

Comparison of the Solid and Liquid Solution States of Representative Phosphoranes by ^{31}P NMR

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Abstract: Cross polarization and magic-angle spinning techniques have been used to obtain ^{31}P chemical shifts for solid samples of several pentacoordinated phosphorus species. Comparison of these results with chemical shifts of solutions of the same compounds indicates that the structures do not differ substantially between the solid and solution phases. This finding is used to apply NMR values for solutions of a large number of phosphoranes to a study of the relation between $\delta_{31\text{P}}$ and geometric structures of the compounds. With use of ^{31}P NMR and conductivity data, the ionic nature of $\text{ClP}(\text{OC}_6\text{H}_5)_4$ is confirmed.

Structural variations in pentavalent phosphorus compounds have received much attention in recent years.¹⁻³ This interest stems from a variety of structural possibilities that range between two limiting structures for pentacoordination, namely, the trigonal bipyramid (TBP) and the square pyramid (SP). In an effort to explain the NMR equivalence of the fluorine atoms in PF_5 , Berry proposed an intramolecular exchange process based on a normal vibrational mode of such D_{3h} molecules.⁴ Holmes and Deiters later considered this process, and postulated that the lowest energy pathway to exchange proceeded through the tetragonal pyramid.⁵ Subsequently, Holmes and co-workers have determined crystal structures of a large number of phosphoranes, and have shown conclusively that the structures fall somewhere along this coordinate between the TBP and SP structures.⁶ They have used the term "percent displacement along the Berry coordinate" (% B). On the Berry coordinate 0% represents the TBP structure, and 100% represents the SP structure.

Pentacoordinate phosphorus species have been implicated as transition states in numerous reactions.⁷ They are postulated as intermediates in biological processes such as the action of ribonuclease upon its substrate.⁸ Dynamic processes of pentacoordinate compounds in which interchange of ligands occurs is another area of interest in these species.

There has been extensive use of ^{31}P NMR in the study of phosphoranes. The structural interpretation of that work has been based largely on structural models provided by X-ray diffraction. This approach is a common and potentially fragile one—i.e., assuming that structures determined by diffraction studies of a crystalline sample apply to the liquid solution state. The recent development of high-resolution NMR on solid samples provides a means of comparing the crystalline and liquid states directly.

As relatively small differences in ligand structure give rise to substantially different structures of phosphoranes in the solid state⁹ one might expect that the patterns of solvation energies can be sufficiently different from the patterns of crystal-packing energies to cause noteworthy structural differences for a given phosphorane

Table I. ^{31}P Chemical Shifts of Phosphoranes in Solution and in the Solid State^a

compound	% B ^b	liquid (solvent) ^c	solid
(I) $\text{P}(\text{OPh})_3$	15.4	-85.4 (CDCl_3) -86.2 (Et_2O) -85.7 (benzene)	-84.2
(II) $\text{ClP}(\text{OPh})_4$		-22.8 (CH_2Cl_2) -21.6 (CDCl_3)	-23.3
(III) $(i\text{-PrO})_3\text{P Pheq}^d$	16.3	-48.6 (CDCl_3) -49.2 (benzene)	-46.0
(IV) $(\text{Cat})_2\text{PR}^e$			
(a) $\text{R} = (\text{OPh})$	87.7	-30.0 (CH_2Cl_2) -29.1 (CDCl_3)	-25.9
(b) $\text{R} = \text{CH}_3$	78.9	+3.17 (CDCl_3) +1.85 (benzene)	+2.43
(c) $\text{R} = \text{Cl}$	71.2	-9.4 (CH_2Cl_2) -8.1 (CDCl_3)	-11.0
(d) $\text{R} = \text{Ph}$	72.1	-9.8 (CDCl_3) -9.0 (benzene)	-9.47
(V) $(\text{Cat})_2\text{P}(\text{Cat})\text{P}(\text{Cat})_2^e$	45 63	-27.6 (CDCl_3) -29.9 (CDCl_3)	-27.9 -29.8

^a Chemical shifts are given with respect to external 85% H_3PO_4 . Positive shift is lower shielding. ^b Percent along the Berry coordinate between TBP and SP geometries as determined by diffraction studies. See text for references. ^c Values for CDCl_3 as solvent were determined in this laboratory; literature values are given for other solvents. ^d Pheq = phenanthrenequinone. ^e Cat = catechol.

between the solid and liquid solution states. Holmes has pointed out that the observed structures of the more than 50 phosphoranes studied appear to correlate with the electronegativity and ring strain rules for such structures.^{6b} He argues that this is evidence that the lattice interactions in the solid are not sufficient to render invalid a comparison of solid and solution properties. Holmes has also shown that the IR and Raman spectra of solid and solution states are very similar.¹⁰

NMR studies can provide a further test of the common assumption that diffraction-determined solid-state structures can serve as useful models for liquid solution chemistry. More specifically, ^{31}P NMR studies of both the solid and liquid states are employed in this investigation to determine the validity of using solid-state structures for interpreting the solution chemistry of phosphoranes and for interpreting ^{31}P NMR data on solutions of this class of compounds.¹⁰

Experimental Section

NMR Spectra. Solution spectra were measured on a Nicolet NT-150 spectrometer at 60.75 MHz. Phosphorus-31 chemical shifts were determined by substitution, and are reported in ppm from 85% H_3PO_4 , more positive values reflecting lower shieldings. The solid-state measurements were made at a frequency of 24.27 MHz on a home-built

- (1) W. S. Sheldrick, *Top. Curr. Chem.*, **73**, 1 (1978).
- (2) D. Hellwinkel, "Organic Phosphorus Compounds", G. M. Kosolopoff and L. Maier, Eds., Vol. 3, Wiley-Interscience, New York, 1972, Chapter 5B, pp 185-339.
- (3) S. Tripett, "Organophosphorus Chemistry", D. W. Hutchinson and S. Tripett, Eds., Vol. 10, The Chemical Society, London, 1979, p 33. See also earlier volumes in this series.
- (4) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
- (5) (a) R. R. Holmes and R. M. Deiters, *J. Am. Chem. Soc.*, **90**, 5021 (1968). (b) R. R. Holmes and R. M. Deiters, *Inorg. Chem.*, **7**, 2229 (1968).
- (6) (a) R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977). (b) R. R. Holmes, *Acc. Chem. Res.*, **12**, 257 (1979).
- (7) (a) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968). (b) K. Mislow, *ibid.*, **3**, 321 (1970).
- (8) R. R. Holmes, J. A. Deiters, and J. C. Gullucci, *J. Am. Chem. Soc.*, **100**, 7393 (1978).
- (9) (a) I. Ugi, D. Marquarding, H. Klusucek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, **4**, 281 (1971). (b) R. Sarma, F. Ramirez, B. McKeever, J. F. Marecek, and S. Lee, *J. Am. Chem. Soc.*, **98**, 581 (1976).

