Angular Dependence of Two-bond Coupling Constant $^{2}J_{\rm PNC}$ in the *NN*-Dimethylaminophosphines

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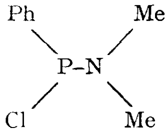
Summary Low-temperature carbon-13 n.m.r. spectra of *NN*-dimethylaminophosphines show the two-bond coupling constant $^{2}J_{\rm PNC}$ to be large and positive when the CN bond is *cis* with respect to the phosphorus lone pair, whilst it becomes small and negative in the *trans*-conformation.

Previous work on P–^{13}C scalar coupling in substituted ethylene phosphines suggested that these coupling constants might be dependent upon conformation,[1] and recently it has been shown that $^{2}J_{\rm PCC}$ are indeed stereospecific in cyclic phosphines.[2] We report here experimental evidence for such an angular dependence of the two-bond coupling constant $^{2}J_{\rm PNC}$ in the aminophosphines.

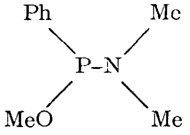
Rotational barriers around the PN bond are high enough (7—10 kcal/mol) to allow observation of fixed conformations at low temperatures. ^{1}H N.m.r. spectra of various *NN*-dimethylaminophosphines indicate that, at low temperature, the two methyl protons become diastereotopic,[3,4] implying a conformation as in (**1**), in agreement with an *X*-ray structure analysis of F_2P-NMe_2.[5] The latter proved nitrogen to be trigonal, thus confirming the existence of a

p_π–d_π bond. It has moreover been shown[4] that the methyl protons (A) *cis* to the phosphorus lone pair resonate at low-field and are more strongly coupled to phosphorus, so that $^{3}J_{\text{PNCH(A)}} > {}^{3}J_{\text{PNCH(B)}}$, the two coupling constants being of the same sign, and probably positive.

^{13}C Fourier transform proton noise-decoupled spectra of aminophosphines (**1**) and (**2**) have been recorded at 25·1 MHz on a Varian XL-100-15 n.m.r. spectrometer, above and below the coalescence temperature. Full experimental details will be published elsewhere.



(**1**)



(**2**)

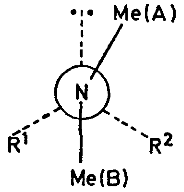
At room temperature, the carbon atoms of the methyl groups are equivalent, and an average coupling constant $^{2}J_{\text{PNC}}$ is observed. The sign of $^{2}J_{\text{PNC}}$ in chloro-*NN*-dimethylaminophenylphosphine can be related to that of $^{3}J_{\text{PNCH}}$, which is known to be positive,[6,7] by the off-resonance technique,[8,9] by irradiation 1·2 p.p.m. downfield from Me_4Si, *i.e.* high-field relative to the proton signal, which resulted in two quartets the one at high-field showing a smaller residual splitting. This proves the phosphorus spin state is the same for the high-field components in the proton and ^{13}C spectra. Therefore $\langle {}^{2}J_{\text{PNC}} \rangle$ has the same sign as $\langle {}^{3}J_{\text{PNCH}} \rangle$, *i.e.* positive, in agreement with the positive value found for $^{2}J_{\text{PNC}}$ in trisdimethylaminophosphine.[6]

TABLE. *$^{2}J_{\text{PC}}$ and ^{13}C chemical shifts in dimethylaminophosphines.*

Compound	Temperature^{a}	$\langle\delta(^{13}C)\rangle^{b}$	$\langle {}^{2}J_{\text{PNC}}\rangle$ /Hz	δ C(A)^{b}	δ C(B)^{b}	$^{2}J_{\text{PNC(A)}}$ /Hz	$^{2}J_{\text{PNC(B)}}$ /Hz
(1)	$+30^{\circ c}$	39·2	+12·0				
	$-60^{\circ c}$			41·8	36·4	+33·9	−11·4
(2)	$+30^{\circ c}$	38·6	+15·6				
	$-100^{\circ d}$			42·8	35·2	+40	−7

[a] Temperatures in °C are accurate to ±5 °C. [b] Chemical shifts are given in p.p.m. downfield from Me_4Si. [c] $C_6D_5{\cdot}CD_3$ solvent. [d] $CFCl_3$–$(CD_3)_2CO$ solvent.

At low temperature, however, slow rotation around the P–N bond renders the two carbon atoms diastereotopic, giving rise to two doublets. Continuous-wave proton decoupling experiments allowed assignment of the carbon resonances in chloro-*NN*-dimethylaminophenylphosphine. Selective irradiation of the high-field proton signal (H_B) left the high-field ^{13}C doublet unchanged, whereas the low-field ^{13}C doublet was not completely proton-decoupled. The same sequence holds therefore as in proton resonance, *i.e.* the ^{13}C signal of CH_3(B), *trans* to the phosphorus lone pair is more highly shielded.



In both compounds, carbon atoms A and B are unequally coupled to phosphorus with $|{}^{2}J_{\text{PNC(A)}}| > |{}^{2}J_{\text{PNC(B)}}|$. The average value of $\langle {}^{2}J_{\text{PNC}} \rangle$ at room temperature is equal to half the difference of the two absolute values observed at low temperature. This proves that $^{2}J_{\text{PNC(A)}}$ and $^{2}J_{\text{PNC(B)}}$ have opposite signs. Since $\langle {}^{2}J_{\text{PNC}} \rangle$ is positive and $^{2}J_{\text{PNC(A)}}$ predominates, $^{2}J_{\text{PNC(A)}}$ is positive like $^{3}J_{\text{PNCH(A)}}$ and $^{3}J_{\text{PNCH(B)}}$ whilst $^{2}J_{\text{PNC(B)}}$ is negative.

These results show the two-bond P–^{13}C coupling constants are related to the dihedral angle as previously observed[2,7] for $^{2}J_{\text{PCC}}$ and $^{2}J_{\text{PCH}}$. This conformational dependence of phosphorus coupling constants in trivalent organophosphorus compounds through two bonds appears to be a general trend and can be described in terms of the dihedral angle θ[7] between the phosphorus lone-pair orbital and the NC (or CC, CH) bond. In *NN*-dimethylaminophosphines, $^{2}J_{\text{PNC}}$ is large and positive when $\theta = 0°$, while it becomes small and negative when $\theta = 180°$.

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