The Carbon-13 and Phosphorus-31 Nuclear Magnetic Resonance Spectra of Some Tertiary Phosphines

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The ^{31}P and ^{13}C n.m.r. spectra for some tertiary phosphines are reported. Factors affecting the chemical shifts and coupling constants are examined, and it is suggested that the major factor involved in determining changes in chemical shifts from one tertiary phosphine to another is the bond angle at the nucleus concerned.

THE growing use of ^{13}C n.m.r. spectroscopy has been reviewed.[1] However, organophosphorus compounds have been neglected, although ^{13}C chemical shifts and ^{31}P–^{13}C coupling constants have been obtained. Retcofsky and Griffin have published the ^{13}C chemical shift of the *para*-carbon atom for ten phenylphosphorus compounds.[2] McFarlane has used ^{1}H–$\{^{13}C\}$ INDOR to measure the ^{13}C n.m.r. spectra of some phosphorus compounds containing methyl or ethyl groups.[3] The ^{13}C n.m.r. spectra of PPh_3, $P(OPh)_3$, and $OP(OPh)_3$ have been reported.[4,5] Thus although different types of phosphorus compound have been examined, there has been no study of the ^{13}C n.m.r. spectra of any one series of organophosphorus compounds. One of the simplest

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[1] E. F. Mooney and P. H. Winson, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 153.

[2] H. L. Retcofsky and C. E. Griffin, *Tetrahedron Letters*, 1966, 1975.

[3] W. McFarlane, *Proc. Roy. Soc.*, 1968, *A*, **306**, 185.

[4] O. A. Gansow and B. Y. Kimura, *Chem. Comm.*, 1970, 1621.

[5] G. C. Levy and J. D. Cargioli, *Chem. Comm.*, 1970, 1663.

series of organophosphorus compounds is that of tertiary alkyl- and aryl-phosphines.

EXPERIMENTAL

The ^{13}C and ^{31}P n.m.r. spectra were measured on a Bruker HFX-90 n.m.r. spectrometer with all proton coupling removed by white noise decoupling at *ca.* 35 °C. The ^{31}P n.m.r. spectra were measured on *ca.* 10% solutions of the phosphine in benzene containing *ca.* 10% perfluorobenzene to provide a ^{19}F field–frequency lock. Calibration was by measurement of the ^{31}P n.m.r. spectrum of $P(OMe)_3$ under the same conditions. The ^{31}P chemical shifts are quoted with respect to 85% H_3PO_4 by taking the chemical shift of $P(OMe)_3$ with respect to 85% H_3PO_4 as $-141{\cdot}0$ p.p.m.[6] The ^{13}C n.m.r. spectra were measured on the neat tertiary phosphine containing *ca.* 10% perfluorobenzene to provide a ^{19}F field–frequency lock and approximately 5% tetramethylsilane as internal ^{13}C calibrant.

All manipulations involving tertiary phosphines were carried out under nitrogen.

RESULTS

Chemical shifts for the tertiary phosphines are in Table 1, and coupling constants in Table 2. The numbering of the carbon and phosphorus atoms is as in (I). Literature values for PMe_3 and PPh_3 are added.[3,4] The assignment of peaks to a given carbon atom was not always straightforward, since the majority of carbons had their ^{13}C resonance split into a doublet by coupling with ^{31}P (see Figure 1). Assignment was assisted by (*a*) use of off-resonance decoupling.[7] This technique gives the number of hydrogen

TABLE 1

^{13}C and ^{31}P N.m.r. chemical shifts for some tertiary phosphines. Atoms are numbered as in (I). The ^{13}C chemical shifts ($\pm 0{\cdot}1$ p.p.m.) are relative to tetramethylsilane and the ^{31}P chemical shifts ($\pm 0{\cdot}2$ p.p.m.) are relative to 85% H_3PO_4 *