- (10) W. Althoff, R. O. Day, R. K. Brown, and R. R. Holmes, *Inorg. Chem.*, **17**, 3265 (1978).

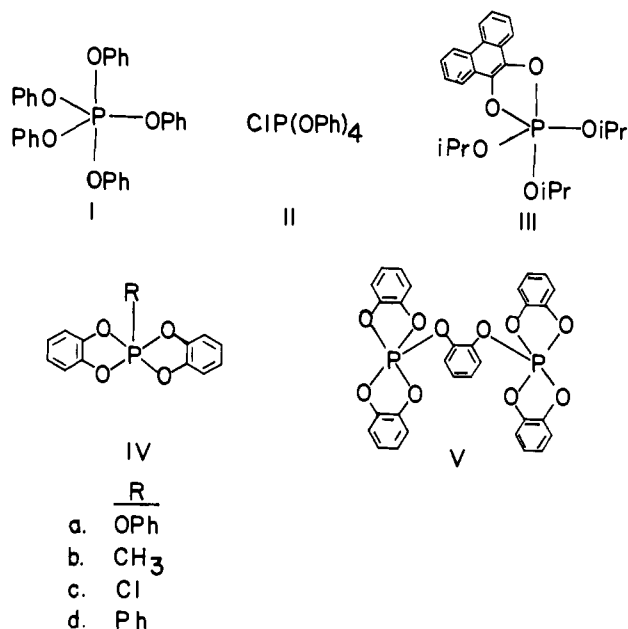


Figure 1. Phosphorus compounds studied in the solid state in this work.

spectrometer based upon a 14-kG Varian HR-60 magnet and a JEOL EC-100 Fourier transform data system. The cross polarization-magic-angle spinning (CP/MAS) experiment has been described previously¹¹ and will not be discussed further here. Typical parameters for the phosphoranes studied were a contact time of 9 ms and repetition times of 8 s, although longer repetition times of up to 30 s were found to be preferable for some of the compounds.

Materials. The compounds studied experimentally in this work are shown in terms of their presumed structures in Figure 1. The compounds I,¹² III,¹³ IVa,¹⁴ IVb,¹⁵ IVc,^{13,16} IVd,¹⁵ and V¹⁷ were prepared by procedures reported in the literature. All reactions were performed in a dry nitrogen atmosphere. Solvents and reagents were purified and dried by standard procedures.¹⁸

Compound II^{12,19} was prepared by adding a benzene solution of phenol dropwise to a stirred suspension of PCl₅ and benzene. After being stirred at room temperature for 3 h, the benzene was removed under vacuum and a white hygroscopic powder was obtained, with a melting point (uncorrected) of 76–78 °C and $\delta_{1p} = -21.6$ ppm (CDCl₃). The ¹³C and ¹H NMR spectra of this compound show resonance patterns characteristic of phenoxy groups, with small impurity peaks. Elemental analysis for chlorine gave values ranging from 14% Cl to 16% Cl (theoretical for ClP(OC₆H₅)₄ is 8.7% Cl). The parent peak in the mass spectrum is found at 408 amu (theoretical for ClP(OC₆H₅)₄ is 407.86 amu).

Results and Discussion

³¹P NMR Results. ³¹P NMR data on the phosphoranes of this study are summarized in Table I, and representative spectra are shown in Figure 2. The ³¹P data show that the chemical shift of each solid is indeed very similar to that of the corresponding solution. Consider, for example, the four PO₅ compounds

(11) J. Schaefer and E. O. Stejskal, *Top. Carbon-13 NMR Spectrosc.*, **3**, 283 (1979).

(12) F. Ramirez, A. J. Bigler, and C. P. Smith, *J. Am. Chem. Soc.*, **90**, 3507 (1968).

(13) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 2268 (1967).

(14) R. Sarma, F. Ramirez, and J. F. Marecek, *J. Org. Chem.*, **41**, 473 (1976).

(15) (a) M. Wieber and W. R. Hoos, *Tetrahedron Lett.* 5333 (1968). (b) M. Wieber and W. R. Hoos, *Monatsh. Chem.*, **101**, 776 (1970).

(16) F. Ramirez, A. J. Bigler, and C. P. Smith, *Tetrahedron*, **24**, 5041 (1968).

(17) A. Schmidpeter, T. von Creigern, W. S. Sheldrick, and D. Schomburg, *Tetrahedron Lett.*, 2857 (1978).

(18) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", Pergamon Press, New York, 1966.

(19) (a) C. K. Tseng, *J. Org. Chem.*, **44**, 2793 (1979). (b) L. V. Nesterov, R. G. Mutalopova, S. G. Salikhov, and E. I. Loginova, *Izv. Akad. Nauk., SSSR., Ser. Khim.*, 414 (1971). (c) G. S. Harris and D. S. Payne, *J. Chem. Soc.*, 3043 (1956).

