for **5** and **6** to assume trigonal geometries which we feel may be responsible for the relatively large values of $^1J_{P-N}$. It is shown below that increasing the NPN bond angles increases $^1J_{P-N}$ and this might also be an important factor. Compounds **7, 8,** and **9** represent situations restricting rotational isomerism through ring formation. The ring nitrogen couplings are sensitive to exocyclic substituent electronegativity. Note that in **7**, a bonding situation apparently very similar to **5,** $^1J_{P-N}$ drops to a value which is 9.3 Hz *smaller* than **1,** consistent with change only in substituent electronegativity at the phosphorus

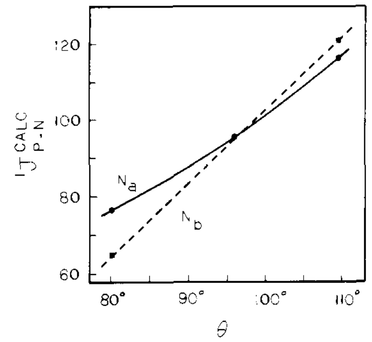
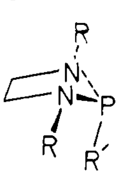


Figure 2. Calculated P-N couplings of trigonal triaminophosphine vs. the N_bPN_b bond angle, θ, defined in 22. These results are from a CNDO/2 spd basis set. Deleting the d orbitals on phosphorus had no effect on the relative trends.

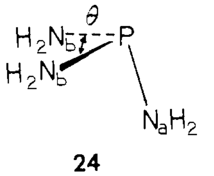
and not any significant trigonal geometry as in **5** or **6**. In the same line of thought, **9** exhibits a larger coupling than does **8**.

In **8** the endocyclic P-N coupling is quite similar to that in **1**. However, the exocyclic P-N coupling is 35.1 Hz smaller than **1**. The closest analogue to **8** for which there is structural data is given by **22**[32] and **23**.[33] In **22** and **23** the NPN angle was



22, R = p-MeC$_6$H$_4$ R' = Ph
23, R = Me R' = Cl

90.2 and 93.9°, respectively, whereas that found for **1** was 96.5° [23f] and that in bis(*N,N*-dimethylamino)chlorophosphine was 96.2 °.[23b] One possibility to consider for the anomalous exocyclic P-N coupling in **8** is that it is a reflection of decreasing the interior PNP bond angle by forming the diazaphospholidine ring. To test this hypothesis CNDO/2 FPT calculations were carried out on **24**. In **24** the HNH angles



24

were kept at 120°. The N_bPN_b angle, θ, was varied keeping the position of the N_a group fixed. Figure 2 shows that as θ is decreased from 96°, $^1J_{P-N}$ for *both* N_a and N_b decrease. The fact that the exocyclic P-N coupling is decreased much more than the endocyclic one relative to **1** argues that this cannot be the sole factor operative in **8**. Another consideration is rotation around the exocyclic P-N bond. One would normally expect a dihedral angle, ϕ, between the lone pair on nitrogen and phosphorus equal to 60-90° for acyclic compounds.[25] However, examination of molecular models of **8** revealed that maintaining this dihedral angle for the exocyclic nitrogen (whether it is pyramidal or trigonal) will bring the hydrogens of one of the methyl groups close to the hydrogens and/or carbon-carbon bond of the diazophospholidine ring. These repulsions will be minimized when ϕ = 180° as in **25**.

