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- (26) The correlation between the chemical shift and average endocyclic bond angle exists irrespective of the question of the rigidity of the ring in solution. Ring conformational changes would not be manifest in ambient temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra: four- and six-membered rings yield singlets because of symmetry regardless of conformational changes, and five-membered rings will yield complex $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in spite of possible conformational changes not involving inversion of the phosphorus lone pair electrons.²⁰ Clearly the average hybridization of the phosphorus atoms, as dictated by the ring size and measured by the endocyclic P–P bond angle, is the dominant factor in the ^{31}P chemical shift.
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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 $(\text{Me}_2\text{N})_3\text{P}$, $(\text{Me}_2\text{N})_3\text{PS}$, and $(\text{Me}_2\text{N})_3\text{PO}$

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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 $(\text{Me}_2\text{N})_3\text{P}$, $(\text{Me}_2\text{N})_3\text{PS}$, and $(\text{Me}_2\text{N})_3\text{PO}$ as +59.1, +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 ^1H 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 cou-

plings, 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 organometallic⁶ 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

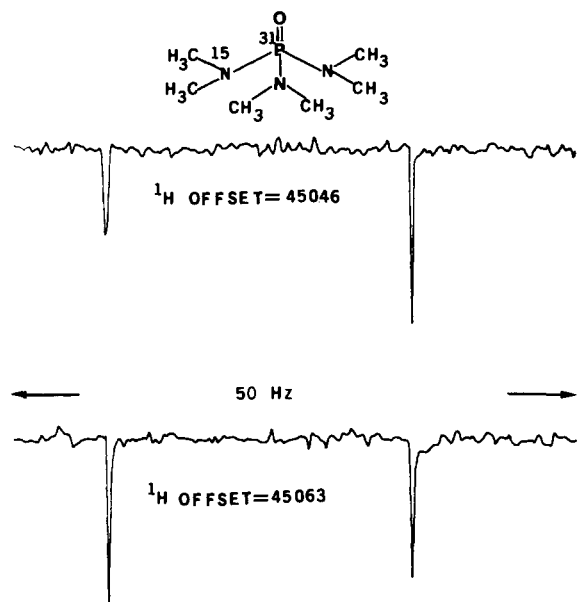


Figure 1. Natural abundance ^{15}N NMR spectra of $[(\text{CH}_3)_2\text{N}]_3\text{PO}$ under conditions of coherent low-power off-resonance proton decoupling. Upper spectrum: 15 098 transients, spectral width 512 Hz, acquisition time 4 s, 20° pulse, no delay. Lower spectrum: 17 670 transients, 256 Hz spectral width, 20° pulse, no delay. Spectra obtained on XL-100 WG12/S-124XL at 10.1 and 25.16 MHz (for $^2J_{\text{PC}}$) locked to 10% internal C_6D_6 in 10-mm tubes at 20°C ; no exponential weighting applied. Decoupler power 80 dB. Spectra are inverted because of significant nuclear Overhauser effect (negative because of negative γ_{N}).

molecular orbital calculations are performed to examine the effect of conformation, substituents, and the importance of the Fermi contact coupling contribution to the directly bonded ^{31}P - ^{15}N couplings.

Experimental Section

NMR Measurements. ^{15}N NMR spectra were obtained at 10.1 MHz using a Varian XL-100 WG/S-124 XL 16K fourier transform spectrometer. Neat solutions (10% C_6D_6 for internal deuterium lock) were run in 10-mm tubes at $\sim 30^\circ\text{C}$. Typical conditions are illustrated in Figure 1 where the double resonance spectra are shown for tris(dimethylamino)phosphine oxide. This method⁷ permitted a sign determination for the ^{15}N - ^{31}P coupling in the oxide via selective irradiation of the phosphorus spin states within the ^{31}P - ^1H multiplet in the *proton* spectrum. Since off-resonance high-frequency irradiation enhances the high-frequency component of the ^{15}N - ^{31}P doublet in the ^{15}N spectrum of the three spin (^1H , ^{15}P , ^{31}P) system the ^{31}P - ^1H and ^{31}P - ^{15}N reduced couplings (K_{PN}) are of the same sign. Since γ_{N} is negative $^1J_{\text{PN}}$ is of opposite sign to $^3J_{\text{PH}}$.⁸ Similar consideration of $^2J_{\text{PC}}$ and $^3J_{\text{PH}}$ allowed sign determination of $^2J_{\text{PC}}$ from off-resonance studies in the ^{13}C spectrum.⁹ These were performed at 25.1 MHz on the same samples as used in the ^{15}N studies. The phosphine, sulfide, and oxide were used as received from Aldrich Chemical Co.

