Conformational Effects on *PNCH, PNC,* and *PNSi* Spin Coupling in Tervalent Phosphorus–Nitrogen Compounds

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The ^{1}H and ^{13}C n.m.r. spectra of a series of tervalent phosphorus–nitrogen compounds having a known conformation about the P–N bond have been obtained. These measurements confirm previous assumptions that the coupling constants *J*(*PNCH*) and *J*(*PNC*) are relatively large and positive for a methyl group having a *cis* relation with the lone pair of electrons on phosphorus. *J*(*PNCH*) is small, and *J*(*PNC*) small and negative when the methyl group is *trans* to the lone pair. The results are discussed by reference to compounds of unknown conformation. The coupling constant, *J*(*PNSi*), in a series of silylaminophosphines, $Ph_2P{\cdot}NR{\cdot}SiMe_3$ (R = Me, Et, Pr^i, or Bu^t), also appears to be related to the conformation adopted by the P–N bond.

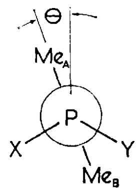

FIGURE 1 The dihedral angle, θ, for an aminophosphine, $P(NMe_2)(X)Y$

IT has been recognised [1-8] for several years that the spin coupling constant, *J*(*PNCH*), in tervalent phosphorus–nitrogen compounds has a marked stereochemical dependence. This was clearly demonstrated by studies of the low-temperature ^{1}H n.m.r. spectra of the aminophosphine, $PPhCl(NMe_2)$, and related compounds [1,5,7] in which rotation about the P–N bond became slow on the n.m.r. time scale and two distinct *P*–N–C–*H* couplings were measurable. Both couplings had the same sign but a problem was posed [1] in relating the individual couplings to the position of the methyl groups relative to the lone pair of electrons on phosphorus. A planar, or near planar, distribution of bonds about nitrogen is generally observed in aminophosphines [9-15] so that the assignment of couplings may be considered by reference to Figure 1. The dihedral angle θ for the aminophosphine, $P(NMe_2)(X)Y$, is that between the plane containing the P, N, and C$_A$ (in Me$_A$) atoms and the plane † which bisects XPY along the P–N axis. After consideration of the ^{1}H n.m.r. spectra of $P(CF_3)_2(NMeH)$ it was proposed [1] that *J*(*PNCH*) is relatively large (±19.2 Hz) for methyl group A (θ *ca.* 0°) and relatively small (±6.7 Hz) for methyl group B (θ *ca.* 180°) in $PPhCl(NMe_2)$. The same relation has been assumed [2] in making assignments to the ^{13}C spectra of $PPh(NMe_2)X$ (X = Cl or OMe); *J*(*PNC*) for X = Cl is relatively large and positive (±33.9 Hz) when θ *ca.* 0°, but smaller and negative (∓11.4 Hz) when θ *ca.* 180°. A similar relation is suggested for *J*(*PNC*) and *J*(*PNCC*) in $PR(Cl)(NPr^i_2)$ (R = Me or Ph),[6] and for *J*(*PNP*) in diphosphinoamines.[16]

In order to extend and, if possible, confirm these proposals for *J*(*PNCH*) and *J*(*PNC*), we have examined the ^{1}H and ^{13}C n.m.r. spectra of several tervalent phosphorus–nitrogen compounds of known crystal structure (or preferred conformation established by electron diffraction), and assumed the preferred structure in solution is the same. The angle θ has not been reported in most structure determinations and, where possible, we have used the fractional co-ordinates to obtain this angle.

RESULTS

Hydrogen-1 and ^{13}C n.m.r. data for the *N*-methyl groups of compounds of known structure are listed in Table 1. The relative signs of the coupling constants were established by ^{1}H-{^{13}C}, ^{1}H-{^{31}P}, and ^{13}C-{^{1}H} double-resonance experiments. *J*(*PNCH*) had the same sign as *J*(*CH*) in selected cases (see Tables 1 and 2) and is always assumed to be positive. In those cases where ^{13}C satellites were too low in intensity to obtain relative sign information from the ^{1}H spectra the relative signs of *J*(*PNC*) and *J*(*PNCH*) were

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† This plane is assumed to bisect the lone pair, but when X ≠ Y this is not strictly correct.