Tertiary phosphine	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	P(11)
PMe_3	$-14{\cdot}3$ [a]										62 [b]
PEt_3	$-19{\cdot}5$	$-10{\cdot}3$									$20{\cdot}1$ [c]
$PBu^n{}_3$	$-29{\cdot}3$	$-28{\cdot}6$	$-25{\cdot}4$	$-14{\cdot}7$							$32{\cdot}7$ [c]
PMe_2Ph	$-14{\cdot}7$				$-143{\cdot}5$	$-130{\cdot}7$	$-128{\cdot}5$	$-128{\cdot}0$			$47{\cdot}6$ [c]
PEt_2Ph	$-20{\cdot}9$	$-10{\cdot}0$			$-139{\cdot}8$	$-132{\cdot}7$	$-128{\cdot}6$	$-128{\cdot}7$			$17{\cdot}6$ [c]
$PPr^n{}_2Ph$	$-31{\cdot}7$	$-20{\cdot}1$	$-16{\cdot}1$		$-140{\cdot}4$	$-132{\cdot}8$	$-128{\cdot}6$	$-128{\cdot}7$			$27{\cdot}3$ [c]
$PBu^n{}_2Ph$	$-29{\cdot}0$	$-29{\cdot}0$	$-25{\cdot}0$	$-14{\cdot}0$	$-140{\cdot}6$	$-132{\cdot}8$	$-128{\cdot}6$	$-128{\cdot}7$			$26{\cdot}0$ [c]
$PMePh_2$	$-12{\cdot}7$				$-141{\cdot}5$	$-132{\cdot}6$	$-128{\cdot}8$	$-128{\cdot}7$			$27{\cdot}7$ [c]
$PEtPh_2$	$-21{\cdot}5$	$-10{\cdot}4$			$-140{\cdot}2$	$-133{\cdot}3$	$-128{\cdot}9$	$-128{\cdot}8$			$12{\cdot}3$ [c]
PMe_2Bu^t	$-9{\cdot}5$								$-26{\cdot}5$	$-26{\cdot}5$	$28{\cdot}7$ [c]
PEt_2Bu^t	$-17{\cdot}7$	$-12{\cdot}3$							$-28{\cdot}1$	$-27{\cdot}8$	$-6{\cdot}9$ [c]
$PPr^n{}_2Bu^t$	$-28{\cdot}8$	$-22{\cdot}1$	$-16{\cdot}3$						$-27{\cdot}8$	$-27{\cdot}8$	$8{\cdot}7$ [c]
$PBu^n{}_2Bu^t$	$-25{\cdot}5$ [e]	$-31{\cdot}2$	$-25{\cdot}4$ [e]	$-14{\cdot}1$					$-27{\cdot}9$	$-27{\cdot}8$	$4{\cdot}4$ [c]
$PMeBu^t{}_2$	$-3{\cdot}2$								$-30{\cdot}7$	$-29{\cdot}4$	$-12{\cdot}0$
$PEtBu^t{}_2$	$-14{\cdot}3$	$-15{\cdot}1$							$-31{\cdot}4$	$-30{\cdot}0$	$-32{\cdot}4$
$PPr^nBu^t{}_2$	$-24{\cdot}4$ [e]	$-24{\cdot}3$ [e]	$-16{\cdot}1$						$-31{\cdot}4$	$-30{\cdot}0$	$-26{\cdot}3$ [c]
$PBu^t{}_3$									$-34{\cdot}7$	$-32{\cdot}8$	$-63{\cdot}3$
PPh_3					$-138{\cdot}3$ [f]	$-134{\cdot}4$	$-129{\cdot}2$ [f]	$-129{\cdot}3$ [f]			$6{\cdot}0$ [d]

[a] From ref. 3. [b] From ref. 10. [c] From ref. 11. [d] From ref. 6. [e] Probable assignment, see text. From ref. 4.

* The sign of the shifts is in the sense that increasing field is taken as positive.