Our CNDO/2 calculations (both with and without d orbitals) predict an energy minimum at this dihedral angle for aminophosphine, although it is well known that CNDO/2 is likely to give erroneous results where adjacent atoms have unshared electron pairs in hybrid orbitals[34] (i.e., there is always likely to be a minimum at ϕ = 180° because of the neglect of overlap). However, recent ab initio calculations have also predicted a minimum at ϕ = 180° for aminophosphine with nitrogen in a pyramidal geometry, as in **21**, although the minimum for **20** was still predicted to be of lower energy.[24c] Therefore, with the steric requirements inherent in **8** it seems likely that **25** may well be the favored conformer. Figure 3 shows a plot of the calculated $^1J_{P-N}$ for aminophosphine as a function of the dihedral angle between the lone pairs, ϕ. This only shows the CNDO/2 FPT calculations with d orbitals on phosphorus. Deleting d orbitals from the basis set produced no changes in the relative trends of the couplings). The calculated $^1J_{P-N}$ for the trigonal geometry (dashed line) has essentially no dependence on ϕ. However, for the pyramidal geometry at nitrogen (solid line) the calculated $^1J_{P-N}$ drops precipitously as ϕ increases from 0 to 180°. Likewise $P_{S_PS_N}{}^2$ (dashed-dotted line) for the pyramidal geometry follows this dependence quite closely. Note that since the magnetogyric ratio of ^{15}N is negative and that for ^{31}P is positive, the reduced P-N coupling in aminophosphine is negative, therefore a larger value for $^1J_{P-N}$ implies a smaller (more negative) reduced coupling. This is the reason for plotting $P_{S_PS_N}{}^2$ in an inverse manner in Figure 3. Therefore, the FPT results indicate that the smaller exocyclic P-N coupling in **8** is due to the enhanced preference for conformation **25**.

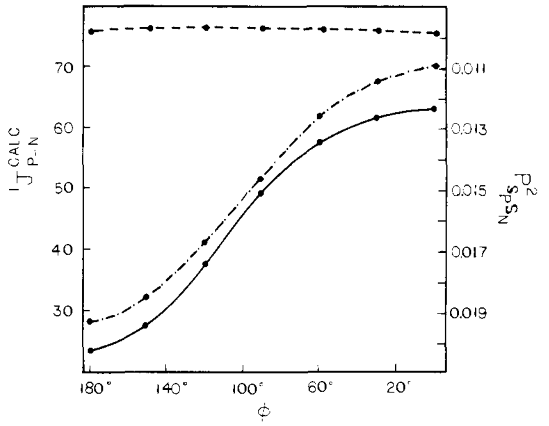
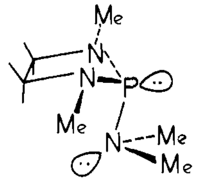


Figure 3. The calculated P-N coupling in aminophosphine as a function of the dihedral angle between the lone pair on phosphorus and nitrogen, ϕ. The solid line refers to a pyramidal geometry at nitrogen, the dashed line to the trigonal geometry. The dashed-dotted line refers to the dependence of the phosphorus s-nitrogen s bond order, squared, $P_{S_PS_N}{}^2$, as a function of ϕ for the pyramidal geometry of nitrogen. Note that the scale for $P_{S_PS_N}{}^2$ is plotted inversely.



25

It is interesting to see to what the physical basis for this dihedral dependence of $^1J_{P-N}$ is due, as well as to be able to predict in what other situations a dihedral dependence on one-bond couplings is likely to be found. A similar dependence on $^1J_{P-P}$ in diphosphine has recently been found,[35] using ab initio wave functions within the Pople-Santry approach (eq 3). Here when ϕ = 0 the calculated $^1J_{P-P}$ is quite small, but as ϕ approaches 180° $^1J_{P-P}$ becomes larger. CNDO/2 and extended Hückel calculations on diphosphine and aminophosphine likewise gave small values of $P_{S_PS_P}{}^2$ and $P_{S_PS_N}{}^2$, respectively, when ϕ = 0°, which then become larger when ϕ goes to 180°. The reason why the s bond order is larger when ϕ = 180° compared to ϕ = 0° can be understood in a simple fashion. In Figure 4 consider the distortion in going from a planar H_2A-AH_2 molecule to either a cis or trans conforma-