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obtained by off-resonance ^{13}C-{^1H} experiments. The signs of the two *J*(*P*N*C*) couplings relative to *J*(*P*N*P*) in Ph_2P·NMe·P(S)Ph_2 were obtained by ^{13}C-{^{31}P} experiments under conditions of ^1H noise decoupling. The case of F_2P·NMe·PF_2 is complicated by the coupling to four fluorine nuclei; however, a single experiment (Figure 2) is sufficient to obtain the relative signs. In Figure 2(*b*) the proton irradiation field is set to high frequency of the *N*-methyl proton signals (the intensities are distorted because of population-transfer effects). Comparison of appropriate residual $^{13}C \cdots {}^1H$ couplings [for example (1—5) < (3—7) and (2—6) < (4—8) shows that *J*(*P*N*C*)/*J*(*P*NC*H*) and *J*(*H*CNP*F*)/*J*(*F*PN*C*) are both positive.

TABLE 1

Hydrogen-1 and ^{13}C n.m.r. data for tervalent phosphorus–nitrogen compounds of known conformation

Compound	*J*(*P*NC*H*) [a]/Hz	*J*(*P*N*C*)/Hz	δ_C/p.p.m.	Structure ref.
$PCl_2(NMe_2)$	±12.9 [b,c]	±21.2 ± 1 [b]	38.3 [b]	1, 12, 21
$PCl(NMe_2)_2$	±11.8 [b,c]	±16.5 ± 1 [b]	38.8 [b]	*d*
$P(NMe_2)_3$	±8.8 [c,e]	±19.0 ± 0.5 [e,f]	38.3 [e,f]	22, 23
F_2P·NMe·PF_2	±3.0 [g]	±2.25 ± 0.1 [g]	21.4 [g]	13
	[*J*(*H*CNP*F*) ± 1.5]	[*J*(*F*NP*C*) ± 7.6]		
ClP·NBu^t·PCl·NMe	±11.1 [b,c]	±15.0 ± 1 [b] (NMe)	28.7 [b]	*cf.* 25
$(ClPNBu^t)_2$		6.6 ± 0.5 [g]	54.1 [g]	25
		[*J*(PNCC) 6.1]		
ClPNMeCH$_2$CH$_2$NMe	±15.1(Me) [e]	±18.8 ± 0.2 [e]	33.1 [e]	
	±7.2(CH_2) [h]	∓10.8 ± 0.2	48.8	24
ClPNMeNMeP(Cl)NMe	12.3(PNMeP) 17.3(PNMeN) [i] (from ref. 28)			35
Ph_2P·NMe·P(S)Ph_2	±1.8 [e]	∓5.0 ± 0.5 [e]	32.1 [e]	15
		[*J*(*P*^{V}N*C*) ± 5.0, *J*(*P*N*P*) ± 99]		
$P(NMeNMe)_3P$	±15.4 [c,i,j]	±12.8 ± 0.2 [e,i,j]	37.3 [e]	33
$ClP(NMeNMe)_2PCl$	16.8 [i] (from ref. 28)			34
$P_4(NMe)_6$	±16.3 [e,j]	±36.4 ± 0.1 [e,j] (see text)	37.3 [e]	37

[a] ±0.1 Hz, except for data from ref. 28. [b] Solutions in CH_2Cl_2. [c] Same sign as *J*(*CH*). [d] N. M. Zaripov, N. A. Naumov, and L. L. Tuzova, *Phosphorus*, 1974, **4**, 179. [e] In $CDCl_3$. [f] In good agreement with the results of R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1908; G. A. Gray and T. A. Albright, *ibid.*, 1976, **98**, 3857. [g] In C_6D_6. [h] Mean value, see ref. 3. [i] \|*J*(*P*NC*H*) + *J*(*P*NNC*H*)\| or \|*J*(*P*N*C*) + *J*(*P*NN*C*)\|. [j] Complex triplet, see text.