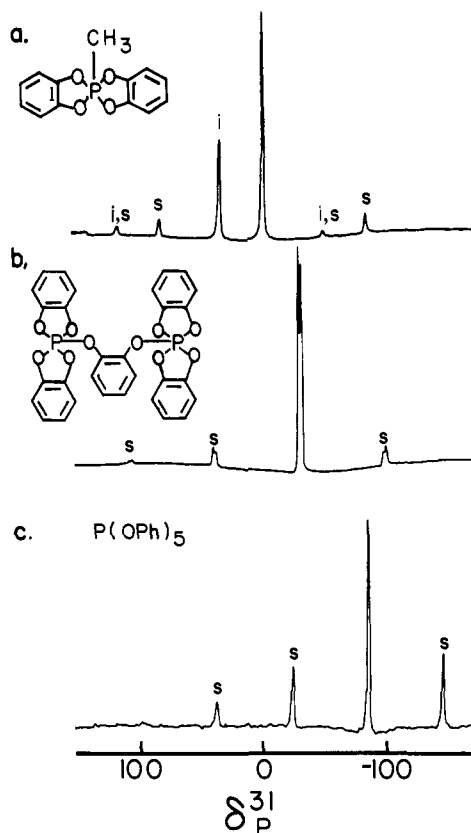


Figure 2. Representative ³¹P NMR spectra of solid samples of penta-coordinated phosphorus compounds. Spinning side bands are indicated by "S". Impurities are indicated by "I". Parameters: (a) 1.5 ms contact time, 8 s repetition rate, 250 scans, (b) 9.5 ms contact time, 8 s repetition rate, 2610 scans, (c) 9 ms contact time, 12 s repetition rate, 372 scans.

(phosphoranes in which each of the atoms directly bonded to phosphorus is oxygen) I, III, V, and IVa. These four have very similar chemical makeup from the point of view of the atoms attached to phosphorus, and differ basically in geometry, as is indicated by the % B values obtained from X-ray data on crystals.^{6,17} For this series of compounds, the chemical shift varies from -85 to -25 ppm, i.e., over a range of 60 ppm; yet the largest solid vs. liquid shift difference is only about 4 ppm for molecule IVa. Hence, it seems clear that the structure of each of these compounds in solution is very close to that in the solid.

It can be seen in Figure 2 that compound V exhibits a doublet in the solid-state ³¹P spectrum. The crystal structure for this compound shows that the two phosphorus atoms are at sites of differing geometry, as indicated by the two % B values given in Table I.¹⁷ It is gratifying that the NMR study is in agreement with the X-ray structural data. When V is dissolved in CHCl₃ and the ³¹P NMR is taken as a function of time, two peaks are observed, at nearly identical chemical shifts to those observed in the solid. The relative intensities of these two lines vary until equilibrium is reached in about 30 min at 30 °C. After equilibrium has been reached, the relative intensities of the two peaks may be altered by varying the sample temperature. The implication of these data is that a structural difference of the two phosphorus atoms in V that is comparable to the difference found in the solid is maintained in solution. Characterizing the exact nature of this time-dependent behavior in solution would require additional study.

Certain of the spectra obtained in the solid state showed peaks which can be identified with decomposition products by the fact that, as time passes, these peaks grow in relation to the main peak. For example, the solid-state spectrum of compound IVb showed an impurity peak at 8.3 ppm with an intensity that was approximately one quarter the intensity of the main peak at 2.4 ppm; the same sample 2 months later, having been kept in a freezer and sealed against moisture, showed nearly equal intensity for

these two peaks. One must, however, guard against making direct estimates of relative concentration of the various components from CP/MAS measurements on these solids. A glaring example of this need for caution is found in the spectrum of solid IVc. The spectrum shows several "extra" peaks over a wide range of chemical shift values. The solution spectrum of this sample, however, shows only one strong line, at -8.1 ppm. Only after 4 h of collecting data on the solution are very small impurity peaks detected which agree in chemical shifts with those of the solid-state spectrum. Apparently the cross polarization process occurs much more efficiently in the sample impurities than in compound IVc. Compound V was one of the impurities that occurred in the sample of compound IVc; and preliminary experiments seem to indicate that the presence of a small amount of V in the solid sample actually enhanced the intensity of the line due to IVc. In an overnight CP/MAS experiment on a highly purified sample of IVc, the spectrum obtained had a very low signal-to-noise figure, and showed very little, if any, V impurity. The CP/MAS spectra of less pure samples of IVc showed more V relative to IVc, but the IVc peak also emerged faster than in the pure samples; i.e., a higher signal-to-noise figure for the IVc resonance was obtained in the same number of pulses. This would tend to indicate that in some way the presence of V enhances the ^{31}P spin polarization in IVc, e.g., either by ^{31}P spin diffusion between V and IVc, or by the proton T_1 values in IVc being reduced by the presence of the impurity, V.

The ^{31}P spectrum of solid $\text{P}(\text{OC}_6\text{H}_5)_5$ yields another interesting case of impurity effects. As can be seen in Figure 2, the CP/MAS spectrum of I shows one peak at -84.2 ppm. If the contact time is changed from 9 ms to about 9 μs , then one line is observed, at -17.7 ppm. This -17.7 ppm resonance is due to the impurity triphenyl phosphate.

$\text{ClP}(\text{OC}_6\text{H}_5)_4$. Compound II has been the subject of some controversy, mainly due to the difficulty of obtaining pure samples. Ramirez¹² reported a white, hygroscopic solid with $\delta_{31\text{P}} = -22.8$ (CH_2Cl_2) as being $\text{Cl}_2\text{P}(\text{OC}_6\text{H}_5)_3$. Tseng^{19a} has recently argued that this compound was probably $\text{ClP}(\text{OC}_6\text{H}_5)_4$. Our Cl content of 14–16% is higher than required for the latter formula. We found that reaction of PCl_5 with 3 equiv of phenol yielded a product substantially contaminated with PCl_5 and with a wide melting point range, 62–70 °C, whereas reaction of PCl_5 with 4 equiv of phenol yielded a product with a narrow melting range, 76–78 °C, which is in agreement with a value quoted by Ramirez, 76–78 °C.¹² In addition, compound II reacted with water to form triphenyl phosphate ($\delta_{31\text{P}} = -17.7$ ppm) and phenol; the proton NMR showed the ratio of phenolic groups in triphenyl phosphate to free phenol to be 3-to-1. This result is consistent with compound II being $\text{ClP}(\text{OC}_6\text{H}_5)_4$, which is also indicated by the mass spectrum. It is our opinion that the high Cl analyses obtained on compound II are due to HCl impurities that are difficult to remove. Maintaining the sample at 60 °C under dry vacuum for 2 days did lower the Cl content to 12.4%.

