¹³C and ³¹P NMR Studies of Some Aminophosphonium Chlorides

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The multinuclear NMR spectral data for an homologous series of tertiary phosphines, $R_{3-n}P(NMe_2)_n$, aminophosphonium ions, $[R_3PNR'R'']^+$, and phosphonium ions, $[R_{4-n}PMe_n]^+$, where R = Me, Et, *n*-Pr and Ph, R' and/or R'' = H, Me and n = 0 and 1 are reported and discussed. Quaternization by alkylation or chloramination causes an increase in the ³¹P chemical shift ($\Delta \delta_P$ is positive), a decrease in the ¹³C chemical shift ($\Delta \delta_C$ is negative) for all carbons, an increase in the magnitudes of ¹J(PC), ³J(PC), ³J(PNCH) and ²J(PCH) and a decrease in the magnitude of ²J(PC). Substitution of a Me₂N group for an alkyl or aryl group produces an increase in the ³¹P chemical shift and in the magnitude of ¹J(PC). α - and β -deshielding and γ -shielding effects are noted in the ¹³C NMR spectra and β -deshielding and γ -shielding effects are noted in the phosphorus and nitrogen atoms.

KEY WORDS ¹³C NMR ³¹P NMR Tertiary phosphines Aminophosphonium ions Phosphonium ions

INTRODUCTION

Several reports have been published on ³¹P and ¹³C nuclear magnetic resonance (NMR) studies of phosphonium salts.¹⁻⁷ However, only three studies⁸⁻¹⁰ considered phosphonium salts containing the P-N bond. Our interest was in conducting a detailed NMR study on a homologous series of aminophosphonium chlorides and related phosphines and phosphonium salts in order to correlate the changes in chemical shift and coupling constant data with structural and electronic effects created by various substituents on the P and/or N atoms. In this paper the multinuclear NMR spectral data of such a series of aminophosphonium ions, $[R_{4-n}PMe_n]^+$, and tertiary phosphines, $R_{3-n}P(NMe_2)_n$, in which R = Me, Et, *n*-Pr and Ph, R' and/or R''= H. Me and n = 0 and 1 are reported.

The changes in the ¹³C and ³¹P chemical shift and the ³¹P—¹³C, ¹³C—¹H and ³¹P—¹H coupling constant data for a given homologous series are discussed in terms of substitution effects produced by the Me₂N moiety and quaternization effects produced by alkylation and chloramination of the respective tertiary phosphines. These processes are represented diagrammatically in Scheme 1.

EXPERIMENTAL

All storage and transfer of the phosphines and the experimental purification work were conducted in a dry nitrogen atmosphere in a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-493 Dri-Train. All reactions were carried out in an atmosphere



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of pre-purified nitrogen or *in vacuo* using literature procedures.^{11,12} All synthesized compounds were characterized by elemental analysis; m.p.; IR; ¹H, ¹³C, and ³¹P NMR; EI-MS; CI-MS; and electrical conductivity.⁹

The procedure for the synthesis of $[R_3PNR'R'']^+$ is described elsewhere.^{9,11} Aminophosphines, R_2PNMe_2 , were either prepared by the reactions of halophosphines with dimethylamine¹² or by the alkylation of Me_2NPCl_2 with RMgX.¹³ Me_4P^+ , Pr_4P^+ and R_3PMe^+ salts were prepared by the addition of the appropriate alkyl halide to a diethyl ether solution of the respective tertiary phosphine. Et₄PI and Ph₄PI were purchased from Alfa, Me_3P and *n*-Pr₃P from Strem Chemical Company and Et₃P from Aldrich, and were used as such.