Calculations

The geometries of the aminophosphines were taken as follows: P-H = 1.414 Å, H-P-H = 93.4° , and H-P-N = 97.5° are from methylphosphine,¹⁰ the P-N bond distance (1.70 Å) and conformations of the amino groups in triaminophosphine were taken from tris(dimethylamino)phosphine.¹¹ For the tetravalent phosphorus compounds a standard geometry of P-H = 1.42 Å and H-P-H = 105° was chosen. CNDO/2 (spd) optimization gave P-N bond distances of 1.69, 1.72, 1.64, and 1.66 Å for **5**, **6**, **7**, and **8**. A P-N bond length for **10**-**16** was set at 1.66 Å from the structure of triaminophosphine oxide.¹² The P-O and P-S bond lengths used were 1.51 and 1.91 Å, respectively. The P-S bond length was taken from the average of several related compounds.¹³ It should be noted that CNDO/2 (spd) energy minimizations gave excellent geome-

Table I. Nuclear Spin Couplings (Hz)

Type	$[(\text{CH}_3)_2\text{N}]_3\text{P}$	$[(\text{CH}_3)_2\text{N}]_3\text{PS}$	$[(\text{CH}_3)_2\text{N}]_3\text{PO}$
$^1J_{\text{PN}}$	$+59.1 \pm 0.1$	$\mp 6.0 \pm 0.2$	-26.9 ± 0.1
$^2J_{\text{PC}}$	$+19.15 \pm 0.05$	$+3.3 \pm 0.05$	$+3.4 \pm 0.1$
$^1J_{\text{PO}}$			145 ^a

^a From 10 000 transient ^{17}O spectrum (G. A. Gray, to be published).

tries for triaminophosphine, its oxide and sulfide.¹⁴ Trigonal bipyramidal geometry at phosphorus was used for the phosphoranes. The P- N_{eq} and P- N_{ax} bond lengths of 1.64 and 1.78 Å, respectively, were taken from the x-ray structures of several related cyclic phosphoranes.¹³ The P- H_{axial} = 1.508 Å and P- H_{eq} = 1.402 Å were taken from ab initio geometry optimizations.¹⁵ The P- F_{ax} and P- F_{eq} bond distances were assumed to be the same as those found for trifluorodimethylphosphorane (1.55 and 1.64 Å, respectively).¹⁶ The dihedral conformations of the amino groups for the phosphoranes were taken from ref 17 and 18. A standard N-H bond distance of 1.01 Å was assumed. All calculations were done on a Burroughs B-6700 computer.

