

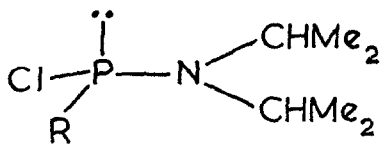
THE STEREOCHEMICAL DEPENDENCE OF $^{31}\text{PNC}^{13}\text{C}$ COUPLING
CONSTANTS IN ACYCLIC AMINOPHOSPHORUS COMPOUNDS

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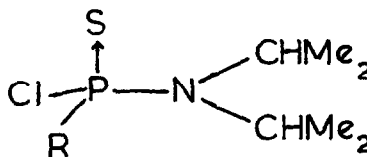
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There has been considerable interest in the stereochemical dependence of two and three-bond phosphorus-proton coupling constants.^{1, 2} Recently it has been reported that the corresponding phosphorus-carbon coupling constants, $^2\text{J}(\text{PCC})$,³ $^2\text{J}(\text{POC})$,⁴ $^2\text{J}(\text{PNC})$,⁵ $^3\text{J}(\text{PCCC})$,⁶ and $^3\text{J}(\text{POCC})$ ⁷ are also markedly stereochemically dependent. We now present preliminary results on the three-bond coupling $^3\text{J}(\text{PNCC})$.



1 a R = C₆H₅
b R = Me



2 a R = C₆H₅
b R = Me

Aminophosphorus compounds of type 1 provide a good substrate for investigating the conformational dependence of $^3\text{J}(\text{PNCC})$ since at low temperature all four methyl groups are diastereotopic due to molecular asymmetry combined with slow rotation around the PN bond.^{2, 8} The low temperature ^{13}C nmr data for some compounds of this type are given in Table I. In the aminophosphines 1a and 1b, $^3\text{J}(\text{PNCC})$ shows a very marked conformational dependence as the value for one methyl group is 23 Hz compared with 0-7 Hz for the other three methyl groups. The range of $^3\text{J}(\text{PNCC})$ values is much smaller in the corresponding sulphides (2a and 2b), though a stereochemical effect is evident. Although the signs of the coupling constants cannot readily be determined

Table I. ^{13}C Chemical Shifts (δ)^a and ^{31}P --- ^{13}C Coupling Constants (J) in Aminophosphorus Compounds.

Compd.	Temp. (°C)		Me(A)	Me(B)	Me(C)	Me(D)	CH(A)	CH(B)	
<u>1a</u>	-40°	J, Hz ^b	4	23	<2	6	25	12	
		(δ , ppm)	(21.4)	(24.6)	(21.5)	(26.6)	(45.0)	(51.9)	
			┌──────────┐		┌──────────┐		┌──────────┐		
	+55°	J, Hz ^b	13		4		7		
		(δ , ppm)	(23.2)		(24.2)		(48.6)		
<u>1b</u>	-50°	J, Hz ^b	4	23	2	7	25	13	
		(δ , ppm)	(21.0)	(24.1)	(21.9)	(26.2)	(45.7)	(48.2)	
			┌──────────┐		┌──────────┐		┌──────────┐		
	+55°	J, Hz ^b	Broad signal at 23.7 ppm ^d					6	
		(δ , ppm)						(47.4)	
<u>2a</u>	-93°	J, Hz ^c	<3	7	7	<3	<3	<3	
		(δ , ppm)	(18.9)	(22.5)	(19.7)	(24.4)	(47.5)	(52.1)	
			┌──────────┐		┌──────────┐		┌──────────┐		
	+35°	J, Hz ^c	4		4		3		
		(δ , ppm)	(21.3)		(22.5)		(50.0)		
<u>2b</u>	-90°	J, Hz ^c	<3	8	7	<3	<3	<3	
		(δ , ppm)	(19.3)	(22.7)	(21.1)	(24.2)	(47.9)	(51.5)	
			┌──────────┐		┌──────────┐		┌──────────┐		
	+32°	J, Hz ^c	5		4		3		
		(δ , ppm)	(21.6)		(22.9)		(49.8)		

^a Relative to internal TMS.