The ¹³C and ³¹P NMR chemical shifts and ³¹P-¹³C, ¹³C-¹H and ³¹P-¹H coupling constants of the tertiary phosphines and the aminophosphonium and phosphonium ions were determined in our laboratory and are given in Table 1. Pertinent literature references are also given in Table 1. The ¹H, ¹³C and ³¹P NMR spectral data were recorded using 0.20 M chloroform-d solutions of the compounds at 25° C, except where noted in the table. The NMR data were obtained using a Nicolet 300 MHz multinuclear Fourier transform NMR spectrometer operating at 75.475 MHz for ¹³C, 300.132 MHz for ¹H and 121.495 MHz for ³¹P. The ¹H and ¹³C NMR data were referenced to tetramethylsilane as an internal standard. An 85% aqueous H₃PO₄ solution was used as an external reference for the ³¹P NMR data. ³¹P NMR spectra were obtained with continuous decoupling (bilevel mode). All coupling constants involving phosphorus were obtained from the ¹H and ¹³C NMR spectra—90° pulses of 8 μ s duration were used for the ¹H NMR and 45° pulses were employed for the ³¹P and ¹³C NMR studies. The proton-decoupled ¹³C NMR spectra were obtained using bilevel decoupling with NOE and the proton-coupled ¹³C NMR spectra with NOE. The digital resolution was generally 0.50, 0.25 and 0.125 Hz per data point for the decoupled ¹³C and ³¹P, coupled ¹³C and ¹H NMR experiments, respectively. The ¹H NMR chemical shift and ¹H-¹H coupling constant data have been reported elsewhere.⁹

RESULTS

Quaternization of the tertiary alkylphosphines, R_3P , to yield the tetraalkylphosphonium salts, R_4P^+ [Scheme 1; process (c)], causes an increase in the ³¹P chemical shift $(\Delta \delta_{\rm P} \text{ is positive})$, a decrease in the ¹³C chemical shift $(\Delta \delta_{\rm C}$ is negative) for all the carbons, an increase in the magnitudes of the ${}^{1}J(PC)$, ${}^{3}J(PC)$, ${}^{3}J(PNCH)$ and $^{2}J(PCH)$ values and a decrease in the magnitude of the $^{2}J(PC)$ value. Typical values are obtained for $^{1}J(CH)$ in the tertiary phosphines, which increase slightly on quaternization. These results are consistent with those previously reported for the formation of R_4P^+ from R_3P .^{14,15} A sign change on quaternization for ¹J(PC), $^{2}J(PC)$ and $^{2}J(PCH)$ has been reported.¹⁴ In this study, only the magnitudes of the coupling constants have been determined. However, the signs of the coupling constants, where known from the literature, are given in Table 1.14,16

Phenylation of Ph_3P to yield Ph_4P^+ gives similar changes in the NMR spectra as for the tertiary alkylphosphines, except that only the C-1 δ_C of the phenyl group

Compound		δ_{c}	δ_{p}	¹J(PC)	²J(₽C)	³ Ј(РС)	¹ Ј(СН)	² J(PCH)	³ J(PCH)	²J(PNC)	³ J(PNCH)	Relevant literature data (nuclei)
Me ₃ P		16.21	-60.50	-10.9	_	_	127.3	+1.7	_	_	_	(H, C, P); ¹⁴ (H, P) ³⁵
Me ₂ PNMe ₂	PMe	13.83	40.27	16.3		_	126.3	4.7	_	_	_	(H, P); ^{28,36} (P) ³⁵
	NMe	39.37	_	_	_	_	134.1	_		11.6	10.4	
[Me₄P] ⁺ (in DMSO)		10.67	26.20	+55.2	_	—	132.6	-15.5	-	—	_	(H, P, C); ¹⁴ (H); ^{36,37} (P) ³⁵
[Me₃PNH₂] ⁺ (in DMSO)		12.86	51.24	65.4	—	_	131.2	14.9	—	_		(H, P) ⁸
[Me ₃ PN(H)Me] ⁺	Me	11.66	53 .17	65.7	_	—	131.7	13.7	-	_	_	
	NMe	26.57	-	_		_	138.9	_		2.7	14.7	
[Me ₃ PNMe ₂] ⁺	Me	10.76	62.53	64.6	_		132.2	13.9	—		_	(H) ³⁸
	NMe	36.99		—		_	139.2		-	2.5	11.5	
Et ₃ P	CH₂	18.26	-17.97	-11.3	_		126.7	0.8			_	(H, P, C) ¹⁴
	CH₃	9.45	—	_	+12.3		126.0		+14.1	_	_	
Et ₂ PNMe ₂	CH₂	21.33	64.42	12.2	_		127.6	_	-	_	_	(H, P); ³⁵ (P) ³⁶
	CH₃	9.58	—	_	15.7	—	127.3	-	15.7	_	-	
	NMe	40.16	-	_	_	_	133.9		-	12.4	8.4	
[Et ₃ PMe] ⁺	CH₂	13.95	37.96	50.2		_	131.4	13.2	-	_	—	(H); ³⁶ (P) ^{28,35}
	CH₃	6.16	-		5.0		130.5	_	18.7	-	-	
	PMe	4.42	—	52.1	_	-	133.2	13.4		_	_	
[Et ₄ P] ⁺	CH₂	12.34	40.56	+48.8	_	_	131.5	12.8	-	_	_	(H, P, C); ¹⁴ (H); ^{28,36,37} (P) ³⁵
	СН _з	6.30			~5.2	_	130.5		+18.0		-	
$[Et_3PNH_2]^+$	CH₂	16.02	60.67	61.4	_		129.9	12.9	_	_	_	
	CH₃	5.41	-	_	4.8	_	130.2		18.6	_	—	
[Et₃PN(H)Me] ⁺	CH₂	14.05	63.74	60.4	_	_	130.0	12.4		-		
	CH₃	5.13	_		4.8	-	130.3	_	18.4	-	_	
	NMe	26.70	_	_			138.9			3.1	12.4	