Tseng^{19a} reported that a CHCl_3 solution containing $\text{BrP}(\text{OC}_6\text{H}_5)_4$ and $\text{ClP}(\text{OC}_6\text{H}_5)_4$ exhibits a ^{31}P signal at -22.5 , and he indicated that this was evidence of the ionic nature of this compound, that is, the chloride salt of the tetraphenoxyphosphonium ion. Nesterov^{19b} showed that the series of compounds $\text{XP}(\text{OC}_6\text{H}_5)_4$, with $\text{X} = \text{Cl}, \text{Br}, \text{I},$ and BF_5 , all have very similar $\delta_{31\text{P}}$ values ($-24, -26, -23, -21$, ppm, respectively), and he interpreted this as evidence that this collection is a series of tetraphenoxyphosphonium salts. If compound II had a pentacoordinated phosphorus structure, it would be expected to have a TBP structure, or very nearly so. However, based on the conclusions of this paper (vide infra), the $\delta_{31\text{P}}$ value of -21.6 is inconsistent with the TBP structure. This may be taken as further evidence of the ionic nature of compound II. Also, noting the similarity of the phosphorus chemical shift for the solution and solid samples of compound II ($\delta_{31\text{P}} = -21.6$ (CDCl_3), $\delta_{31\text{P}} = -23.2$ (solid)), we conclude that the solid-state and solution structures of the $\text{ClP}(\text{OC}_6\text{H}_5)_4$ are essentially the same.

In order to test the hypothesis that the structure of compound II is the ionic tetraphenoxyphosphonium chloride structure,

Table II. Conductivity and ^{31}P Chemical Shifts

compound	solvent	concn, M	Λ , $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$	$\delta_{31\text{P}}$, ppm
$\text{ClP}(\text{OC}_6\text{H}_5)_4$	CHCl_3	0.0929	1.38	-21.6
$\text{ClP}(\text{OC}_6\text{H}_5)_4$	CH_3CN	0.144	92.2	-21.8
$\text{BrP}(\text{C}_6\text{H}_5)_4$	CHCl_3	0.00502	2.94	23.9
$\text{BrP}(\text{C}_6\text{H}_5)_4$	CH_3CN	0.0274	101	24.5
$\text{P}(\text{OC}_6\text{H}_5)_5$	CH_3CN	0.0488	0.48	-84.0
$\text{P}(\text{OC}_6\text{H}_5)_5$	CHCl_3	0.0256	<0.08	-85.4

conductivity experiments were carried out on $\text{ClP}(\text{OC}_6\text{H}_5)_4$ and on $\text{P}(\text{OC}_6\text{H}_5)_5$ and $\text{BrP}(\text{C}_6\text{H}_5)_4$ as models of molecular and ionic substances, respectively. The results and related ^{31}P chemical shifts in solution are summarized in Table II. From the table it is seen that, as expected, the equivalent conductances of $\text{P}(\text{OC}_6\text{H}_5)_5$ are very low in either CHCl_3 or CH_3CN solution. By contrast, both $\text{ClP}(\text{OC}_6\text{H}_5)_4$ and $\text{BrP}(\text{C}_6\text{H}_5)_4$ show small equivalent conductances in CHCl_3 , but very large equivalent conductances in CH_3CN . ^{31}P chemical shifts of the same solutions on which conductivity experiments were carried out give very nearly the same values for a given solute in both solvents. Our interpretation of these results is that both $\text{ClP}(\text{OC}_6\text{H}_5)_4$ and $\text{BrP}(\text{C}_6\text{H}_5)_4$ are ionic substances, which exist largely as ion pairs in CHCl_3 solution, but largely as separated ions in CH_3CN solution. The ^{31}P chemical shift is apparently not very sensitive to that distinction. The sample of $\text{ClP}(\text{OC}_6\text{H}_5)_4$ is thought to have an impurity of HCl, and some triphenyl phosphate. These impurities are the reaction products of hydrolysis of $\text{ClP}(\text{OC}_6\text{H}_5)_4$, and can affect the accuracy of the conductivities reported in Table II. $\text{ClP}(\text{OC}_6\text{H}_5)_4$ is very susceptible to reaction with moisture, and when nonrigorously dried solvents were used, much lower conductivities were measured. This is not the behavior one would expect if the measured conductivity were primarily due to an HCl impurity, and the conclusion regarding the ionic nature of $\text{ClP}(\text{OC}_6\text{H}_5)_4$ is therefore not affected by the impurity HCl in the sample. Harris and Payne have made the same kind of argument.^{19c}

The Relationship between Molecular Structure and ^{31}P NMR Chemical Shift. The structures of a large number of pentacovalent phosphorus species have been determined by X-ray diffraction. Most of the known structures are summarized in Figures 1 and 3. As stated previously, Holmes has interpreted the structures of these molecules in terms of the Berry coordinate,⁴ and has shown that they fit somewhere along the coordinate between the TBP and the SP structures. Table III^{20–55} gives the % B value, i.e.,