^b Data obtained in CDCl_3 solution.

^c Data obtained in CD_2Cl_2 solution.

^d Chlorine exchange appears to become rapid above ambient temperature, inverting configuration at phosphorus and rendering all four methyl groups isochronous.

since $^4J(\text{PNCCH})$ is close to zero, some relative sign information may be obtained by observing the spectra at higher temperature where rotation around the PN bond is fast on the NMR time-scale. Thus it appears from the time averaged J value for Me(A) and Me(B) in 1a at 55° that the individual coupling constants have the same sign for these two carbon nuclei in different isopropyl groups.

The $^{31}\text{P}^{13}\text{C}$ coupling constants for the anisochronous methine carbon atoms are also reported in Table I. In the aminophosphines 1a and 1b these $^2J(\text{PNC})$ couplings clearly differ in sign as the time-averaged value obtained at 55° is approximately equal to half the difference between the two low-temperature values. Simonnin *et. al.* have previously reported⁵ similar results for the methyl carbon atoms in chloro-N,N-dimethylaminophenylphosphine, $\text{C}_6\text{H}_5\text{P}(\text{Cl})\text{NMe}_2$ (2). It is interesting that in the phosphine sulphides 2a and 2b, $^2J(\text{PNC})$ is very small for both methine carbon nuclei.

It has been suggested that a large positive value for $^3J(\text{PNCH})$ and $^2J(\text{PNC})$ in 3 is associated with the N-methyl group cis to the phosphorus lone pair.^{2, 5} Indeed, it appears that a proximate lone pair of electrons usually makes a positive contribution to reduced coupling constants by a "through space" effect.⁹ Thus the large value of $^3J(\text{PNCC})$ observed for Me(B) in 1a and 1b could result from a preferred molecular conformation that places this methyl group close to the phosphorus lone pair.

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REFERENCES

1. For leading references see: J. P. Albrand, D. Gagnaire, J. Martin and J. B. Robert, Bull. Soc. Chim. France, 40 (1969); J. P. Albrand, D. Gagnaire, M. Picard, and J. B. Robert, Tetrahedron Letters, 4593, (1970); D. W. White and J. G. Verkade, J. Magn. Resonance, 3, 111 (1970); B. J. Blackburn, R. D. Lapper, and I. C. P. Smith, J. Amer. Chem. Soc., 95, 2873 (1973); W. G. Bentrude and H. W. Tan, J. Amer. Chem. Soc., 95, 4666 (1973); L. Evelyn, L. D. Hall, P. R. Steiner, and D. H. Stokes, Org. Magn. Resonance, 5, 141 (1973).
2. A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, J. Amer. Chem. Soc., 92, 5206 (1970).
3. G. A. Gray and S. E. Cremer, Chem. Comm., 367 (1972); J. Org. Chem., 37, 3458 (1972); ibid., 37, 3470 (1972); J. J. Breen, S. I. Featherman, L. D. Quin, and R. C. Stocks, Chem. Comm., 657 (1972); S. Sorensen, R. S. Hansen, and H. J. Jakobsen, J. Amer. Chem. Soc., 94, 5900 (1972).
4. M. Haemers, R. Ottinger, D. Zimmermann, and J. Reisse, Tetrahedron Letters, 2241 (1973).
5. M. P. Simonnin, R. M. Lequan, and F. W. Wehrli, Chem. Comm., 1204 (1972).
6. G. A. Gray and S. E. Cremer, Tetrahedron Letters, 3061 (1971).
7. W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, J. Amer. Chem. Soc., 93, 797 (1971); R. D. Lapper, H. H. Mantsch, and I. C. P. Smith, ibid., 95, 2878 (1973); R. D. Lapper and I. C. P. Smith, ibid., 95, 2880 (1973); A. A. Borisenko, N. M. Sergeyer, E. Y. Nifant'ev, and Y. A. Ustynyuk, Chem. Comm., 406 (1972).
8. W. B. Jennings, Chem. Comm., 867 (1971)
9. W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Bradley, and D. M. Jerina, J. Amer. Chem. Soc., 94, 8501 (1972), and references therein.