Table 1. NMR Data (δ , ppm; J, Hz) for $R_{3-n}P(NMe_2)_n$, $[R_3PNR'R'']^+$ and $[R_{3-n}PMe_n]^+$ compounds

Table 1. cont'd

C		•		1 ((20)	2 ((20)	3 (19.0)	1	2 ((55))	3 // 50/11	2 ((2)) (2)	3 ((5)) ((1))	Relevant literature data
Compound		δ_{c}	δ_P	'J(PC)	²J(PC)	³J(PC)	'Ј(СН)	² J(PCH)	°J(PCH)	*J(PNC)	°J(PNCH)	(nuclei)
[Et ₃ PNMe ₂]	CH₂	14.18	72.07	59.1		_	130.7	11.9	_	_		
	CH₃	5.35			5.0		130.4	_	18.4	—		
	NMe	37.64	_	—	_	—	139.2			1.7	9.4	45 07 05
n-Pr ₃ P	PCH ₂	29.74	-32.02	11.6	—	—	127.2	<0.2	—	—		(C); ¹⁵ (P) ^{27,35}
	CH₂	19.35	-		13.3	-	126.6		_	_		
	CH3	16.08	_			11.4	125.0		_	_		
[n-Pr ₄ P]	PCH ₂	21.45	32.08	46.9		_	131.2	12.7	_		—	
	CH₂	15.87	-	_	4.6		128.8	_	—	_		
	CH₃	15.64				16.0	127.0		_			
[<i>n</i> -Pr ₃ PMe] ⁺	PCH ₂	22.80	30.87	48.6	_	—	131.5	12.8	_		-	
	CH₂	15.75	—	—	3.5	—	129.0	_	_	_	—	
	CH₃	15.47	-		_	16.4	127.1	—	_	_		
	PMe	5.79	—	51.7	_	—	133.2	13.4	—			
$[n-\Pr_3PNH_2]^+$	PCH ₂	25.27	54.31	59.1	_	_	128.6	12.7	_	_	_	
	CH₂	14.89			3.8	—	128.8			_		
	CH₃	15.21	—		_	16.4	126.7	_	_	_	_	
$[n-Pr_3PN(H)Me]^+$	PCH ₂	23.44	57.46	59.0	—		129.0	12.3	—	—	—	
	CH₂	14.90			3.8	_	128.9					
	СН ₃	15.16	—	—	_	16.4	126.8	_	-			
	NMe	26.81	—	—	—	-	138.7	_	_	3.1	12.7	
[n-Pr ₃ PNMe ₂] ⁺	PCH₂	23.14	66.06	57.1			129.8	-		_	-	
	CH₂	14.99	—	—	4.4	_	128.9		_			
	СН3	14.85	-	—	_	16.4	127.0	_	_	_	—	
	NMe	37.60	_	—	_		139.1			1.8	9.5	
Compound		δο	δο	¹ J(PC)	² J(PC)	³ J(PC)	4 J/00)	¹ J(CH)	² J(PNC)	³ J(PNCH)	Rele	evant literature data (nuclei)
	~ ^	107.10			- ()	- (/	- (FC)	- (,	. (,	,	(11 - 5) 3	$\frac{1}{2}$
Ph ₃ P	C-1	137.12	-4.84	-10.8	-	_	-		-	_	(H, P);"	⁻ (C, P); ∺41
	C-2,6	133.67	_	_	+19.4	_	_	160.3	_		(C); ^{10,00}	
	C-3,5	128.43	-	_	_	+6.9	_	160.2	_	_	(P)**	
	C-4	128.64	_				<1	160.2	-	_		
Ph ₂ PNMe ₂	C-1	138.7	64.95	15.2	_	—			_	_	(H, P);*	° (P) ^{35,42}
	C-2,6	131.9	_		19.4		_	160.0	_			
	C-3,5	128.0	-		—	5.7	—	159.7	_	_		
	C-4	128.3	—	—	—	—	<1	160.2		-		
	NMe	41.8	—		-	_	—	134.9	14.7	9.6	2	29 4 20 40
[Ph₄P] ⁺	C-1	117.3	23.5	89.5			_	—	_	_	(C, P); ³	²⁰ (C); ^{4,39,40}