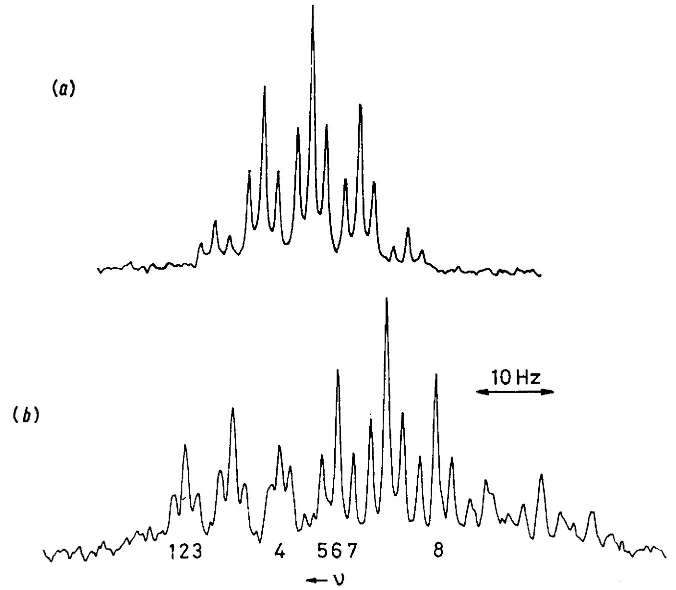

FIGURE 2 Carbon-13 n.m.r. spectra of F_2P·NMe·PF_2: (*a*) with proton noise decoupling; (*b*) with proton irradiation to high frequency of *N*-methyl signals (see text). Both spectra were recorded with the same offset

The ^{13}C n.m.r. spectra of the phenyl groups of the diphosphinoamines, Ph_2P·NR·PPh_2 (R = Me, Et, or Pr^i), are of the AA′X type (or ABX in the event of a small ^{13}C isotope shift). Of the six-line pattern expected for the X(^{13}C) spectrum,[17] we observed a deceptively simple triplet (R = Me or Et), the separation of the outer components of which is $|J(PC^n) + J(PNPC^n)|$. The triplet structure shows that $|J(PNP)| \gtrsim |J(PC^n) + J(PNPC^n)|$. However, when R = Pr^i, C^1 and C^2 were doublets and C^3 had triplet structure. This places a value of *ca.* 10 Hz on $|J(PNP)|$ (*i.e.* between 6.3 and 13.3 Hz). The small value of $|J(PC^1) + J(PNPC^1)|$ when R = Me, relative to R = Et or Pr^i [or *J*(PC^1) in PPh_3 (Table 3)] suggests that *J*(*P*NP*C*^{1}) is significant. ^1H-{^{31}P} INDOR results[16] on Ph_2P·NR·PPh_2 (R = Et or Pr^i) indicated that $|J(PNP)|$ is < *ca.* 50 Hz.

TABLE 2

Hydrogen-1 and ^{13}C n.m.r. data for selected tervalent phosphorus–nitrogen compounds

Compound	*J*(*P*NC*H*) [a]/Hz	*J*(PNC)/Hz	δ_C/ p.p.m.
Cl_2P·NMe·PCl_2	±3.0 [b,c]	∓1.6 ± 0.3 [a,d]	28.8 [b]
Cl_2P·NMe·P(O)Cl_2	±1.6 [b]	∓2.8 ± 0.2 [b]	31.5 [b]
	[*J*(*P*^{V}NC*H*) ±15.5]	[*J*(*P*^{V}N*C*) ±1.8]	
PCl_2(NMePh)	±4.8 [b]	∓3.8 ± 0.3 [b]	35.3 [b]
PPh_2(NMePh)	±1.7 [b]	∓8.7 ± 0.3 [b]	35.7 [b]
Cl_2P·NMe·$SiMe_3$	±6.8 [c,e]	∓4.2 ± 1 [e]	30.5 [e]
Ph_2P·NMe·PPh_2	±3.0 [f]	∓5.4 ± 0.2 [f]	32.6 [f]

[a] ±0.1Hz. [b] In C_6D_6. [c] Same sign as *J*(*CH*). [d] −2.0 ± 0.5 Hz in I. J. Colquhoun and W. McFarlane, *J.C.S. Faraday II*, 1977, 722. [e] In CH_2Cl_2. [f] In $CDCl_3$.