TABLE 2

^{13}C–^{31}P Coupling constants (Hz) for some tertiary phosphines. The carbon atoms are numbered as in (I). All coupling constants are accurate to $\pm 0{\cdot}2$ Hz

Tertiary phosphine	$^1J(C^1–P)$	$^2J(C^2–P)$	$^3J(C^3–P)$	$^1J(C^5–P)$	$^2J(C^6–P)$	$^3J(C^7–P)$	$^1J(C^9–P)$	$^2J(C^{10}–P)$
PMe_3 [a]	$-13{\cdot}6$							
PEt_3	$14{\cdot}0$	$13{\cdot}8$						
$PBu^n{}_3$	$13{\cdot}8$	$14{\cdot}8$	$11{\cdot}1$					
PMe_2Ph	$14{\cdot}6$			$15{\cdot}6$	$17{\cdot}5$	$5{\cdot}8$		
PEt_2Ph	$12{\cdot}5$	$14{\cdot}7$		$17{\cdot}9$	$18{\cdot}6$	$6{\cdot}7$		
$PPr^n{}_2Ph$	$12{\cdot}8$	$15{\cdot}4$	$12{\cdot}2$	$17{\cdot}6$	$20{\cdot}4$	$6{\cdot}7$		
$PBu^n{}_2Ph$	$12{\cdot}7$ [c]	$15{\cdot}2$ [c]	$11{\cdot}5$	$17{\cdot}7$	$19{\cdot}2$	$6{\cdot}7$		
$PMePh_2$	$15{\cdot}4$			$14{\cdot}1$	$18{\cdot}8$	$6{\cdot}4$		
$PEtPh_2$	$17{\cdot}1$	$11{\cdot}6$		$14{\cdot}9$	$18{\cdot}9$	$6{\cdot}5$		
PMe_2Bu^t	$19{\cdot}8$						$10{\cdot}7$	$13{\cdot}4$
PEt_2Bu^t	$18{\cdot}2$	$21{\cdot}0$					$13{\cdot}0$	$13{\cdot}4$
$PPr^n{}_2Bu^t$	$19{\cdot}1$	$20{\cdot}8$	$12{\cdot}7$				$12{\cdot}4$	$13{\cdot}6$
$PBu^n{}_2Bu^t$	$19{\cdot}4$ [c]	$18{\cdot}8$	$12{\cdot}3$ [c]				$12{\cdot}9$	$13{\cdot}4$
$PMeBu^t{}_2$	$25{\cdot}2$						$21{\cdot}8$	$14{\cdot}1$
$PEtBu^t{}_2$	$22{\cdot}0$	$28{\cdot}3$					$23{\cdot}2$	$13{\cdot}8$
$PPr^nBu^t{}_2$	$21{\cdot}8$ [c]	$27{\cdot}9$ [c]	$13{\cdot}4$				$23{\cdot}5$	$14{\cdot}2$
$PBu^t{}_3$							$33{\cdot}9$	$13{\cdot}3$
PPh_3 [b]				21	20	7		

[a] From ref. 3. [b] From ref. 4. [c] Probable assignment, see text.

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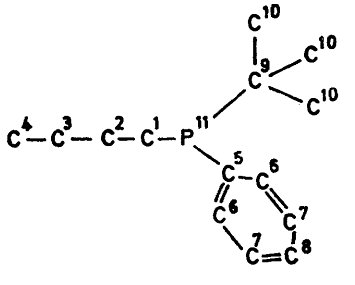
[6] 'Topics in Phosphorus Chemistry,' vol. 5, ^{31}P Nuclear Magnetic Resonance, ed. M. Grayson and E. J. Griffith, Interscience, New York, 1967, and references therein.

[7] R. A. Archer, R. D. G. Cooper, P. V. Demarco, and L. R. F. Johnson, *Chem. Comm.*, 1970, 1291.

atoms attached to a particular carbon atom. It proved especially useful for $PEtBu^t_2$ where the doublets due to the carbon of the ethyl group overlapped. (*b*) Use of intensities.



(I)

Intensities were used with caution on account of enhancements due to the nuclear Overhauser effect. However, the effect appeared to be approximately equal for the *o*-, *m*-, and *p*-carbons of the phenyl ring. (*c*) Use of measurements on other compounds. For a monosubstituted phenyl ring, the *m*-carbon ^{13}C chemical shift is least moved from the position of benzene.[8] The *o*- and *m*-carbons were assigned on this basis. The assignment of the CH_2 carbons of alkyl chains were based on the chemical shifts reported for alkanes [9] and the magnitude of phosphorus–carbon coupling constants in other tertiary phosphines.