	C-2,6	134.3		_	10.3	_		164.4		_	(P) ^{6,35}	
	C-3,5	130.8	-	—	—	12.8	—	166.8	—			
	C-4	135.7	—				2.9	164.4		_		40.00 00
[Ph ₃ PMe] ⁺	C-1	118.8	22.2	88.7	—	—					(C, P);'	^{10,28} (H); ³⁶
	C-2,6	133.3	—	_	10.7	_	_	163.8	—		(C); ^{4,7,4}	³ (P) ^{6,27,35}
	C-3,5	130.6		-		12.9	—	166.0	—			
	C-4	135.3		_		_	2.2	161.2		_		
	PMe	11.6	_	57.2	—	_	_	134.9	_			
[Ph ₃ PNH ₂] ⁺ (in DMSO)	C-1	123.41	36.18	103.1	—	—	_	_	·	_	(H); ⁴⁵ (P) ^{2,44}
	C-2,6	129.61	—	—	11.4	—		164.4	—	-		
	C-3,5	132.68		-	—	13.1	—	165.6	—			
	C-4	132.4	_				2.8	163.5				
[Ph ₃ PN(H)Me] ⁺	C-1	121.14	39.35	102.9	—	—	—	—	—			
	C-2,6	133.21	_	_	10.9		—	163.0	_			
	C-3,5	129.67	_	_	_	13.1	_	165.3				
	C-4	134.47	—	—	—	—	2.9	163.0	_	_		
	NMe	28.04	_		—	—	—	139.9	2.3	13.8	1	
$[Ph_3PNMe_2]^+$	C-1	119.17	47.55	101.9	_			_	-	-	· (H) ⁴⁵	
	C-2,6	133.46	_	_	10.7	_	_	163.8	_	_		
	C-3,5	130.29			_	13.2	_	166.0	_	_		
	C-4	135.35	_				2.9	166.0	_	_		
	NMe	39.22		_	_			140.4	3.2	10.5	i	
[Ph ₂ P(Me)NMe ₂]*	C-1	120.66	50.79	101.3	_	_	_	_	_	_		
	C-2,6	132.80			11.1	—	_	163.8	_	_		
	C-3,5	130.49	-	_	-	13.1		165.8		_		
	C-4	135.35	_				2.5	163.3	_			
	NMe	38.94	_		_	_	_	140.0	3.1	11.0	1	
	PMe	12.51		67. 2		_	_	133.2			-	
	-	-										

Interestingly, quaternization of R_3P by chloramination [Scheme 1; processes (d), (e) and (f)] yields relative changes in the NMR spectra in agreement with those for processes (a) and (c) above. However, the magnitudes of the changes, in certain cases, are quite different. The dependence of the chemical shift and coupling constant changes on R, R' and R" on quaternization will be discussed below. Quaternization of an aminophosphine, R_2PNMe_2 , by alkylation or phenylation to yield $R_3PNMe_2^+$ yields similar changes in the NMR data, except that for formation of $Ph_3PNMe_2^+$ from Ph_2PNMe_2 where the δ_P decreases rather than increases. Substitution of a Me₂N group for an alkyl or aryl group in R_3P to give R_2PNMe_2 [Scheme 1; (b)] or in R_3PMe^+ to yield $R_3PNMe_2^+$ produces an increase in δ_P and in the magnitude of ${}^1J(PC)$.