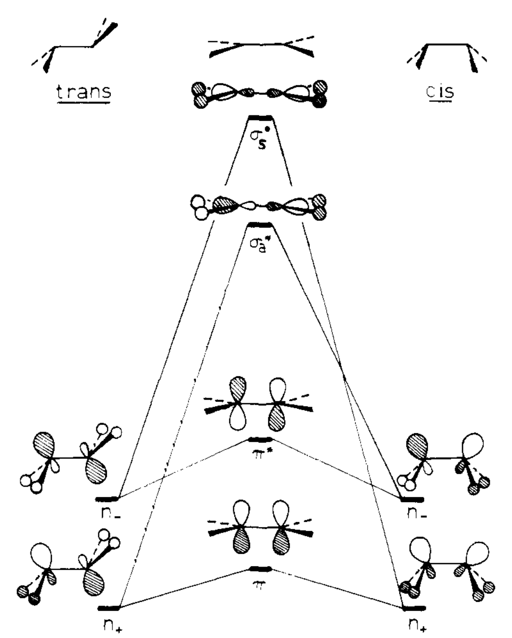


Figure 4. Relative mixings of a planar $H_2A\text{-}AH_2$ upon bending.

tion.[36] For $H_2P\text{-}PH_2$ (or $H_2P\text{-}NH_2$) the highest occupied molecular orbital in the planar geometry is π^*. As the distortion from the planar to cis geometry occurs σ_a^* mixes into π^*, while σ_s^* mixes into π. In the reduced C_{2v} geometry of the cis conformer σ_a^* and π^* belong to the b_2 representation, while σ_s^* and π transform as a_1. The important fact is that since π^* always lies above π in energy, the mixing of σ_a^* into π^* is larger than that of σ_s^* into π when the distortion leads to the cis geometry. (In EHT calculations σ_a^* also lies lower in energy than σ_s^*, although this ordering makes no crucial difference in the discussion.) On the other hand, bending to the trans geometry mixes σ_s^* into π^* and σ_a^* into π; in the C_{2h} geometry σ_a^* and π are of b_u symmetry, while σ_s^* and π^* transform as a_g. Here the mixing of σ_s^* into π^* will be larger than that of σ_a^* into π. In aminophosphine the symmetry of the cis and trans conformations is only C_s; therefore, mixing between σ_a^* and σ_s^* into π^* in both conformations is allowed. However, the nodal structure of the levels given in Figure 4 is the same for aminophosphine and diphosphine. This means that relative mixings upon bending will still basically be dominated by those factors given before. Table II presents the mixing coefficients derived from first and second order perturbation theory using the approach outlined by Imamura.[37] The results (from extended Hückel calculations) do indeed bear out the analysis given above. Breaking up σ_s^* and σ_a^* into their atomic contributions result in the designations below. The extent to which σ_a^* mixes into the π or π^* levels will decrease the s bond order between the two central atoms, since the s orbitals are of opposite phases. However, when σ_s^* mixes into π or π^* the s bond order will increase. The final result is that in the cis geometry mixing with σ_a^* dominates; in the trans geometry σ_s^* dominates, therefore, the s bond order between the central atoms is larger in the trans geometry than it is in the cis. The preceding discussion has also neglected the highest unoccupied level, **26.** This acts in a completely analogous fashion to σ_a^* in Figure 4, i.e., reducing the s bond order preferentially in the cis over the trans geometry. When $P_{S_AS_B}{}^2$ follows $^1J_{A-B}$ for molecules of this type, the reduced coupling between A and B should be smaller in the cis than in the trans geometries (i.e., $^1J_{^{15}N-^{15}N}$ in hydrazines or diimides should also show this trend).[38] Our CNDO/2 FPT calculations on diphosphine also give $^1J_{P-P}$ as much larger in the trans than in the cis conformation both with and without d orbitals on phosphorus (spd and sp basis sets, respectively), which is in agreement with the ab initio calculations.[35] However, as Figure 5 shows, there are major differences between the calculations. $P_{S_PS_P}{}^2$ for the CNDO/2 sp and spd calculations follow the dependence on $^1J_{P-P}$ as given by ab initio calculations; however, the FPT method is *not* dependent on a direct relationship to $P_{S_AS_B}{}^2$. It is interesting to note that the calculated values of $^1J_{P-P}$ by both FPT methods at the experimental geometry of diphosphine ($\phi = 75°$)[39] are much closer to experiment ($^1J_{P-P} = -108$ Hz;[40] calculated $^1J_{P-P} = -127.0$ and -123.3 Hz for the CNDO/2 spd and sp basis sets, respectively) then the ab initio value (-164.5 Hz). The name is true when one includes 10% of the trans conformation.[41]

