Nuclear Magnetic Resonance Studies of Scrambling Reactions in Solutions of Tetra-alkyl- and Tetra-aryl-diphosphanes

By **Robin K. Harris** * and **Elizabeth M. Norval (née McVicker)**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ
Manfred Fild, Lehrstuhl B für Anorganische Chemie der Technischen Universität, 33 Braunschweig, Pockelsstrasse 4, German Federal Republic

The ^{31}P-{^1H} nuclear magnetic resonances of certain tetra-alkyldiphosphanes are broadened on dissolution in methylene dichloride, the effect increasing with time. Simultaneously, the ^{13}C-{^1H} and ^1H spectra indicate ' decoupling ' from ^{31}P. These observations suggest breakage of the P–P bond, and mixtures of certain diphosphanes give n.m.r. spectra which indicate exchange of parts, with the formation of new mixed species. The ^{31}P chemical shifts and P–P coupling constants for such species are presented and discussed. In two cases ^{13}C data have also been obtained.

In 1972 McFarlane and McFarlane [1] reported an interesting effect for the ^1H n.m.r. spectrum of tetramethyldiphosphane, when in solution in dichloromethane. For neat diphosphane samples the spectrum showed a deceptively simple triplet pattern for an $[AX_6]_2$ spin system.[2] However, McFarlane and McFarlane [1] found that for solutions containing increasing proportions of CH_2Cl_2 the lines broadened and merged to form a single line, which sharpened so that for 14% P_2Me_4 in CH_2Cl_2 the width at half-height ($\Delta\nu_{\frac{1}{2}}$) was 1.5 Hz. Decreasing the diphosphane concentration further caused the signal to broaden again, and it was suggested that the triplet pattern was reformed in very dilute solutions. These workers also found that mixing symmetrical diphosphanes P_2Me_4 and P_2Ph_4 in dichloromethane gave a single proton peak, which changed over a period of days to a doublet of doublets, as the unsymmetrical diphosphane Me_2PPPh_2 was produced.

Several other unsymmetrical diphosphanes $R^1_2PPR^2_2$ have been prepared,[3] either by boiling a disubstituted phosphine PR^1_2H with a disubstituted phosphinous chloride, PR^2_2Cl, in presence of tertiary amines, or by the reaction of an organic halide and a disubstituted phosphide $M(PR_2)$ (M = an alkali metal). Generally, the unsymmetrical diphosphanes are unstable and eventually revert to the symmetrical compounds, but in a few cases ^{31}P n.m.r. data have been obtained.[4-7]

Using dichloromethane as the solvent we have been able to form eight unsymmetrical diphosphanes and record their ^{31}P spectra *in situ*. The values of $^1J(PP)$ and $\delta(P)$ provide interesting comparisons with those of symmetrical diphosphanes, and can be related to the bulk of the substituents on phosphorus. Prior to mixing the compounds in dichloromethane, the ^{31}P spectra of the individual symmetrical diphosphanes were recorded in dichloromethane. More extensive n.m.r. studies were carried out on the effect of the solvent on P_2Et_4. Solutions of diphosphanes, whether of individual species or of mixtures, in benzene or toluene appear to be stable.

EXPERIMENTAL

All samples of diphosphanes were made up under nitrogen in a dry-box. The solvent was *ca.* 30% CD_2Cl_2 and 70% CH_2Cl_2 (v/v). The CH_2Cl_2 was distilled over P_4O_{10} and stood over $K_2[CO_3]$ prior to use, but CD_2Cl_2 was used as obtained commercially. Samples were placed in n.m.r. tubes (outside diameter, 12 mm), degassed by the freeze–pump–thaw method, and sealed. They were stored at 4 °C when not being studied. Since the diphosphanes with lower alkyl substituents were very reactive and relatively volatile it was not possible to measure amounts accurately, so, where quoted below, the concentrations (as a percentage of the total volume) are only approximate.

Phosphorus-31, ^{13}C, and ^1H spectra were recorded at 40.51, 25.41, and 100.06 MHz, respectively, using a Varian XL100 spectrometer. Proton-noise decoupling was applied for the ^{31}P and ^{13}C spectra. Temperatures were calibrated using a standard methanol sample. Chemical shifts are given with respect to 85% H_3PO_4 for ^{31}P and $SiMe_4$ for ^{13}C and ^1H. They were measured by the indirect method,[8] using $\Xi_P(85\%\ H_3PO_4) = 40\,480\,720$ Hz and $\Xi_C(SiMe_4) = 25\,145\,004$ Hz. The standardized lock frequency was $\Xi_D(CD_2Cl_2) = 15\,350\,688$ Hz.