- (20) R. K. Brown and R. R. Holmes, *Inorg. Chem.*, **16**, 2294 (1977).
- (21) J. V. Weiss, R. Schmultzler, D. Schomburg, and W. S. Sheldrick, *Chem. Ber.*, **112**, 1464 (1979).
- (22) T. E. Clark, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **18**, 1668 (1979).
- (23) C. B. Cong, A. Munoz, M. Koenig, and R. Wolf, *Tetrahedron Lett.*, 2297 (1977).
- (24) M. Weiber, K. Foroughi, and H. Klingl, *Chem. Ber.*, **107**, 639 (1974).
- (25) D. D. Swank, C. N. Caughlan, F. Ramirez, and J. F. Pilot, *J. Am. Chem. Soc.*, **93**, 5236 (1971).
- (26) D. Hellwinkel and W. Krapp, *Chem. Ber.*, **111**, 13 (1978).
- (27) T. E. Clark, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **18**, 1660 (1979).
- (28) H. L. Carrell, H. M. Berman, J. S. Ricci, Jr., W. C. Hamilton, F. Ramirez, J. F. Marecek, L. Kramer, and Ivan Ugi, *J. Am. Chem. Soc.*, **97**, 38 (1975).
- (29) R. K. Brown, R. O. Day, S. Husebye, and R. R. Holmes, *Inorg. Chem.*, **17**, 3276 (1978).
- (30) G. V. Rosenthaler, K. Sauerbrey, and R. Schmultzler, *Isr. J. Chem.*, **17**, 141 (1978).
- (31) P. Narayanan, H. M. Berman, F. Ramirez, J. F. Marecek, Y. Chaw, and V. A. V. Prasad, *J. Am. Chem. Soc.*, **99**, 3336 (1977).
- (32) J. A. Howard, P. R. Russel, and S. Tripett, *J. Chem. Soc., Chem. Commun.*, 856 (1973).
- (33) R. K. Oram and S. Tripett, *J. Chem. Soc., Perkins Trans. 1*, 1300 (1973).
- (34) Y. Segall and I. Granoth, *J. Am. Chem. Soc.*, **100**, 5130 (1978).
- (35) P. J. Wheatly, *J. Chem. Soc.*, 2206 (1964).
- (36) H. P. Latscha, *Z. Naturforsch., B*, **23B**, 139 (1968).

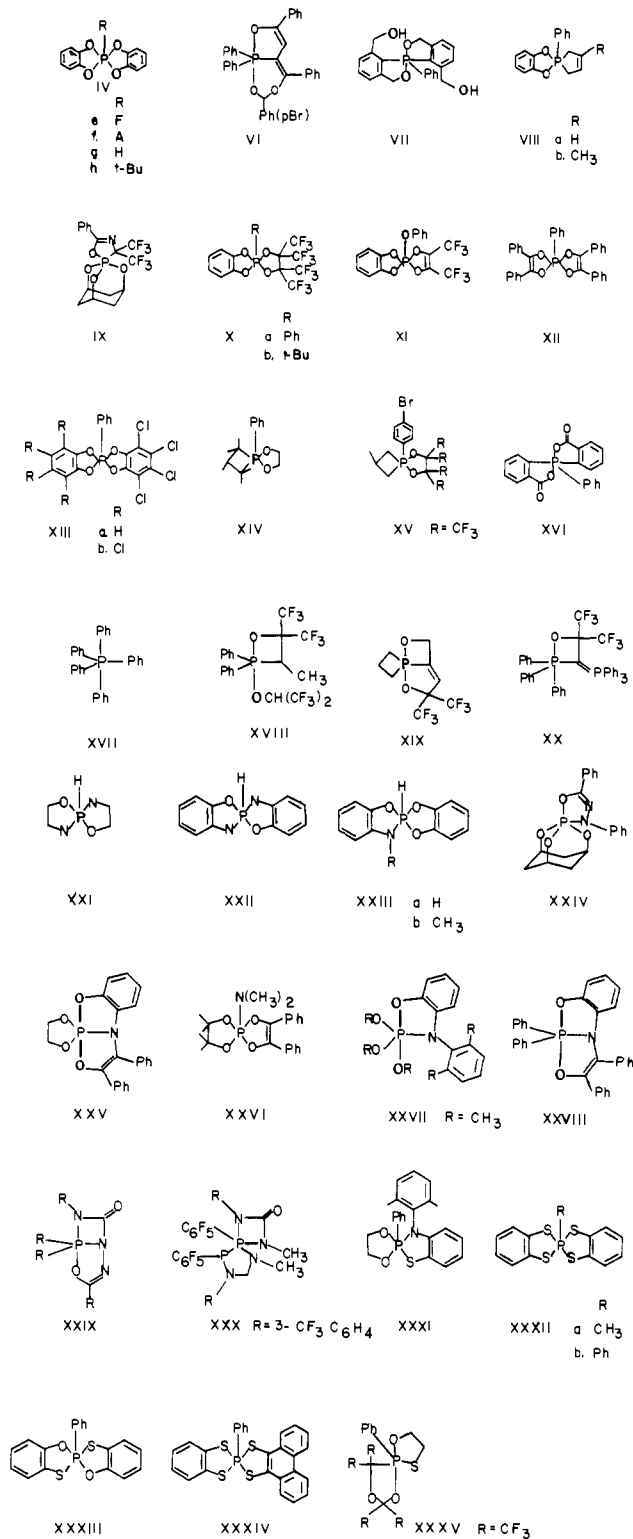


Figure 3. Pentacoordinated phosphorus compounds for which X-ray-determined structures are known.

the percent along the Berry coordinate, for each of the X-ray-determined structures of some 47 compounds. Also given in Table

- (37) M. Ul-Hagnue, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Am. Chem. Soc.*, **93**, 5229 (1971).
 (38) H. A. E. Aly, J. H. Barlow, D. R. Russel, D. J. H. Smith, M. Swindles, and S. Tripett, *J. Chem. Soc., Chem. Commun.* 449 (1976).
 (39) G. Chioccola and J. J. Daly, *J. Chem. Soc. A.*, 568 (1968).
 (40) C. H. Birum and C. N. Matthews, *Chem. Commun.*, 137 (1967).
 (41) R. Burgada and C. Larrenco, *J. Organomet. Chem.*, **66**, 255 (1974).
 (42) P. F. Meunier, R. O. Day, J. R. Devillers, and R. R. Holmes, *Inorg. Chem.*, **17**, 3270 (1978).