Results and Discussion

Table I contains the experimental ^{15}N - ^{31}P couplings, as well as several others of interest. Although a sign change was observed^{4a} in going from tricoordinate P(III) in $(\text{CF}_3)_2\text{PNH}_2$ to the tetracoordinate P(V) in $\text{F}_3\text{P}=\text{NPF}_2$ or pentacoordinate P(V) in $\text{F}_3\text{P}(\text{NH}_2)_2$, these highly fluorinated phosphorus may not be typical for most organophosphorus compounds not containing highly electronegative groups, and therefore their coupling behavior does not necessarily define a general oxidation-state dependence. The tris(dimethylamino) substituents provide an unchanging array at the phosphorus which experiences change only at the unique fourth coordination site. (This is also true for the anilino dimethyl compounds recently reported.⁵) The sign change observed here closely follows the change in reduced coupling (^{15}N has a negative magnetogyric ratio, ^{13}C positive) observed in the series $(\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_3\text{PS}$, and $(\text{CH}_3)_3\text{PO}$ which exhibits one-bond ^{13}C - ^{31}P couplings of -13.6 ,^{7a} $(+56.1)$,¹⁷ and $(+68.3)$ Hz.¹⁷ The change from positive $^1J_{\text{PN}}$ to negative in P(III) \rightarrow P(V) has been explained^{4a} in terms of greater Fermi contact contribution resulting from substantial increase of 3s bonding character in the phosphorus hybrid orbitals, sp^3 in the case of the tetrahedral P(V) in $\text{F}_3\text{P}=\text{NPF}_2$. Corroborative evidence for this viewpoint in ^{13}C - ^{31}P coupling has recently been obtained¹⁸ for the trigonal bipyramidal $(\text{CH}_3^{\text{eq}})_3\text{P}(\text{CH}_3^{\text{ax}})(\text{OCH}_3^{\text{ax}})$ where $^1J_{\text{CP}^{\text{eq}}} = 116.0$ Hz and $^1J_{\text{CP}^{\text{ax}}} = 7.3$ Hz, which is consistent with phosphorus sp^2 hybrid bonding orbitals within the equatorial plane and essentially p bonding to the axial ligands.

The large two-bond ^{13}C - ^{31}P coupling in the P(III) compound is similar to the $+12$ - 15 Hz couplings previously observed in *N,N*-dimethylaminophosphines.²¹ These are average values for the appropriate rotameric distributions. As has been shown for $^2J_{\text{PCC}}$ ²²⁻²⁴ and $^2J_{\text{PNC}}$ ²¹ there is a dihedral angle dependence of $^2J_{\text{PC}}$ in phosphines with respect to the orientation of the coupled carbon and the phosphorus lone pair, large and positive for a cis relationship, small and negative for trans (-7 for trans $^2J_{\text{PNC}}$, $+40$ Hz for cis).²¹

The parallels observed here, along with the consistencies observed in different oxidation states, substituent arrays, and symmetries argue that the ^{13}C - ^{31}P coupling behavior may have significant *experimental* correspondence in ^{15}N - ^{31}P couplings. This prospect should encourage the acquisition of new data to explore further their behavior in different bonding and conformational situations. On the theoretical side it is critical to