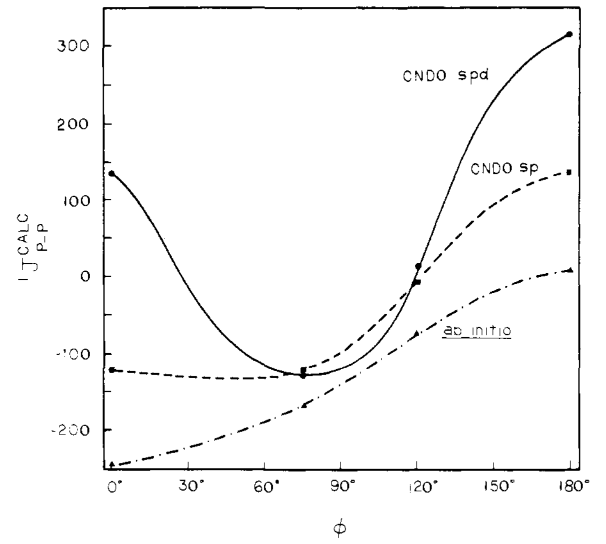
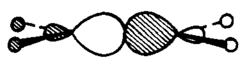


Figure 5. The calculated $^1J_{P-P}$ of diphosphine as a function of the dihedral angle between the adjacent lone pairs on phosphorus, ϕ.

Table II. Mixing Coefficients to Second Order for the Levels Indicated in Figure 4

	Diphosphine		Aminophosphine	
	Cis	Trans	Cis	Trans
σ_s^*, π^*	0	0.3477	0.1801	0.2578
σ_a^*, π^*	0.3390	0	0.2475	0.0053
σ_s^*, π	0.2182	0	0.1979	0.1144
σ_a^*, π	0	0.1784	0.0140	0.1460



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$^{17}O\text{-}^{31}P$ Couplings. The $^{17}O\text{-}^{31}P$ couplings for various phosphine oxides are collected in Table I. A determination of these couplings is severely hampered by the line broadening associated with the ^{17}O quadrupole. Nevertheless, as shown in Figures 6 and 7, narrow lines are possible particularly for highly symmetrical molecules. However, we have observed ^{17}O resonances for several POR molecules where the extreme line widths (~1000 Hz) totally obscured any $^{31}P\text{-}^{17}O$ couplings, as shown in Figure 6a. It is of interest that these couplings were