DISCUSSION

³¹P chemical shifts

For any given parent phosphine, R₃P, quaternization of the phosphorus via methylation [Scheme 1; process (a)] to give R₃PMe⁺ or via chloramination [Scheme 1; processes (d), (e) and (f)] to yield R₃PNR'R"⁺ produces a large increase in δ_P . The ordering of the magnitude of this increase for each R₃PMe⁺, R₃PNH₂⁺, R₃PNHMe⁺ and R₃PNMe₂⁺ series depends on the nature of R (Ph < Et < *n*-Pr < Me). This trend parallels that of the δ_P of the parent phosphines and the bond angle changes that result on quaternization of the phosphorus.⁵ The bond angles at phosphorus have been reported, or are expected, to be approximately tetrahedral¹⁷⁻¹⁹ in all the phosphonium compounds.

The δ_P NMR data also indicate that for a given R₃P series, quaternization via chloramination produces a larger positive $\Delta\delta_P$ than that produced via methylation [Scheme 1; processes (d), (e) or (f) vs (a)]. This reflects the effect that the relative electronegativities of the R'R"N and Me moieties (theoretical electronegativities: Me, 2.27; NH₂, 2.61; NHMe, 2.45; NMe₂, 2.40)^{20,21} have on the shielding at phosphorus. This increased deshielding of the phosphorus nucleus on quaternization also correlates with the observed negative $\Delta\delta_H$ of the C-1 protons upon quaternization⁹ and the positive $\Delta\delta_C$ of the C-1 carbons, as discussed below.

The $\Delta \delta_P$ values for the respective methyltrialkylphosphonium and dimethylaminotrialkylphosphonium salts are essentially constant (35 ppm), which suggests that substituting a Me₂N group for a Me group [Scheme 1; process (g)] produces a constant deshielding and stereochemistry effect at the phosphorus. Analogous effects are noted for the substitution of an NH₂ or NHMe moeity for a Me group. Additionally, substitution of a Me₂N group in the parent phosphine to form the aminophosphine [Scheme 1; process (b)] produces a large positive $\Delta \delta_P$.

The ordering of the magnitude of $\Delta \delta_P$, aminophosphonium relative to parent phosphine, [Scheme 1; processes (d), (e) and (f)] in going from the NH₂ to the

NHMe to the NMe₂ derivative correlates with a β -effect produced by replacing each H with a Me group. This β -effect is partially offset by the shielding influence that the decreasing electronegativity^{20,21} of the R'R"N moiety has on the phosphorus nucleus. Hence it is reasonable to expect somewhat smaller $\Delta \delta_P$ values to occur on substitution of the first Me group as compared with those observed with substitution of the second Me group, where the theoretical electronegativities of the NHMe and NMe₂ groups are very similar.

Quaternization of R_2PNMe_2 (R = alkyl) via alkylation to yield $R_3PNMe_2^+$ [Scheme 1; process (c)] produces a smaller $+\Delta\delta_P$ than does chloramination of R_3P to yield $R_3PNMe_2^+$ [Scheme 1; process (f)]. A positive $\Delta\delta_P$ is also observed in the quaternization of Ph₃P. However, a negative $\Delta\delta_P$ results on quaternization of Ph₂NMe₂ to yield Ph₃PNMe₂⁺ and Ph₂P(Me)NMe₂⁺. These $\Delta\delta_P$ trends parallel the ordering of δ_P of the parent phosphines and the expected bond angle changes that result on quaternization.⁵

 $\delta_{\rm P}$ increases as R is changed from methyl to propyl to ethyl for any given R₃PMe⁺ or R₃PNR'R"⁺ series. This trend is a consequence of the β - and γ -effects² that successive carbon chain lengthening has on the phosphorus atom. The $\delta_{\rm P}$ values for the phenyl derivatives in these two series are smaller than those for the analogous alkyl derivatives, as expected owing to the greater electronegativity of the phenyl group.^{2,5,8}

¹³C chemical shifts

Quaternization of the phosphorus causes a decrease in $\delta_{\rm C}$ (2-7 ppm) for all the alkyl carbon atoms, as previously observed for phosphonium compounds.^{7,14} Typical intrachain α - and β -deshielding and interchain γ -shielding effects are noted at the C-1 carbon on lengthening of the hydrocarbon chain.^{4,22} Shielding occurs at C-1 for the R'R"N derivatives on replacing a hydrogen with a Me in going from R₃PNH₂⁺ to R₃PNHMe⁺ to R₃PNMe₂⁺.