Table II. Calculated Nuclear Spin Couplings^a

Compound	A-B		Nitrogen geometry				
			Trigonal		Pyramidal		
			J_{AB}	$P_{S_A S_B}$	J_{AB}	$P_{S_A S_B}$	
H ₂ PNH ₂	PH	1 ^b	-128.0	0.2691	2 ^c	-116.2	0.2720
	PN		+75.6	0.1315		+57.7	0.1136
	PNH		-0.2			+7.1	
(H ₃ N) ₃ P	PN	3 ^d	+95.9	0.1271	4 ^e	+57.1	0.1230
	PNH		-4.3			+3.3	
	PH	5	+508.8	0.4876	6	+475.9	0.4805
H ₃ P ⁺ -NH ₂	PN		-17.4	0.2263		+23.3	0.1840
	PNH		0.5			-4.0	
	PH	7	+397.8	0.4698	8	+359.4	0.4631
H ₃ P=NH	PN		+106.5	0.2013		+141.1	0.1735
	PNH		-0.3			-4.8	
	PF	9	-1566.3	0.1850			
F ₃ P=NH	PN		+494.8	0.2048			
	PNH		+17.3				
	PH	10	+604.6	0.5154	11	+592.6	0.5117
H ₂ P(O)NH ₂	PN		-6.2	0.2419		-0.3	0.2162
	PO		+157.7	0.1948		+147.4	0.1945
	PNH		-3.9			-5.3	
(H ₂ N) ₃ P=O	PN	12	-39.0	0.2651	13	-12.0	0.2285
	PO		+330.9	0.2050		+261.4	0.2051
	PNH		+0.1			-4.1	
H ₂ P(S)NH ₂	PH	14	+543.0	0.4883	15	+539.5	0.4886
	PN		+7.0	0.2267		-2.4	0.2112
	PS		-50.8	0.1706		-48.3	0.1702
(H ₂ N) ₃ P=S	PNH		-4.1			-3.9	
	PN	16	-28.9	0.2473	17	-9.3	0.2158
	PS		-83.7	0.1781		-70.2	0.1783
H ₄ P-NH ₂ (equatorial NH ₂)	PNH		+0.6			-2.1	
	PH	18	+348.3	0.4068	19	+308.1	0.4008
	PH ^{ax}		+482.2	0.4843		+490.6	0.4830
H ₄ P-NH ₂ (axial NH ₂)	PN ^{eq}		-1.4	0.2240		+12.7	0.1944
	PNH		-2.9			-5.6	
	PH	20	+80.6	0.3762	21	+100.2	0.3799
F ₃ P(NH ₂) ₂	PH ^{ax}		+588.6	0.4859		+567.3	0.4815
	PN ^{eq}		+50.1	0.1660		+36.5	0.1423
	PNH		-9.0			-8.0	
F ₃ P(NH ₂) ₂	PF ^{eq}	22	-229.7	0.1644	23	-351.5	0.1555
	PF ^{ax}		+20.5	0.2015		-222.8	0.1949
	PN ^{eq}		-134.1	0.2963		+28.7	0.1917
	PNH		+12.5			-10.8	

^a Values for averages over several conformations, except where noted. In Hz. PO couplings refer to ³¹P-¹⁷O coupling. ^b Without d orbitals: $J_{PH} = -197.7$, $J_{PN} = +67.9$, and $J_{PNH} = +3.1$. ^c Without d orbitals: $J_{PH} = -177.5$, $J_{PN} = +60.2$, and $J_{PNH} = +13.0$. ^d Without d orbitals: $J_{PN} = +96.3$ and $J_{PNH} = -3.0$. ^e Without d orbitals: $J_{PN} = 50.3$ and $J_{PNH} = +7.4$.

assess the importance of the Fermi contact mechanism for ¹⁵N-³¹P coupling, especially since interpretation of such couplings within the contact formalism has already commenced.^{4,5} The large magnitudes for the phosphine and oxide ¹⁵N-³¹P couplings give ample encouragement for theoretical prediction since such predictions will not be severely hampered by very small observed couplings as are found, for example, for ¹³C-¹⁵N couplings. With these factors in mind we here report the first systematic theoretical analysis of ¹⁵N-³¹P coupling using modern SCF-MO finite perturbation methods.

Calculation of ¹⁵N-³¹P Couplings. There have been several studies of the Fermi contact contribution in P-H, P-C, and P-P couplings²⁵⁻²⁷ using molecular orbital calculations within the Pople-Santry formalism.²⁸ This formalism requires that the calculated couplings be directly proportional to the "s character" comprising the directly bonded atoms. In addition, it requires a judicious assignment of an "average triplet excitation energy", or a more exacting sum-over-states method. A much more promising and productive approach which avoids this problem is the finite perturbation technique²⁹ (FPT) used

in conjunction with SCF molecular orbital wave functions in the INDO (intermediate neglect of differential overlap) or CNDO (complete neglect of differential overlap) approximations. The coupling is computed in the presence of a contact perturbation:

$$h_B = \frac{8\pi}{3} \cdot \beta \mu_B S_B^2(0)$$

The coupling constant is then computed as

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

where $\rho_{s_A}^2$ is the diagonal spin density matrix element for the valence s orbital of atom A. This method has given reliable P-C and P-H couplings, in general, for a wide variety of organophosphorus compounds.³⁰⁻³² Here we use the CNDO/2 approximation to examine the effect of conformation, substituent, and the extent of contribution of the Fermi contact mechanism.