On account of the overlap of doublets, assignment is not conclusive in three cases. For example Figure 1 shows part of the ^{13}C n.m.r. spectrum of $PBu^n_2Bu^t$. From the observed chemical shifts of alkanes and other tertiary phosphines, the four peaks can be assigned to the doublets of C(1) and C(3). It would be expected that $^1J(P–C^1)$ and $^3J(P–C^3)$ will be approximately the same as those measured for $PPr^n_2Bu^t$ where $^1J(P–C^1) = 19·1$ Hz and $^3J(P–C^3) = 12·7$ Hz. Of the possible assignments only two have coupling constants close to those of $PPr^n_2Bu^t$, namely $^1J(P–C^1)$ 19·4 Hz and $^3J(P–C^3)$ 12·3 Hz or $^1J(P–C^1)$ 17·9 Hz and $^3J(P–C^3)$ 13·8 Hz. The first pair appear the most likely, and these values are given in Table 2 with the corresponding chemical shifts in Table 1, but the second assignment cannot be completely ruled out. Similar problems exist for PBu^n_2Ph and $PPr^nBu^t_2$.

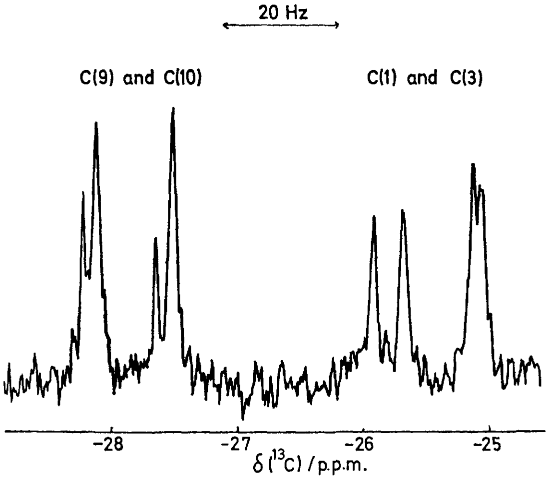


FIGURE 1 Part of the 22·62 MHz ^{13}C n.m.r. spectrum of $PBu^n_2Bu^t$, with all the proton coupling removed

DISCUSSION

The ^{31}P *Chemical Shifts.*—Most of the ^{31}P chemical shifts have been reported previously,[10,11] but are reported for the first time for $PMeBu^t_2$, $PEtBu^t_2$, and PBu^t_3. It is however pertinent to discuss the ^{31}P as well as the ^{13}C chemical shifts. Factors that affect ^{31}P chemical shifts of phosphines appear to be very closely related to those that affect the ^{13}C chemical shifts of alkanes.[9] For example if the ^{13}C chemical shift [9] of RCH_3 (R = alkyl or phenyl) is plotted against the ^{31}P chemical shift [10] of $RPPh_2$, R_2PPh, or R_3P a steady curve is produced, (*e.g.* Figure 2). Factors affecting ^{31}P chemical shifts have been examined previously.[6] It was concluded that three factors were involved: (*a*) the electronegativity of the substituent(s), (*b*) the bond angle(s) at the phosphorus, and (*c*) π-bonding between the substituent and the phosphorus. The order of substituent effect $Me < Bu^i < Pr^n < Bu^n < Et < Ph < Pr^i < Bu^t$ does not seem to have been satisfactorily explained. A similar order is found for both tertiary phosphines and alkanes (Figure 2). It is significant that the phenyl group lies on the same line as the alkyl groups. This does not happen if $R_3{}^{11}B$ is plotted against $R^{13}CH_3$ or $R^{17}OH$ against $R^{13}CH_3$. There are significant deviations when R = Ph, but boron–phenyl and oxygen–phenyl π-bonding would be expected.[12] Thus phenyl–phosphorus π-bonding seems to be unlikely in tertiary phosphines. Confirmation of this conclusion comes from the ^{13}C chemical shifts