Table III. Summary of Structures and ^{31}P NMR Chemical Shifts of Pentacoordinate Phosphorous Compounds from This and Other Studies

compd	% B ^a	$\delta_{31\text{P}}$, ^b ppm	structure and NMR ref ^c
I	15.4	-85.4	6a, 12
III	16.3	-48.6	6a, 13
IVa	87.7	-29.1	6a, 14
IVb	78.9	3.17	6a, 15b
IVc	71.2	-8.1	20, 16
IVd	72.1	-9.8	6a, 15b
IVe	64.8		6a
IVf	73.0	-1.7 (toluene)	6a, 21
IVg	1.7	-21	22, 23
IVh	82.4	5.6	21, 24
V	45	-29.9	17, d
	63	-27.6	
VI	6.6	-50.2 (benzene)	6a, 25
VII	26.5	-26.7	6a, 26
VIIIa	82		27
VIIIb	93.3		6a
IX	11.9	-17.9 (CH ₂ Cl ₂)	6a, 28
Xa	52	-12.4 (?)	29, 30
	37	6.1 (?)	29, 30
XI	57	-29.5 (CH ₂ Cl ₂)	29
XII	86		27
XIIIa	93.7		22
XIIIb	94.3		22
XIV	87	14.14 (benzene)	10, 10
XV	61.6	3.7 (benzene)	32, 33, e
XVI	3.6	-60.8	34
XVII	9	-88.7 (?)	35, 36, e
XVIII	26.7	-32.1 (benzene)	37, 37, e
XIX		30.0	38, e, f
XX	25	-54 (CH ₂ Cl ₂)	39, 40
XXI	27.7	-53.6 (CH ₂ Cl ₂)	6a, 41
XXII	25	-47.5 (CH ₂ Cl ₂)	42, 41
XXIIIa	5.5	-35 (CH ₂ Cl ₂)	43, 41
XXIIIb	11.2	-36 (CH ₂ Cl ₂)	43, 41
XXIV	29.0	-56.8 (CH ₂ Cl ₂)	6a, 28
XXV	35.0	-16.4 (CH ₂ Cl ₂)	6a, 44
XXVI	30.7	-35	45, 46
XXVII	14.5	-57	47, 48, e
XXVIII	29.2	-33.4 (CH ₂ Cl ₂)	6a, 49
XXIX	31	-30.2 (CH ₂ Cl ₂)	50, e
XXX	21	-72.6 (?)	51
XXXI	49.3	-10.6	52, e
XXXIIa	78.9		6a
XXXIIb	35.2		53
XXXIII	43	18.2	53, 54
XXXIV	93	29.5	53, 54
XXXV	36	3.0	55, e

^a See ref 6a and text. ^b Solvent is CDCl₃ unless indicated. (?) indicates solvent not specified in the report. ^c First reference is to structure, second is to ^{31}P NMR. Where only one reference is given, either no ^{31}P NMR is available, or it is given in the structure paper. ^d Assignment of two % B values to two $\delta_{31\text{P}}$ values is based on internal trend in PO₅ compounds. See text. ^e The % B values for these molecules were calculated in this lab from reported structural parameters. ^f This molecular structure does not fit on the Berry coordinate.

III are the ^{31}P NMR chemical shifts, where known, as determined on liquid solutions.

- (43) T. E. Clark, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **18**, 1653 (1979).
 (44) A. Schmidpeter, D. Schomburg, W. S. Sheldrick, and J. H. Weinmaier, *Angew. Chem.*, **88**, 851 (1976).
 (45) J. S. Szobota and R. R. Holmes, *Inorg. Chem.*, **16**, 2299 (1977).
 (46) D. Bernard and R. Burgado, *Tetrahedron*, **31**, 797 (1975).
 (47) J. I. G. Cadogan, R. O. Gould, S. E. B. Gould, P. A. Sandler, S. J. Swire, and B. S. Tait, *J. Chem. Soc., Perkin Trans. 1*, 2392 (1975).
 (48) J. I. G. Cadogan, D. S. B. Grace, P. K. K. Lim, and B. S. Tait, *J. Chem. Soc., Perkin Trans. 1*, 2376 (1975).
 (49) A. Schmidpeter and J. H. Weinmaier, *Chem. Ber.*, **111**, 2086 (1978).
 (50) A. Schmidpeter and J. Zuber, *Chem. Ber.*, **109**, 3581 (1976).
 (51) H. W. Roesky, K. Ambrosins, and W. S. Sheldrick, *Chem. Ber.*, **112**, 1365 (1979).

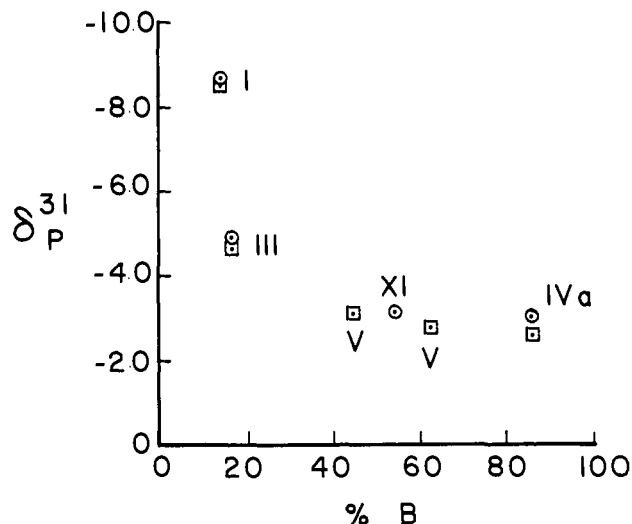
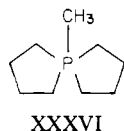


Figure 4. Plot of ^{31}P chemical shift vs. percent along the Berry coordinate (%B) for PO_5 compounds. Solution data are represented as circles. Solid-state data are represented as squares. Point labels are from Table II.

In order to consider the effect of molecular geometry on the ^{31}P chemical shift, one wishes to study sets of compounds within which there are minimal ligand variations that are nongeometrical. Each set chosen should have several compounds therein to give a reasonable representation of any trends that may exist. In order to find a reasonable number of ^{31}P data, and because of the close similarity found in this work between the solid-state and solution-state ^{31}P chemical shifts, solution-state ^{31}P data from the literature are used for these comparisons. Despite this inclusion and the large number of compounds considered in Table III, only three sets of compounds are found in sufficient number to warrant consideration in this light. These three sets are (1) the PO_5 group (compounds in which each of the five ligands is bonded to phosphorus through a ligand oxygen), (2) the PO_4C group, and (3) the PO_2C_3 . After brief consideration of certain general features of Table II, these three groups are considered in turn.