The calculated nuclear spin couplings³³ are given in Table II. A description of the geometry chosen for these compounds

is given in the Experimental Section. Table II also lists the phosphorus 3s–nitrogen 2s bond orders. Calculations for tetravalent or pentavalent phosphorus atoms did not converge properly without d orbitals; therefore, these calculated values have not been included in Table II.

The immediate difficulty in calculating ^{15}N – ^{31}P couplings for the compounds in Table II is that the coupling is sensitive to the planarity at nitrogen. (The P–N couplings are insensitive to rotation about the P–N bond.) It has been established that the inversion barrier at nitrogen is markedly reduced by the substitution of an adjacent second row atom.³⁵ Our CNDO/2 calculations indicate that there is little difference (<4 kcal/mol) in the energy between the pyramidal and trigonal conformations for the compounds in Table II, with the exception of **12**. A good example of this dilemma is provided by **1** and **2**. When the . . .P–N–H dihedral angle ϕ is 0° , the CNDO/2 (spd) calculations favor trigonal **2** over pyramidal **1** by 1.0 kcal/mol. This is in reasonably good agreement with ab initio calculations on this molecule which included d orbitals on phosphorus and nitrogen.³⁵ However, upon rotation of the amino group by 60° , the pyramidal form is now favored by 1.9 kcal/mol. This effect has also been found in ab initio calculations.³⁷ Deleting the d orbitals in the CNDO/2 basis set inordinately stabilizes the pyramidal form. This is also a common feature when the inversion barriers at carbon are calculated for phosphonium ylides using the CNDO/2 approximation.³² However, extended Hückel calculations without d orbitals also suggest that trigonal **1** is more stable than pyramidal **2** when $\phi = 0^\circ$. They furthermore show that a large share of this stabilization occurs in the HOMO, basically a lone pair on nitrogen, in that the σ_{π^*} orbital on the phosphine fragment interacts strongly with the filled p orbital on nitrogen. Thus, the σ_{π^*} orbital is behaving in a completely analogous fashion to d orbitals on phosphorus. Substitution of electronegative groups on phosphorus will lower the energy of the σ_{π^*} level, and, therefore, allow greater interaction with the filled p orbital on nitrogen. This is supported by the microwave structure of difluoramino phosphine.³⁸ Here the nitrogen is trigonal with the amino group exactly bisecting the F–P–F angle. These calculations, of course, correspond to the gas phase and since the experimental ^{15}N – ^{31}P couplings are from the liquid state at room temperature, intermolecular interactions may be important and the energy differences will become more obscured. One conceivable exception to this occurs with **22**. Here trigonal **22** is calculated to be 11.1 kcal/mol more stable than the pyramidal **23**. This tendency has been discussed elsewhere on the basis of ab initio¹⁷ and extended Hückel calculations.¹⁸ (See ref 39 for experimental details on this compound; here the rotational and/or inversion barrier is found to be 11.1 kcal/mol.)

From Table II, it is seen that the substitution of two amino groups for hydrogens causes $^1J_{^{15}\text{N}-^{31}\text{P}}$ to become more negative for tetravalent phosphorus compounds. Since the magnetogyric ratio of ^{15}N is negative, this means that the reduced coupling constant for this substitution is becoming more positive. This is similar to what is found for $^1J_{^{31}\text{P}-^{13}\text{C}}$. This substitution in the case of trivalent phosphorus compounds does not seem particularly clear (i.e., compare **1** with **3** and **2** with **4**). The substitution of fluorine atoms for hydrogens generally causes $^1J_{\text{P-H}}$ and $^1J_{\text{P-C}}$ to increase. The CNDO/2 FPT calculations exaggerate this effect.³² Therefore, the calculated $^1J_{\text{N-P}}$ for **22** and **23** are likely to be overestimated (vide infra). The directly bonded P–H coupling for phosphine **1** is likely to be positive, based on sign determinations for several types of phosphines.⁴⁰ However, our calculations incorrectly predict it to be negative. This seems to be a common failing of the CNDO/2 FPT method.³² The $^1J_{\text{P-H}}$ calculated couplings for the other compounds in Table II are quite reasonable, with the magnitudes and relative orders in agreement with experimental