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The ^{13}C spectrum of $P(NMeNMe)_3P$ was a deceptively simple triplet (Table 1), but for reasons which are not clear the centre component of the triplet was much broader than the outer components. Similar effects were apparent in the ^{13}C spectra of $P_4(NMe)_6$ (Figure 3). The results of spectra simulations of this $AX_2X'_2$ spin system do not give an upper estimate of $J(PNP)$, but they do show that the inclusion of a four-bond coupling, $J(PNPNC)$, doubles up the outer components of the triplet. The observed separation of the outer sharp lines (72.8 Hz) is therefore a close approximation to $2J(PNC)$.

TABLE 3

Carbon-13 data [a] for diphenylphosphinoamines, $Ph_2P{\cdot}NR{\cdot}PPh_2$

R	δ(NC) p.p.m.	$J(PNC)$ Hz	δ(C^1) p.p.m.	J(PC^1) Hz	δ(C^2) p.p.m.	J(PC^2) Hz	δ(C^3) p.p.m.	J(PC^3) Hz
Me	32.6	−5.4	138.5	6.5	132.4	20.7	128.2	6.3
Et	47.2	+11.3	139.6	12.5	132.6	22.2	128.0	6.0
Pr^i	51.9	+10.3	139.9 [b]	13.3	132.9 [b]	22.8	128.0	6.3
PPh$_3$ [c]				−12.51		+19.65		+6.80

[a] In $CDCl_3$ at ambient temperatures. C^1, C^2, and C^3 signals appeared as deceptively simple triplets, and the separation of the outer components of these triplets gave $|J(PC^n) + J(PNPC^n)|$ (±0.7 Hz); see text for interpretation in terms of individual couplings. C^4 was a singlet at δ 128.6 ± 0.1 in all three cases. [b] Doublet. [c] S. Sørensen, R. S. Hansen, and H, J. Jakobsen, *J. Amer. Chem. Soc.*, 1972, **94**, 5900.

^{1}H-{^{29}Si} and ^{1}H-{^{31}P} double-resonance experiments on the ^{29}Si satellites of the SiMe$_3$ signals of the compounds listed in Table 4 showed that $J(PNSi)$ and $J(SiCH)$ have opposite signs (taking into account [18] a negative magnetogyric ratio for ^{29}Si). The latter coupling is known [19] to be positive in $SiMeCl_2H$, so we deduce that $J(PNSi)$ has a negative sign. The four-bond coupling $J(PNSiCH)$ is also positive. It was possible to check these assignments in the case of $PCl_2[NMe(SiMe_3)]$ since ^{29}Si satellites of the *N*-methyl signals were observable and the relative signs of $J(PNCH)$ and $J(PNSi)$ could be established by ^{1}H-{^{29}Si} double-resonance experiments.

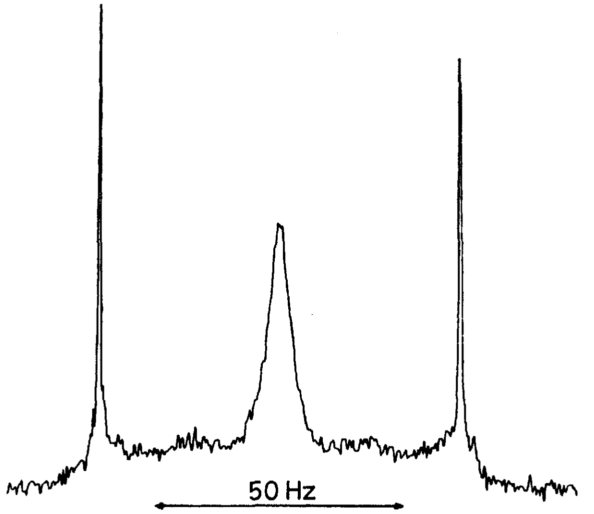

FIGURE 3 ^{13}C-{^{1}H} n.m.r. spectrum of $P_4(NMe)_6$, obtained without exponential weighting of Free Induction Decay

DISCUSSION

Both $J(PNCH)$ and $J(PNC)$ decreased with increasing values of n in the series $PCl_{3-n}(NMe_2)_n$ (n = 1—3). This trend has previously been reported for $J(PNCH)$.[20] In order to relate these couplings to the approximate conformations adopted about the P–N bonds, about which there has been some dispute for $PCl_2(NMe_2)$ [1,21] and $P(NMe_2)_3$,[22,23] it is necessary to establish whether the sum of the two 90° couplings is greater than the sum of the couplings for θ = 0 and 180°. This is not possible, but there is little doubt that the larger couplings, for $n = 1$, most closely represent the latter combination of angles in solution.[1]