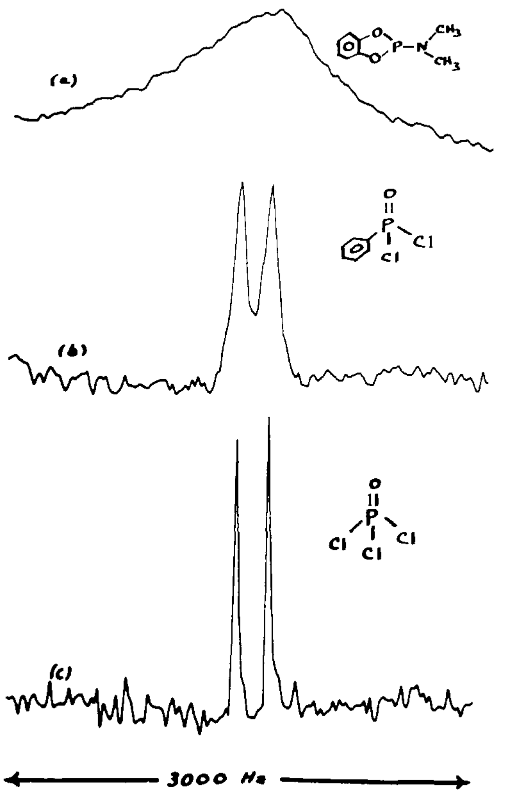

Figure 6. Natural abundance ^{17}O NMR spectra of the neat liquids in 12-mm tubes using external ^{19}F lock: (a) 77 676 transients, acquisition time 0.05 s, exponential time constant −0.01; (b) 26 289 transients, acquisition time 0.05 s, exponential time constant −0.02; (c) 5237 transients, acquisition time 0.05 s, exponential weighting not used.

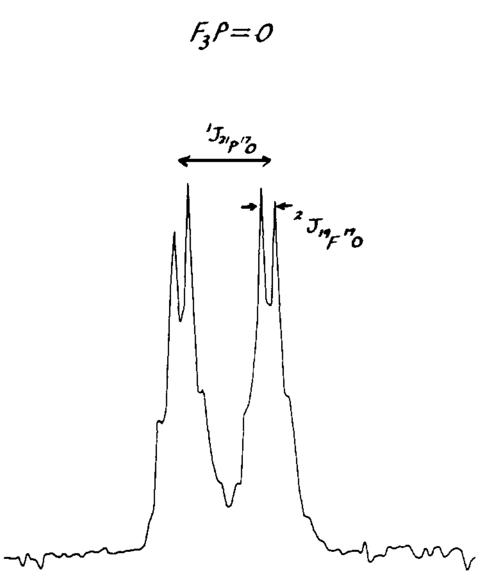

Figure 7. Natural abundance ^{17}O NMR spectrum of neat F_3P=O at −40 °C in a 12-mm tube, external ^{19}F lock. Transients (25 130) were accumulated using 0.1-s acquisition time and no exponential weighting.

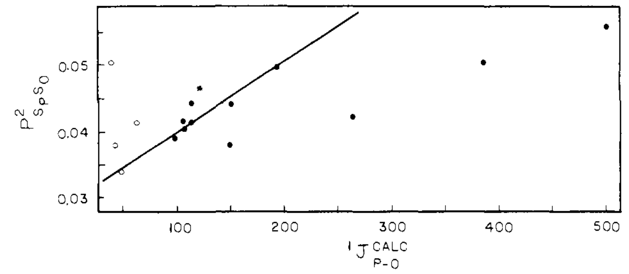

Figure 8. Calculated $^1J_{P-O}$ vs. $P_{S_PS_O}{}^2$. The closed circles refer to P=O coupling, all others are designated by open circles. The values are taken from Table III.

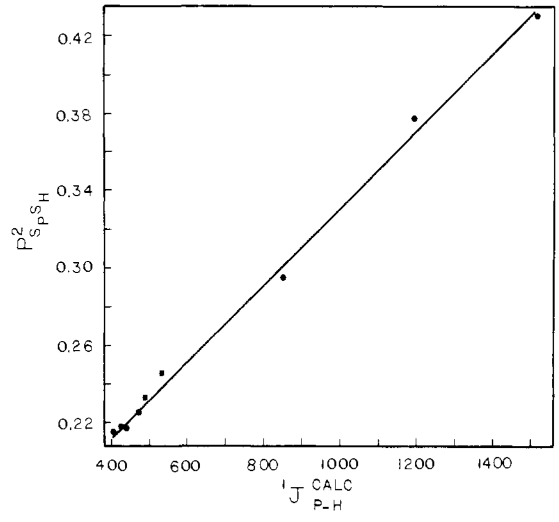

Figure 9. Calculated $^1J_{P-H}$ vs. $P_{S_PS_H}{}^2$. The values are taken from Table IV.