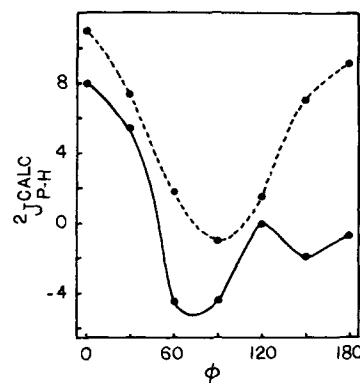


Figure 2. Calculated couplings for **1** (solid line) and **2** (dashed line) versus the . . .P–N–H dihedral angle ϕ .

findings.⁴⁰ Note in particular the very small $^1J_{\text{P-H}}$ calculated for the axial hydrogen when the amino group is also axial for **20** and **21**. A novel tricyclic phosphorus–nitrogen phosphorane which has this conformation has recently been reported to exhibit an unusually low $^1J_{\text{P-H}}$.⁴¹ The ^{31}P – ^{17}O couplings for **10** and **11** are in fair agreement with that found for tris(dimethylamino)phosphine oxide (Table I); however, the addition of two more amino groups causes the calculated $^1J_{^{31}\text{P}-^{17}\text{O}}$ to become too large. The magnitudes of $^2J_{\text{P-N-H}}$ are likely to be suspect, since two-bond couplings are only adequately described with the inclusion of one-center exchange integrals.²⁹ However, previous calculations on $^2J_{\text{P-C-H}}$ have given fairly reliable trends for these couplings.³² In Figure 2 the calculated $^2J_{\text{P-N-H}}$ for **1** and **2** is plotted for various . . .P–N–H dihedral angles (ϕ). The solid line refers to **1** and the dashed to **2**. The average of the pyramidal and trigonal conformations will make $^2J_{\text{P-H}}$ large at small ϕ , a minimum at $\phi \sim 75^\circ$, and finally at $\phi \sim 90^\circ$ $^2J_{\text{P-H}}$ will become larger but fairly insensitive to ϕ . This is similar to the INDO FPT calculations of $^2J_{\text{P-H}}$ in trimethylphosphine.³¹

In Figure 3 the calculated $^1J_{^{15}\text{N}-^{31}\text{P}}$ couplings are plotted against the phosphorus 3s–nitrogen 2s bond orders from Table II. Figure 3 was drawn for equal sensitivity to changes in P^2_{SPN} and $^1J_{\text{P-N}}$. Compounds **7**, **8**, and **9** are significantly displaced from the line (**8** and **9** are not shown for convenience). The values of $^1J_{\text{P-N}}$ for these compounds seem to be greatly overestimated. The displacement of trifluorodiaminophosphorane (**22**) can be seen to be a result of the CNDO/2 FPT tendency to exaggerate the inductive effects of fluorine substituents (as described above). In other words, from the line in Figure 3 and the P^2_{SPN} for **2** a $^1J_{\text{P-N}}$ of -80 Hz is expected. This agrees well with the value of -81.5 Hz given experimentally.^{4a} The other compounds fall fairly close to the line giving support to the notion that the $^1J_{\text{P-N}}$ couplings can be tentatively related to the percent s character comprising the P–N bonds.³⁷ This situation is also evident for $^1J_{\text{P-C}}$ ^{30,32} and $^1J_{\text{P-H}}$.³²

A comparison of the experimental and calculated $^1J_{\text{P-N}}$ couplings is given in Table III. Here for the triamino-substituted compounds we have taken the average of the pyramidal and trigonal calculated couplings since the inversion barriers for these compounds are calculated to be very small (note that there will be two pyramidal conformers for each trigonal one). Since the gas phase structure for aniline shows the nitrogen to be close to the trigonal conformation⁴² and the presence of a phosphorus-containing group adjacent to the nitrogen will greatly add to the stability of the trigonal form, we have compared the calculated P–N couplings for only the trigonal geometry with those found for the anilindimethyl-substituted phosphorus compounds. At any rate, a Boltzmann distribution of these compounds at room temperature should be highly