In a recent electron-diffraction study [13] it was established that $F_2P{\cdot}NMe{\cdot}PF_2$ adopts a preferred conformation in which both angles θ = 180°. Also, the crystal structure of the diphenylphosphino-derivative, $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$,[15] shows that θ = 160°. Whilst correlations involving these compounds require an extrapolation between the vapour or solid phase and solution, the relatively small $PNCH$ couplings are consistent with the proposals for $PPh(Cl)(NMe_2)$.[1] The negative PNC coupling for $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$ is also to be expected on this basis, but it is surprising that $F_2P{\cdot}NMe{\cdot}PF_2$ has a positive PNC coupling, albeit small.

TABLE 4

N.m.r. data for silylaminophosphines [a]

Compound	δ(^{31}P) [b] p.p.m.	δ(^{29}Si) [c] p.p.m.	$J(PNSi)$ [d,e] Hz	$J(PNSiCH)$ [d,f] Hz
$Cl_2P{\cdot}NMe{\cdot}SiMe_3$	173.5	15.8	−44	+2.8
$Cl(Ph)P{\cdot}NMe{\cdot}SiMe_3$	137.6	15.9	−34	+1.9
$Ph_2P{\cdot}NMe{\cdot}SiMe_3$	48.5	12.1	−32	+1.4
$Ph_2P{\cdot}NEt{\cdot}SiMe_3$	45.8	10.7	−33	+1.3
$Ph_2P{\cdot}NPr^i{\cdot}SiMe_3$	42.1	9.0	−10	+0.8
$Ph_2P{\cdot}NBu^t{\cdot}SiMe_3$	46.9	8.3	$|<10|$	$|<0.2|$

[a] In CH_2Cl_2 solution at ambient temperatures, measured using ^{1}H-{^{31}P} and ^{1}H-{^{29}Si} double-resonance methods. [b] Downfield from 85% H_3PO_4. [c] Downfield from internal SiMe$_4$. [d] Sign assumes $J(SiCH)$ and $J(PNCH)$ positive. $J(SiCH)$ was *ca.* 8 Hz in each case. [e] ±2 Hz. [f] ±0.1 Hz.

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Intermediate values of θ are to be found in the diazaphospholan,[24] $ClPNMeCH_2CH_2NMe$ which probably has an envelope conformation in the vapour phase from which angles θ of 70 ± 20 and 150 ± 20° may be estimated for N–Me and N–CH_2 groups respectively. In the cyclodiphosphazane $ClP{\cdot}NBu^t{\cdot}PCl{\cdot}NMe$, θ is *ca.* 70°, provided that the compound retains a conformation similar to that of $ClP{\cdot}NBu^t{\cdot}PCl{\cdot}NBu^t$.[25] The $P^{III}NC\mathit{H}$ couplings for *N*-methyl groups which form part of a four-,[26] five-,[3,27,28] or six-membered [29-31] ring generally occur in the range 10—19 Hz, with some of the largest couplings observed in 2-phospha-1,3-diazacyclohexanes.[29] Apparently, the only exceptions are to be found with the dimethylamino-derivatives $Me_2N{-}POCH_2CH(Me)NMe$ and $Me_2N{\cdot}P(NMeNMe)_2P{\cdot}NMe_2$, where $|J(PNCH)|$ 7.5 (ref. 32) and an apparent 6.9 Hz (see below) [28,31] respectively.

The crystal-structure data [33] for the cage diphosphine $P(NMeNMe)_3P$ may be used to give θ = 49.5° for an apparent $P \cdots H$ coupling of 15.4 Hz.[30] In $ClP(NMeNMe)_2PCl$ θ is 65°,[34] and in $ClPNMeNMeP(Cl)NMe$ θ is 42.6 (PNMeP) and 68.1° (PNMeN),[35] for which couplings of 16.8,[35] 12.3, and 17.3 Hz (ref. 28) respectively have been obtained. The couplings which relate to the PNMeNMeP group are $|J(PNCH) + J(PNNCH)|$ and may not bear a straightforward relation to θ if $J(PNNCH)$ is significant. It is worth noting that $J(PNNCH)$ is zero in *NN*-dimethylhydrazino-derivatives of phosphines.[36] The apparent 16.3 Hz coupling observed in the ^1H spectrum of $P_4(NMe)_6$ is also complicated by long-range coupling effects. Its crystal structure has been established,[37] and this indicates that θ is *ca.* 0°.