The ^{31}P chemical shifts summarized in Table III cover a range from -89 to 14 ppm, a span of more than 100 ppm. Chemical shifts of -40 ppm to -90 ppm seem to indicate a pure or distorted TBP (% B < 30), whereas for signals at lower shielding than -40 ppm almost any structure seems to be possible. Another interesting pattern is the fact that $\text{P}(\text{C}_6\text{H}_5)_5$ ($\delta_{31P} = -80.3$),⁵⁶ PCl_5 ($\delta_{31P} = -80.7$)¹², and $\text{P}(\text{OEt})_5$ ($\delta = -70.7$)⁵⁷ should all have such similar ^{31}P chemical shifts. This would seem to predict that the recently synthesized compound XXXVI with $\delta_{31P} = -91.7$ would have a



TBP structure.⁵⁸ Schmidbauer, Hall, and Kohler report that both ^{13}C and ^1H NMR spectra of this compound show no splitting due to distribution between equatorial and axial positions, even at -105°C , and take this as a possible indication of SP structure. They leave open the possibility of rapid polytopic rearrangement due to very low energy barriers, which would seem likely on the basis of the above mentioned ^{31}P chemical shift pattern. Perhaps

(52) J. I. C. Cadigan, R. O. Gould, and N. J. Tweedle, *J. Chem. Soc., Chem. Commun.*, 773 (1975).

(53) R. O. Day, A. C. Sau, and R. R. Holmes, *J. Am. Chem. Soc.*, **101**, 3790 (1979).

(54) A. J. Sau and R. R. Holmes, *J. Organomet. Chem.*, **156**, 253 (1978).

(55) E. Puff, P. R. Russel, and S. Tripett, *Phosphorus*, **4**, 203 (1974).

(56) L. Maier and R. Schmutzler, *Chem. Commun.*, 961 (1969).

(57) D. B. Denny and H. M. Relles, *J. Am. Chem. Soc.*, **86**, 3897 (1964).

(58) H. Schmidbauer, P. Hall, and F. H. Kohler, *Angew. Chem.*, **89**, 748 (1977).

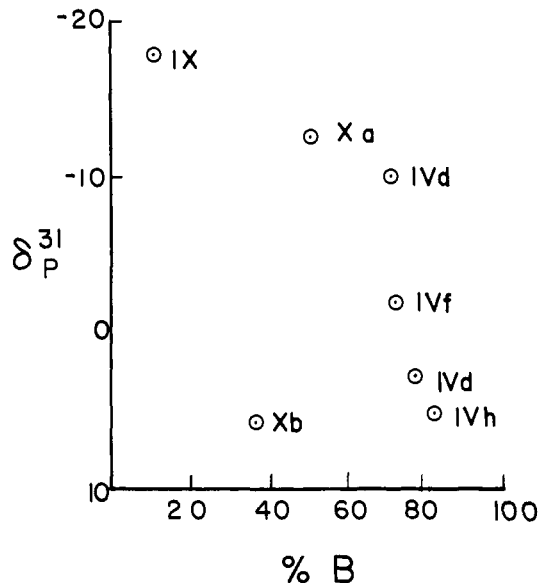


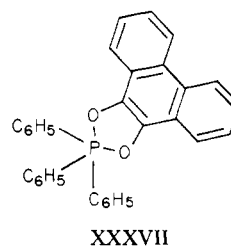
Figure 5. Plot of ^{31}P chemical shift vs. percent along the Berry coordinate (%B) shift for PO_4C compounds. Point labels are from Table II.

solid-state ^{13}C NMR experiments could solve this problem.

Figure 4 gives a plot of the % B of various PO_5 structures from Table III against δ_{31P} . Ramirez has attributed the shift to lower shielding on going from acyclic to monocyclic to bicyclic oxyphosphoranes to inhibition of π bonding.¹² A great many PO_5 type compounds and their δ_{31P} values are known, and they all seem to follow the pattern shown in Figure 4. For many of these compounds the parameter % B is not known (not represented in Figure 4); yet one can guess the range in which % B is expected from the general structural type of a given compound, especially if δ_{31P} is known. For example, consider triphenoxycatechol-phosphorane, for which δ_{31P} is -60.8 . This type of molecule would be expected to have a structure similar to that of the triisopropoxyphenanthrenequinone phosphorane (III, % B = 16.3, $\delta_{31P} = -48.6$). So it is apparent that a δ_{31P} value of -60.8 ppm is in reasonable agreement with the trend in Figure 4.

Figure 5 shows % B plotted against δ_{31P} for a group of PO_4C compounds. It is clear that no simple relationship is present. The scatter in this plot is apparently due to the different ways that variations in the chemical nature of the C atom (which varies among methyl, *tert*-butyl, adamantyl, phenyl, and $\text{C}(\text{CF}_3)_3$) are manifested in ^{31}P shielding and in molecular geometry. It is interesting to note that the two *tert*-butyl derivatives have very different % B values, and yet very similar chemical shifts. Note also the two corresponding phenyl derivatives; in one case the substitution of *tert*-butyl for phenyl has influenced the structure toward SP, whereas in the other the same substitution has influenced the structure toward TBP. Indeed this figure shows the difficulty in predicting structural effects of ligands.