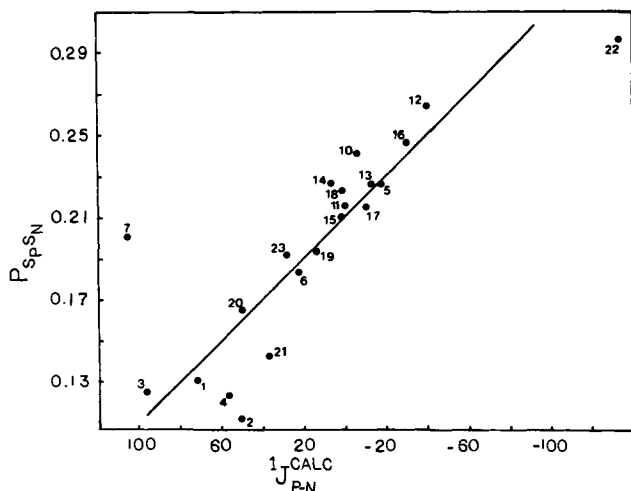


Figure 3. Relationship of calculated $^1J_{P-N}$ and the $P_{3s}-N_{2s}$ bond order. 8 and 9 are omitted.

Table III. Comparison of Experimental and Calculated $^{31}P-^{15}N$ Couplings^a

Exptl compd	J^{Exptl}	J^{Calcd}	Calcd compd
$(Me_2N)_3P$	+59.1	+70.0 ^b +65.6 ^{b,c}	$(H_2N)_3P$
$(Me_2N)_3P=O$	-26.9	-21.0 ^b	$(H_2N)_3P=O$
$(Me_2N)_3P=S$	(\mp)6.0	-12.7 ^b	$(H_2N)_3P=S$
Me_2PNHPh	+53.0 ^e	+75.6 ^d +67.9 ^{c,d}	H_2PNH_2
$Me_2P(O)NHPh$	-0.5 ^e	-6.2 ^d	$H_2P(O)NH_2$
$Me_2P(S)NHPh$	+11.3 ^e	+7.0 ^d	$H_2P(S)NH_2$
$F_3P=NPf_2$	-53.2 ^f	+494.8 ^d	$F_3P=NH$
$F_3P(NH_2)_2$	-81.5 ^f	-134.1 ^d	$F_3P(NH_2)_2$

^a Including d orbitals, unless otherwise noted. ^b These values represent the average between pyramidal and trigonal geometries at nitrogen. ^c Without d orbitals. ^d These values represent those calculated for trigonal geometries at nitrogen. ^e Values taken from ref 5. ^f Values taken from ref 4a.

weighted in favor of the trigonal geometry.⁴³ The calculated couplings for the molecules in Table III agree very nicely in sign and magnitude with the experimental ones, with the exception of the trifluorophosphinimine. As it has been noted previously, the CNDO/2 FPT calculations break down completely for the phosphinimines. The trifluoroaminophosphorane had been shown not to undergo pseudorotation at room temperature.³⁹ We have compared the calculated $^1J_{P-N}$ value for the trigonal geometry only, in view of the computed large stabilization of this geometry. Note that the oxides have a smaller (i.e., more negative) $^1J_{P-N}$ than the sulfides. This is correctly predicted by the calculations, including the sign reversal for the anilindimethyl-substituted compounds. We predict that the coupling of the tris(dimethylamino)phosphine sulfide should remain negative, however. The replacement of two alkyl groups with amino groups does little to affect $^1J_{P-N}$ for phosphines. However, this substitution for the phosphine oxides and sulfides makes $^1J_{P-N}$ become more negative. Our calculations accurately reflect these trends. Additionally, in view of the good correlation of these couplings with the experimental values, changes in the Fermi-contact contribution to P-N couplings are likely to be those producing the dominant effects.

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References and Notes

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