The separation of the outer components of the triplet in the ^{13}C n.m.r. spectrum of $P_4(NMe)_6$ gives $J(PNC)$ +36.2 Hz (see above); this is good evidence for a relatively large and positive θ *ca.* 0° coupling. The +12.8 Hz separation of the outer components of the triplet obtained in the ^{13}C spectrum of $P(NMeNMe)_3P$ is $|J(PNC) + J(PNNC)|$. Trial simulations show that, whilst $J(PNNC)$ affects the intensity and position of the combination lines (which were not seen), it could assume values approaching that of $J(PNC)$ and still leave the spectrum as a triplet.

In Figure 4 $J(PNCH)$ is plotted against estimated values of θ, and this shows that there is no doubt that the assignment [1,2] applied to $PPh(Cl)(NMe_2)$ and related compounds is correct. Indeed, the ^1H and ^{13}C n.m.r. data obtained [1,2] for this molecule would fit that in Figures 4 and 5 quite well making the approximation that θ = 0 and 180°. A scatter of points is to be expected in view of (*i*) the changes in electron-supplying power of the phosphorus and nitrogen substituents, (*ii*) the approximate values of θ in some cases, and (*iii*) the uncertainties involved in extrapolating solid-state data to solution. It is clear, however, that the conformation adopted by the P–N bond is the most important factor determining the magnitude of $J(PNCH)$. When $J(PNC)$ is plotted against θ (Figure 5) the scatter of points is as great as that for $J(PNCH)$, but the general form of the relation with θ is established. Less significance may be placed on point (*b*) $P(NMeNMe)_3P$ (see above), and on points (*d*), $ClPNMeCH_2CH_2NMe$, and (*f*)

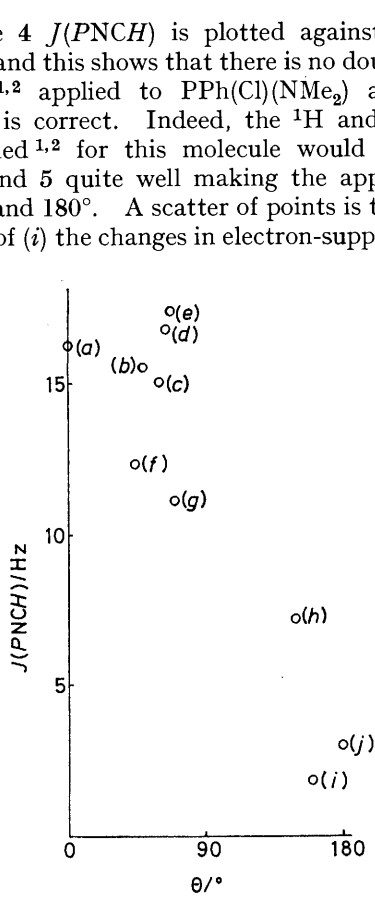

FIGURE 4 Graph of $J(PNCH)$ against θ for (*a*) $P_4(NMe)_6$, (*b*) $P(NMeNMe)_3P$, (*c*) $ClPN\mathit{Me}CH_2CH_2N\mathit{Me}$, (*d*) $ClP(NMeNMe)_2PCl$, (*e*) $ClPN\mathit{Me}N\mathit{Me}P(Cl)NMe$, (*f*) $ClPNMeNMeP(Cl)N\mathit{Me}$, (*g*) $ClP{\cdot}NBu^t{\cdot}PCl{\cdot}NMe$, (*h*) $ClPNMeC\mathit{H}_2C\mathit{H}_2NMe$, (*i*) $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$, and (*j*) $F_2P{\cdot}NMe{\cdot}PF_2$

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$(ClPNBu^t)_2$, which refer to CH_2– and $(CH_3)_3C$–carbon couplings respectively.