Spectrometer conditions varied as the occasion demanded, but ^{31}P-{^1H} spectral widths (s.w.) were in the range 1—5 kHz, with acquisition times (t_{ac}) 0.8—4.0 Hz and pulse angles 20—80°; the number of pulses varied from 50 to 10 000.

RESULTS

(*a*) *Studies of Individual Diphosphanes.*—The ^{31}P-{^1H} and ^{13}C-{^1H} spectra of samples containing tetraethyl-

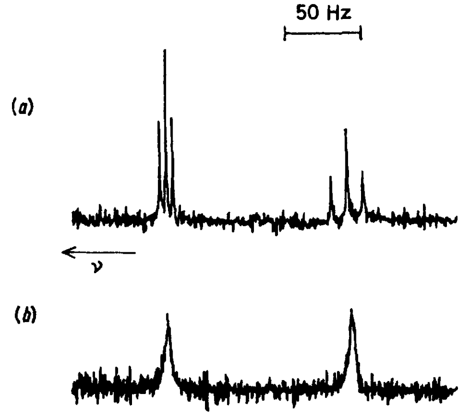


FIGURE 1 ^{13}C-{^1H} n.m.r. spectrum of Et_2PPEt_2 in dichloromethane at 36 °C as a function of concentration, with s.w. = 250 Hz and t_{ac} = 8.0 s in both cases: (*a*) neat (58 pulses); (*b*) *ca.* 15% v/v solution (590 pulses) diphosphane at different concentrations (100, 85, 15, 8, and $<5\%$) in CH_2Cl_2–CD_2Cl_2 were recorded at various intervals of time after preparation and at a range of low temperatures. At ambient probe temperature (36 °C) the linewidths of the ^{31}P singlet or of the deceptively simple triplets in the ^{13}C spectra increased as the diphosphane concentration was reduced. The linewidths also increased with time to the extent that after 6 weeks the ^{31}P signal of the 15% solution was barely distinguishable from the baseline. Decreasing the temperature reduced the linewidths, and in the ^{13}C spectra the triplet pattern re-appeared, whereas at ambient temperature only one broad band was seen in each of the CH_3 and CH_2 regions for (see Figure 1) samples of $\leqslant 15\%$. The proton spectra also showed an increase in linewidth as the concentration was lowered; after 1 week the spectrum of the 15% solution at ambient temperature was that of an A_3B_2 system, associated with the Et groups, apparently totally decoupled from the phosphorus nuclei. At lower temperatures splittings due to coupling to phosphorus were restored.

The only other diphosphanes which showed effects similar to those of P_2Et_4 in dichloromethane were P_2Me_4, as reported by McFarlane and McFarlane,[1] and $(EtMeP)_2$. In an inert solvent (benzene) two sets of signals for ^{31}P were observed [9] for the latter compound due to the presence of the two diastereoisomers, but in CH_2Cl_2–CD_2Cl_2 the signals broadened and only one resonance appeared at the midpoint of those for the isomers. Diphosphanes having any heavier substituents were unaffected by the solvent.