The shielding trends are complicated by the influence of the relative electronegativities of the R'R"N groups and interchain γ -shielding effects.²³ Quaternization by chloramination causes $\delta_{\rm C}$ of the phenyl C-1 carbon to decrease whereas that of the C-4 carbon increases. These data suggest that the R'R"NP< group polarizes the electron density in the phenyl ring so as to increase the electron density at C-1 and reduce it at the C-4 (*para*) carbon.^{24,25}

The $\delta_{\rm C}$ values for the >NMe group in the $R_3 PN(H)Me^+$ and $R_3 PNMe_2^+$ derivatives are essentially invariant with respect to the nature of the alkyl group attached to phosphorus. When R = Ph, the $\delta_{\rm C}$ of the >NMe group is greater than that observed when R = alkyl, suggesting that the more electronegative Ph groups polarize the electron density in the R'R"N moiety so as to decrease the electron density in the Me group.

A deshielding β -effect on the carbon nucleus of the NHMe moiety ¹³C chemical shift results when the proton is replaced with a Me group to give the NMe₂ derivative. A relatively constant deshielding effect of about 10 ppm is observed for each R₃P series, indicating that the deshielding is independent of the nature of the R group.

³¹P-¹³C, ¹³C-¹H and ³¹P-¹H coupling constants

The large increase in the magnitude of ${}^{1}J(PC)$ that accompanies quaternization of the phosphorus has been previously noted and generally explained by the greater s character of the P—C bond in the phosphonium salts as compared with the tertiary phosphines.²⁶⁻²⁸ The magnitude of ${}^{1}J(PC)$ in a given phosphonium series is dependent on the nature of the R group (Ph>Me>Et> *n*-Pr).^{1,28} The greater s character (sp² hybridization) associated with the C-1 carbon attached to phosphorus in the phenyl case as compared with the alkyl cases (sp³ hybridization) is indicative of the very large ${}^{1}J(PC)$ observed for the phenyl derivatives.²⁷

For the R₃PNR'R"⁺ and R₃PMe⁺ phosphonium ions, the ordering of the magnitude of ¹J(PC) parallels the theoretical electronegativities of the R'R"N and Me groups attached to the R₃P moiety. Thus decreasing the electronegativity of the group attached to the R₃P moiety decreases the s character in the P—C bond of the more electropositive R group attached to the phosphorus.^{27,29} A similar comparison of the ¹J(PC) values for the analogous R₂PNMe₂ and R₂PMe phosphines indicates that substitution of the Me₂N group for the Me group also produces an increase in the magnitude of ¹J(PC). An analogous argument, based on Bent's rule,²⁹ has been

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proposed for tertiary phosphines.^{30,31} However, since ${}^{1}J(PC)$ for P^{III} compounds may be composed of several terms, and not necessarily Fermi contact dominated,²⁷ Bent's rule may not be applicable in this case.³²

 ${}^{2}J(PC)$ is slightly larger in magnitude than ${}^{1}J(PC)$ in all the tertiary phosphines. On quaternization, the magnitude of ${}^{2}J(PC)$ decreases, in contrast to that of ${}^{1}J(PC)$, and the relative order of magnitudes in the phosphonium ions becomes ${}^{1}J(PC) \gg {}^{2}J(PC)$. The decrease in ${}^{2}J(PC)$ has been related to the increase in the P-C-C dihedral bond angle²⁷ that occurs on rehybridization of the phosphorus atom.

There is an increase in the magnitude of ${}^{2}J(PCH)$ on quaternization. Quaternization of $R_{2}PNMe_{2}$ to $R_{3}PNMe_{2}^{+}$ produces a decrease in the magnitude of ${}^{2}J(PNC)$. Replacement of a hydrogen with a methyl group in the $R_{3}PNR'R''^{+}$ series is accompanied by a decrease in the magnitude of ${}^{2}J(PNC)$. These changes can be explained by changes in the respective dihedral angles that accompany quaternization.^{27,33,34}

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