An attempt was also made to relate the position of *N*-methyl groups to the phosphorus lone pair in PPh(Cl)(NMe_2) (ref. 1) and in the cyclodiphosphazane Me_2N-P·NBu^t·PCl·NBu^t (ref. 38) by the Nuclear Overhauser Effect. Homonuclear double-resonance experiments involving irradiation of the phenyl and t-butyl protons respectively at low temperatures had no discernible effects on the *N*-methyl signals, which were non-equivalent because of slow rotation about the P–N bond.

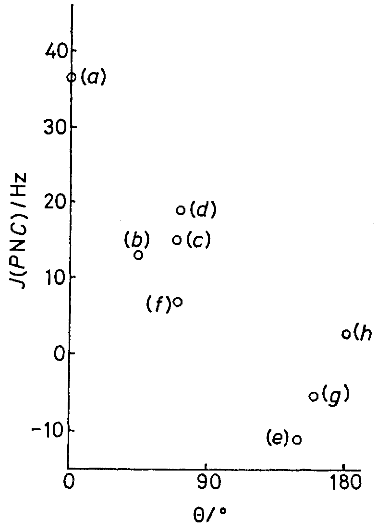

FIGURE 5 Graph of *J*(*P*N*C*) against θ for (*a*) $P_4(NMe)_6$, (*b*) $P(NMeNMe)_3$, (*c*) ClP·NBu^t·PCl·NMe, (*d*) ClPN*Me*CH_2CH_2N-*Me*, (*e*) ClPNMeCH_2CH_2NMe, (*f*) $(ClPNBu^t)_2$ [*J*(*P*N*C*) assumed positive], (*g*) Ph_2P·NMe·P(S)Ph_2, and (*h*) F_2P·NMe·PF_2

Hydrogen-1 and ^{13}C n.m.r. data for other tervalent phosphorus–nitrogen compounds are listed in Table 2, where, in general, structural information is lacking. In the light of the foregoing discussion, Cl_2P·NMe·PCl_2 (ref. 39) would be expected to have a preferred conformation close to that of its fluorinated analogue (θ *ca.* 180°).[13] A similar preferred conformation may be expected for the P^{III}–N bond in Cl_2P·NMe·P(O)Cl_2.[40] The relatively small changes in *J*(*P*NC*H*) and *J*(*P*N*C*) on passing from Cl_2P·NMe·PCl_2 to Cl_2P·NMe·P(O)Cl_2 could be the result of conformational or electronic effects (which are doubtless interdependent anyway). The more negative *J*(*P*N*C*) in (PPh_2)(NMePh) relative to (PCl_2)(NMePh) could be viewed in terms of steric interactions resulting in a more preferred θ *ca.* 180° conformation in the former molecule. However, the effect of more *s* character in the P–N bond as a result of the relatively electronegative phosphorus substituents[41] is difficult to predict. There is only a very general correlation between *J*(*P*N*C*) and *J*(*P*NC*H*) for the data in Tables 1 and 2.

The *P*N*P* coupling constants in bis(diphenylphosphino)amines, Ph_2P·NR·PPh_2, have been related to the approximate conformations adopted by the P–N bonds.[16] The large positive *P*N*P* coupling observed when R = Me suggests that the preferred angles θ are near 180°, a result also expected from the small value of *J*(*P*NC*H*) and negative *J*(*P*N*C*). The *P*N*C*(alkyl) coupling in Ph_2P·NR·PPh_2 is much more positive when R = Et or Pr^i than when R = Me. For R = Et or Pr^i this suggests a small angle θ, which is in good accord with the relatively small *P*N*P* couplings (< *ca.* 50 Hz) observed[16] for these compounds.

The ^1H n.m.r. spectra of a series of silylaminophosphines[42,43] (Table 4) were examined to try to establish whether the coupling constant *J*(*P*N*Si*) also has a conformational dependence. This type of coupling involving tervalent phosphorus has been reported for $(Me_3Si)_2N$·P⁚N·$SiMe_3$,[44] where |*J*(PNSi)| is greater for the ⁚N·$SiMe_3$ group (26.8 Hz) than for the ·$N(SiMe_3)_2$ group (9.1 Hz). During the course of this work the crystal structure of the dimeric form of this phosphazene, namely $[(Me_3Si)_2N\cdot PNSiMe_3]_2$, was reported[45] and this shows that the $N(SiMe_3)_2$ groups have a planar distribution of bonds about nitrogen and that the $SiMe_3$ groups lie *cis* (θ 0°) and *trans* (θ 180°) to the lone pairs on phosphorus. In solution, rotation about the exocyclic P–N bonds is slow on the n.m.r. time scale, and two couplings, |*J*(*P*N*Si*) + *J*(*P*NPN*Si*)| of 3.4 and 31.0 Hz, are observed. Several examples of *P*N*Si* coupling involving quinquevalent phosphorus have been reported.[46,47]