Table III. Theoretical Calculations of ^{31}P-^{17}O Couplings

Compd		$^1J_{P-O}{}^{calcd}$	$P_{S_PS_O}{}^2$
$H_3P=O$		98.5	0.0390
$H_2P(O)Me$		106.2	0.0407
$H_2P(O)NH_2{}^a$		150.2	0.0379
$(H_2N)_3P=O^a$		264.6	0.0421
$H_2P(O)OH$	P=O	150.0	0.0444
	POH	41.5	0.0383
$(HO)_3P=O$	P=O	384.5	0.0501
	POH	33.8	0.0504
$H_2P(O)F$		121.1	0.0468
$F_3P=O$		501.9	0.0554
$H_2P(O)Cl$		112.4	0.0444
$Cl_3P=O$		193.0	0.0498
$H_2P(OH)$		113.8	0.0128
$(HO)_3P$		147.1	0.0101
$H_3P^+(OH)$		48.3	0.0336
$(HO)_3{}^+PH$		60.8	0.0419

[a] These values correspond to an average between trigonal and pyramidal geometries at the nitrogen.

observed in an early study (i.e., **12** and **17**).[9] The phosphoryl oxygen couplings in **12** and **13** are in good agreement with our values. Additionally, in **12** the P=O coupling is assigned the value of 145 Hz because of the similarity to that observed in **10** and **11**. It is readily apparent that the couplings to the phosphoryl oxygen in **10–16** are sensitive to the electronegativity of the substituents around phosphorus. This increase in $^1J_{P-O}$ with increasing electronegativity of the substituents draws parallels with several other couplings to phosphorus. For example, P-C,[42] P-H,[43] P-Se,[44] and P-W,[45] follow this trend. P-B[46] couplings also show that substitution of fluorine groups decrease $^1J_{P-B}$ relative to other highly electronegative groups, which is similar to that found for P-O couplings in Table I.

The CNDO/2 FPT calculations (spd basis set) of $^1J_{P-O}$ for several types of phosphorus compounds are summarized in Table III. The electronegativity effect on the phosphoryl oxygen coupling is also quite apparent with $^1J_{P-O}$ increasing quite markedly from H_3P=O to F_3P=O. A comparison of the experimental values in Table I with the theoretical ones indi-

Table IV. Theoretical and Experimental $^{31}P-^{1}H$ Couplings

Compd	$^1J_{P-H}{}^{calcd}$	$P_{S_PS_H}{}^2$	$^1J_{P-H}{}^{expt}$	Expt compd	Ref
H_3P^+H	430.2	0.2172	548	H_3P^+H	*a*
H_3P^+Me	439.1	0.2165	527.1	H_3P^+Me	*a*
$H_3P^+NH_2$	486.9	0.2332			
$(NH_2)_3P^+H$	506.2	0.2933			
H_3P^+OH	531.6	0.2461			
$(HO)_3P^+H$	1194.1	0.3782	826.2	$(MeO)_3P^+H$	*b*
F_3P^+H	1526.2	0.4303	1109.6	F_3P^+H	*c*
Cl_3P^+H	847.9	0.2944	911.1	Cl_3P^+H	*c*

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cates that as the groups around phosphorus become more electronegative, the FPT method consistently gives a much larger value of $^1J_{P-O}$. This is especially evident for the analogues of **11** and **12,** where the theoretical values are approximately twice as large as the experimental ones. Notice that the calculations do predict a much smaller value for the R*O*P(O) coupling, in accord with that found in **12.** They also predict, correctly, that in **17** this coupling should increase again. Correcting the P-O coupling for changes in effective nuclear charge in the usual manner[11] did not bring the P-O couplings in closer agreement to the experimental ones. Ab initio calculations have indicated that d orbitals on phosphorus are important for several properties in phosphine oxides.[47] We have, unfortunately, not been able to ascertain the importance of d orbitals on phosphorus with respect to P-O coupling. The preliminary calculations without d orbitals did not converge to acceptable limits. Previous calculations employing the Pople-Santry approach within the extended Hückel method[17,18] have given magnitudes of $^1J_{P-O}$ which are much too small (e.g., −58 Hz for **10**). They furthermore predict the sign of $^1J_{P-O}$ to be negative, whereas in the CNDO/2 FPT they are all predicted to be positive. It has been established that the orbital and spin dipole contributions to $^1J_{P-O}$ are negligible,[19] therefore, the Fermi contact term appears to be dominant.