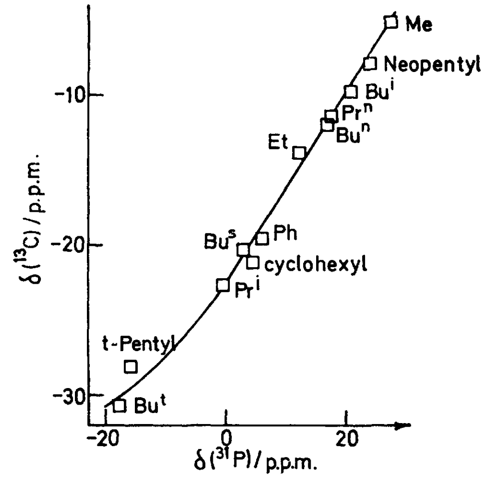


FIGURE 2 A plot of the ^{13}C chemical shift of $R^{13}CH_3$ against the ^{31}P chemical shift of $R^{31}PPh_2$

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[8] G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, 1965, **42**, 2427.

[9] D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 1964, **86**, 2984.

[10] S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781, and references therein.

[11] B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971,1104.

[12] 'Organic Chemistry,' L. F. Fieser and M. Fieser, Reinhold, New York, 3rd edn., 1956, p. 568.

of the *m*- and *p*-carbons of the phenyl ring. Maciel and Natterstad have shown that the *p*-carbon π-electron density is linearly related to the difference in ^{13}C chemical shift between the *m*- and *p*-carbons.[8] In the case of the phenylphosphines reported here, this difference is always less than 0·5 p.p.m. compared with the much larger differences found, *e.g.*, for $PhNMe_2$ (12·5 p.p.m.),[13] where π-bonding is generally accepted. It is therefore concluded that there is almost certainly negligible phosphorus–carbon π-bonding in our tertiary phosphines.

The relative importance of bond angles and electronegativity on ^{31}P chemical shifts of tertiary phosphines is more difficult to assess. However, there are measurements on related compounds that indicate that bond-angle changes are dominant: (*a*) in the case of the PR_4^+ cation, where the C–P–C bond angle is fixed, the change in ^{31}P chemical shift [6] on going from PMe_4^+ (−25·1 p.p.m.) to PEt_4^+ (−33 p.p.m.) is small compared with the change on going from PMe_3 (+62 p.p.m.) to PEt_3 (+20·1 p.p.m.); (*b*) the ' theoretical ' electronegativities of Me and Bu^t are very similar (2·27 and 2·29 respectively [14]) yet there is a considerable chemical-shift difference between PMe_3 (+62 p.p.m.) and PBu^t_3 (−63·3 p.p.m.); (*c*) ^{13}C n.m.r. spectra are known to be relatively insensitive to the electronegativity of the β-substituent. On the basis of the linear plot between the ^{13}C chemical shift and the β-substituent [15] it would be expected that no more than 1 p.p.m. of the 42 p.p.m. change on going from PMe_3 to PEt_3 can be attributed to electronegativity changes; and (*d*) if the computer programme to calculate ^{31}P chemical shifts due to Van Wazer and Letcher is used,[16] then to account for the change in ^{31}P chemical shift on going from PMe_3 to PBu^t_3, without making any allowance for changes in electronegativity, the C–P–C bond angle has to increase from the known value [17] for PMe_3 of 98·6° to 105·7° in PBu^t_3. This is not unreasonable.

We conclude that the ^{31}P chemical shifts of tertiary alkyl- or aryl-phosphines are dominated by bond-angle changes. As a corollary from the relationship shown in Figure 2, the ^{13}C chemical shifts of alkanes (excluding cases where electronegativity of substituents is possibly changed, *e.g.*, changing H to Me on going from CH_4 to C_2H_6) are also dominated by bond-angle changes.

^{13}C *Chemical Shifts*.—The ^{13}C chemical shifts in the tertiary phosphines appear to behave in a similar way to the alkanes.[9] The changes in C(1), C(2), C(3), and C(4) chemical shifts for a series such as PR_2Ph (R = Me, Et, Pr^n, and Bu^n) are analogous to those observed for alkanes. It seems likely from the earlier discussion on ^{31}P chemical shifts that ^{13}C chemical shifts of alkanes are also dominated by changes in bond angle. However, too few data are available to justify a detailed discussion.