It is clear that *J*(*P*N*Si*) is also dependent on the steric bulk of the R group in the series Ph_2P·NR·$SiMe_3$. It is not clear whether the more negative result for X = Cl than Ph in X_2P·NMe·$SiMe_3$ can be related to the electronegativity of the phosphorus substituents. The trend for the diphenylphosphino-derivatives suggests that *J*(*P*N*Si*) will be most negative if a preferred conformation in which θ is small is adopted. Increasing size of the R group would be expected to increase the importance of those conformations where θ approaches 180°. The trend to less negative *P*N*Si* couplings is paralleled by the trend to less positive *P*NSiC*H* couplings. The conformational dependence of the latter coupling has recently been recognised[48] in $P(CF_3)_2[N(SiMe_3)_2]$ and in $[(Me_3Si)_2N\cdot PNSiMe_3]_2$[45] (see above), where the only *P*NSiC*H* coupling (2.8 Hz) observed in the former compound was assigned to the $SiMe_3$ group *cis* to the lone

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pair on phosphorus (θ *ca.* 0°). Our findings add further weight to this assignment.

EXPERIMENTAL

Continuous-wave ^1H and pulsed-Fourier-transform ^{13}C n.m.r. spectra were obtained on JEOL C60HL (60 MHz) and Varian XL-100 (25.2 MHz) spectrometers respectively. Values of $J(PNC)$ were obtained from spectra with a digital resolution of 0.25 Hz or better. ^1H-$\{^{13}C\}$, ^1H-$\{^{31}P\}$, and ^1H-$\{^{29}Si\}$ experiments on the C60HL were carried out as previously described.[16] ^{13}C-$\{^1H,^{31}P\}$ triple-resonance experiments were performed using the XL-100; the decoupler transmitter coil was double-tuned to accept 100 MHz from the power amplifier of the Gyrocode decoupler and 40 MHz direct from the output of a ND-100M Schomandl frequency synthesiser. Spectral simulations were calculated using the Simeq II program of C. W. F. Kort and M. J. A. De Bie on the Varian computer of the XL-100 spectrometer. The compounds $PCl_{3-n}(NMe_2)_n$ (n = 1—3),[49] $Cl_2P{\cdot}NMe{\cdot}PCl_2$,[39] $F_2P{\cdot}NMe{\cdot}PF_2$,[39] $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$,[40] $PCl_2(NMePh)$,[49] $Cl_2P{\cdot}NMe{\cdot}SiMe_3$,[42] $Cl(Ph)P{\cdot}NMe{\cdot}SiMe_3$,[42] $PPhCl(NMe_2)$,[1] $Cl\overline{PNMeCH_2CH_2N}Me$,[50] $P(NMeNMe)_3P$,[31,51] $P_4(NMe)_6$,[52] $Cl\overline{P{\cdot}NBu^t{\cdot}PCl{\cdot}N}Me$,[53] $(ClPNBu^t)_2$,[42] Me_2N-$\overline{P{\cdot}NBu^t{\cdot}PCl{\cdot}N}Bu^t$,[38] $PPh_2(NMePh)$,[49] $Ph_2P{\cdot}NR{\cdot}SiMe_3$ [R = Me, Et, Pr^i, or Bu^t: b.p. 55—60 °C (0.1 mmHg)],[43] $Ph_2P{\cdot}NR{\cdot}PPh_2$ (R = Me,[54] Et,[54] or Pr^i [16]), and $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$ [43] were prepared by literature methods.

We thank the S.R.C. for the award of a studentship (to G. B.) and assistance with the purchase of n.m.r. equipment, and Dr. P. Mallinson for the calculation of dihedral angles from fractional co-ordinates.

[7/1559 *Received*, 31*st August*, 1977]

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