Figure 6 illustrates the relationship between structure and δ_{31P} for a series of PO_2C_3 compounds. Examination of the formulas reveals that the chemical nature varies from $\text{PO}_2(\text{Ar})_3$ (Ar = aryl) to $\text{PO}_2(\text{Ar})(\text{R})_2$ (R = aliphatic). In considering PO_2C_3 compounds, one must also distinguish between two situations, those which have the two oxygen atoms equatorial (VI, VII, XVI, XVIII) and those which have the two oxygens axial-equatorial (XV, XIV). For example, consider the compound XXXVII, which



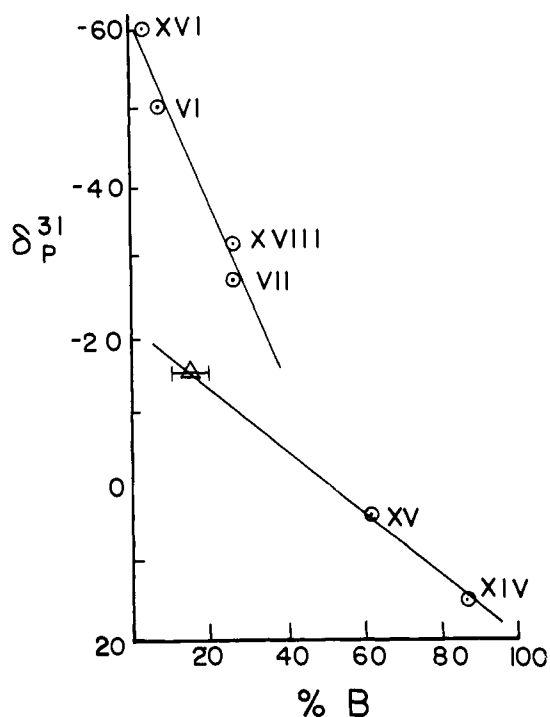


Figure 6. Plot of ^{31}P chemical shift vs. percent along the Berry coordinate for PO_2C_3 compounds. Point labels are from Table II. The triangle plotted point is for an estimated structure. (See text.)

has $\delta_{\text{P}}^{31} = -1.5^2$. On the basis of structural data on similar compounds (e.g., see Table III), one would expect this molecule to have a % B value of 10–20. If the reported δ_{P}^{31} value is plotted at % B = 15 on Figure 6, we see that this point falls on a straight line containing the points for compounds XIV and XV, and this line is different from the line through the remaining four points. Thus, it appears that for PO_2C_3 species there are two distinct correlation lines in Figure 6. The compounds of these two correlations can be distinguished on the basis of the relative orientations of their P–O bonds. The relative orientations can be

discussed in terms of the orientations that the P–O bonds would have if a Berry rotation converted the species to a pure SP configuration or a TBP configuration. The species represented on the upper line of Figure 6 would have two axial P–O bonds in the TBP configuration. Those represented on the lower line would have axial/equatorial orientations in the TBP arrangement or two adjacent basal P–O bonds in the SP. A definite structure vs. chemical shift relationship is apparent in this figure, but whether it is due to changes in geometry or changes in the electronic substituent effects of individual substituents is not clear. There is, in any case, a large change in chemical shift for chemically similar compounds. This variation shows again that one must take care in using phosphorus chemical shifts to determine molecular structures.

The principal purpose in presenting the data in Table III has been to stimulate and lay groundwork for further studies. As can be seen in Figures 4, 5, and 6, not enough points are on the plots to establish unequivocally any explicit relationships between chemical shift and molecular structure. With more data on well-characterized compounds these relationships could be tested more definitively. Such relationships could be important in providing a sound basis for the use of NMR parameters to characterize molecular structure. A more fundamental use of the relationships would be their interpretation in terms of the nature of bonding in these types of molecules. In any case, the present work has demonstrated the ability of NMR to provide a bridge between the crystalline states and liquid (e.g., solution) states. In the present application it has been shown that the structures of representative phosphoranes are very similar in solution to the X-ray-characterized solid-state structures.

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Registry No. I, 19613-06-0; II, 32394-39-1; III, 3009-75-4; IVa, 19579-02-3; IVb, 21229-04-9; IVc, 6857-81-4; IVd, 21229-05-0; V, 60011-07-6; XV, 79734-98-8; XVII, 2588-88-7; XVIII, 79768-48-2; XIX, 79734-99-9; XXVII, 38575-00-7; XXIX, 61733-80-0; XXXI, 58498-98-9; XXXV, 54554-57-3; $\text{BrP}(\text{C}_6\text{H}_5)_4$, 24038-30-0.

5-Methyladenine: A Transient Intermediate in a Translocative Rearrangement

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Abstract: A synthetic approach to 5-methyl-5*H*-adenine by closure of a pyrimidine ring onto 5-amino-4-cyano-4-methyl-4*H*-imidazole, by mild treatment with formamidine at 20 °C, resulted in rearrangement to 4-amino-8-methylimidazo[1,5-*a*]-1,3,5-triazine. This constitutes a “translocative rearrangement” in which the overall result is to remove a $\text{C}\equiv\text{N}$ group from the quaternary carbon of the original 4*H*-imidazole ring and to translocate it efficiently and with ease to a ring nitrogen two atoms removed, where it becomes attached as a $>\text{CNH}_2$ function. An intramolecular route is postulated, proceeding through 5-methyl-5*H*-adenine (and/or its tautomers) as a transient intermediate. Application of semiempirical molecular orbital MINDO/3 calculations revealed the relative instability of the intermediate 5-methyladenine and the stability of the final rearrangement product. They also provided insight into the probable loci of bond breaking and into the structures of the potential intermediates in the ring opening of 5-methyladenine. The imidazotriazine structure of the rearrangement product, indicated by spectroscopic data, was established by unequivocal synthesis.

Previous experimental results in this laboratory have indicated that the existence of a C5-alkylated guanine would be transient and that an intermediate of this type, if formed, would tend to undergo facile ring cleavage and/or rearrangement.¹⁻³ While

it is altogether possible that a C5-alkylated adenine would also be destabilized, the electron-donating 6-amino group might offer greater hope for the recognition of such a species. The least

(1) Golankiewicz, B.; Holtwick, J. B.; Holmes, B. N.; Duesler, E. N.; Leonard, N. J. *J. Org. Chem.* 1979, 44, 1740.

(2) Holtwick, J. B.; Golankiewicz, B.; Holmes, B. N.; Leonard, N. J. *J. Org. Chem.* 1979, 44, 3835.

(3) Holtwick, J. B.; Leonard, N. J. *J. Org. Chem.* 1981, 46, 3681.