The influence of phosphorus on ^{13}C chemical shifts appears to be small. For example the ^{13}C chemical shift of PMe_3 of −14·3 p.p.m. is very similar to that observed [9] for $HC(^{13}CH_3)_3$ of −13·65 p.p.m., yet very different from NMe_3 of −46·8. These differences are probably predominantly due to electronegativities,[14] *e.g.*, $-PMe_2$; −2·28, $-CHMe_2$: −2·28; and $-NMe_2$: −2·40.

^{13}C–^{31}P *Coupling Constants*.—The magnitude of $^1J(^{13}C-^{31}P)$, $^2J(^{13}C-^{31}P)$, and $^3J(^{13}C-^{31}P)$ for the alkyl side-chains are all approximately equal, and are therefore of little assistance for assignments. $^1J(^{15}N-^{13}C)$ has been interpreted on the basis of the Fermi contact term.[18] It is therefore possible that $^1J(^{13}C-^{31}P)$ can be interpreted similarly. The presence of negative values of $^1J(^{13}C-^{31}P)$, although forbidden by the simple Fermi contact treatment, has recently been explained.[19] The *s*-character, s_c, in the hybrid carbon orbital can be estimated on the normal basis, *i.e.*, sp^3 carbon $s_c = 0{\cdot}25$; and sp^2 carbon $s_c = 0{\cdot}33$. The *s*-character, s_p, in the hybrid phosphorus orbital can be estimated for PMe_3 and PPh_3 from the known C–P–C bond angles, θ, from relationship (1). The C–P–C bond angles

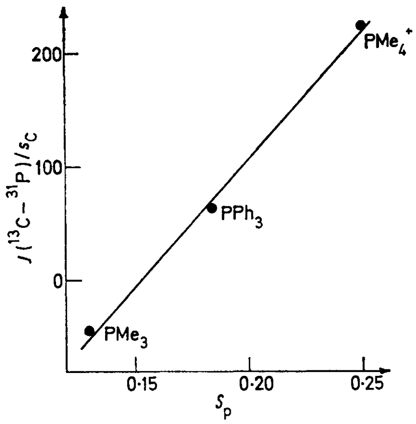

FIGURE 3 A plot of $^1J(^{13}C-^{31}P)/s$-character of the carbon bonding orbital, s_c, against the *s*-character of the phosphorus bonding orbital, s_p, for PMe_3, PPh_3, and PMe_4^+

$$s_p = \frac{\cos\theta}{\cos\theta - 1} \qquad (1)$$

and $^1J(^{13}C-^{31}P)$ are known for PMe_3,[17] PPh_3 [20] [$^1J(^{13}C-^{31}P)$ assumed positive], and PMe_4^+. For these three compounds, a plot of $^1J(^{13}C-^{31}P)/s_c$ against s_p is straight (Figure 3). If we assume a positive value of $^1J(^{13}C-^{31}P)$ for PBu^t_3, this requires a C–P–C bond angle of 105·7°, in good agreement with 105·7° calculated

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[13] C. P. Nash and G. E. Maciel, *J. Phys. Chem.*, 1964, **68**, 832.

[14] J. E. Huheey, *J. Phys. Chem.*, 1965, **69**, 3284.

[15] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 722.

[16] Ref. 6, p. 217.

[17] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, 1960, **32**, 512.

[18] G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 5564.

[19] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1969, **51**, 2790.

[20] J. J. Dally, *J. Chem. Soc.*, 1964, 3799.

from ^{31}P chemical shifts. In view of the approximations this agreement is probably fortuitous, but indicates that the dominant factor with tertiary phosphine chemical shifts and coupling constants is the C–P–C bond angle.

Conclusions.—The major factor affecting ^{31}P and probably ^{13}C chemical shifts appears to the bond-angle changes at the nucleus in question. This only applies when there is a negligible change in the electronegativity of the substituent, *e.g.*, when methyl is changed to t-butyl, but not when hydrogen is changed to methyl.

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