The lack of any definite relationship of $^1J_{P-O}$ to $P_{S_PS_O}{}^2$ is evident from Figure 8. Here the closed circles represent P=O couplings and the open ones all others in Table III. The line drawn in this figure should, of course, be regarded with some caution. Assuming, for the moment, that there is a relationship of $^1J_{P-O}$ for P=O couplings to $P_{S_PS_O}{}^2$ and remembering that the CNDO/2 FPT method consistently overestimates $^1J_{P-O}$ for compounds with highly electronegative groups around phosphorus, it is not too surprising that the points falling far from the line in Figure 8 are $H_2P(O)NH_2$, $(H_2N)_3P{=}O$, $(HO)_3P{=}O$, and $F_3P{=}O$. In order to check if this overestimation of couplings to phosphorus occurs in general, a similar series of P-H couplings to phosphonium cations are presented in Table IV. It is also seen that the couplings which are in poorest agreement with experiment are the trifluoro and trihydroxyphosphonium cations. However, the relative errors in the CNDO/2 FPT calculations (spd basis set) are much less for $^1J_{P-H}$ than those in $^1J_{P-O}$. Another difference to be noted is that, as can be seen in Figure 9, there is a good relationship to $^1J_{P-H}$ and $P_{S_PS_H}{}^2$ for the compounds in Table IV.

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Appendix

The geometries for the aminophosphines, phosphine oxides, and phosphonium cations used in the CNDO/2 FPT calculations[48] have been given previously.[3] A standard P=O bond length was taken to be 1.47 Å. The P-O(H), P-F, P-Cl, and P-H bond lengths were 1.60, 1.52, 1.99, and 1.42 Å, respectively.[50] The angles around phosphorus were taken from close analogues.[50] The rest of the bond lengths and angles were taken from a standard geometric model.[51] The geometry for diphosphine was that used in ref 20. The parameters used in the extended Hückel calculations have been listed elsewhere.[52] All calculations were done on a Burroughs B-6700 computer.

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Carbon-13 Magnetic Resonance Spectra of 8-Substituted Purine Nucleosides. Characteristic Shifts for the Syn Conformation

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Abstract: Carbon-13 magnetic resonance spectra of 8-substituted purine nucleosides were measured. Substitution of the 8-position of adenosine with various substituents (-Br, -Cl, $-SCH_3$, $-SCH_2CH_3$, -SH, $-OCH_3$, -OH, and $-CH_3$) caused characteristic upfield shifts (-2 to -3 ppm) of the 2′-carbon signal. The same phenomena was also observed in the case of 8-substituted guanosines (-Br, $-SCH_3$, -OH, and $-CH_3$), 8-substituted inosines (-Br, -OH, and $-CH_3$), and 2-ethylthio-8-methylinosine. This upfield shift of the 2′-carbon signal for these nucleosides was assumed to be due to their syn conformation placing the lone pair of electrons of base N(3) close to the sugar C(2′)-H(2′) bond. The effects of 8-substituents on the chemical shifts of base carbons are also discussed.

The direction of the base plane relative to the sugar moiety, the glycosidic torsion angle, in a nucleoside is one of the most important parameters determining its conformational properties. It is well known that most of the natural nucleosides take an anti[1] conformation in crystals[2] and in solution.[3] A syn[1] conformation, in which the base direction is reversed with re-