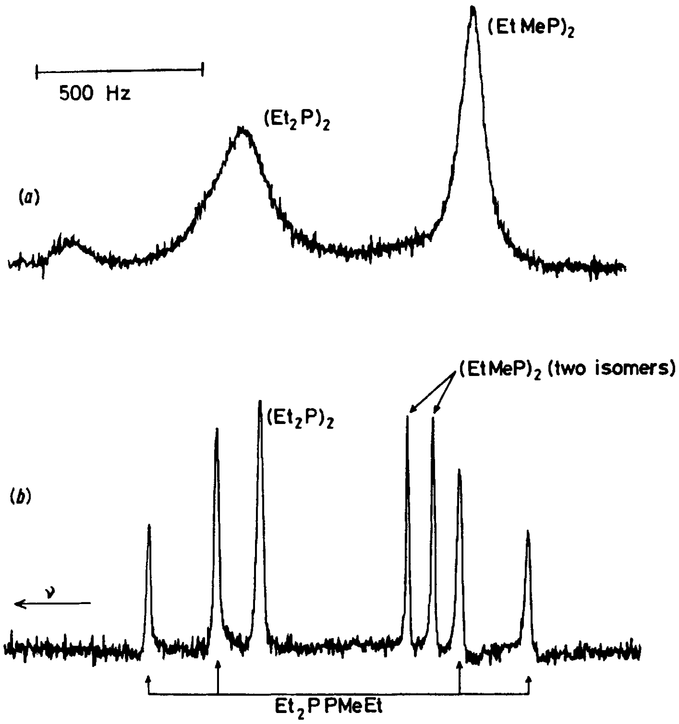


FIGURE 2 ^{31}P-{^1H} n.m.r. spectrum of a mixture of $(EtMeP)_2$ and $(Et_2P)_2$ *ca.* 7 h after mixing, as a function of temperature at s.w. = 2 500 Hz and t_{ac} = 1.6s: (*a*) 36 °C (4 000 pulses); (*b*) −50 °C (54 pulses)

(*b*) *Studies of Mixtures of Diphosphanes.*—Pairs of diphosphanes of general types $(R_2P)_2$ or $(R^1R^2P)_2$ were mixed in solution in CH_2Cl_2–CD_2Cl_2. The ^{31}P-{^1H} spectra were recorded as soon as possible after mixing. In most cases these spectra showed AB patterns indicating that mixed diphosphanes of general types $R^1{}_2PPR^2{}_2$ [from $(R^1{}_2P)_2 + (R^2{}_2P)_2$] or $R^1R^2PPR^3{}_2$ [from $(R^1R^2P)_2 + (R^3{}_2P)_2$] had been formed. Their n.m.r. parameters [δ(P) and $|^1J(PP)|$] were determined and are presented in Table 1.

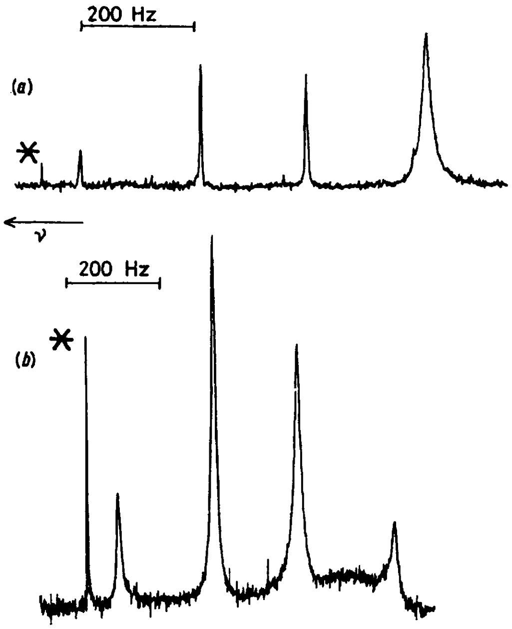


FIGURE 3 ^{31}P-{^1H} n.m.r. spectrum of a mixture of P_2Et_4 and P_2Ph_4 at 36 °C as a function of time after mixing, with s.w. = 1 kHz and t_{ac} = 2s: (*a*) 90 min (887 pulses); (*b*) 3 weeks (2 200 pulses). The peak marked with an asterisk is an impurity. Note that (*a*) and (*b*) do not have the same scale

Usually peaks from the reactants were also present, indicating that an equilibrium had been set up. Figures 2 and 3 show examples. These figures also indicate two typical features concerning the linewidths of the resonances, *viz.* their dependence on temperature (Figure 2) and on the time delay between mixing the diphosphanes and recording the spectra (Figure 3). Carbon-13 spectra were also recorded for two of the systems, and the results are presented in Table 2. We shall now comment on the characteristics of particular systems of diphosphane mixtures.

When the lightest diphosphanes, P_2Et_4 and $(EtMeP)_2$ or

TABLE 1

Phosphorus-31 n.m.r. data [a] for mixed diphosphanes $R^1{}_2PPR^2R^3$, in solution in methylene dichloride

Compound	θ_c/°C	$\lvert ^1J(PP)\rvert$/Hz	$\delta(P_\alpha)$/ p.p.m.	$\delta(P_\beta)$/ p.p.m.
$Me_2P_\alpha P_\beta Et_2$	−50	191.5	−67.63	−22.99
$Me_2P_\alpha P_\beta Pr^i{}_2$	*ca.* 36	238.5	−74.78	11.18
$Me_2P_\alpha P_\beta Bu^t{}_2$	*ca.* 36	319 [b] ±1.0	−62.24	38.92
	−30	327.3	−62.82	32.62
$Me_2P_\alpha P_\beta MeBu^t$	*ca.* 36	205 ±5	−74.02	−5.53
$Et_2P_\alpha P_\beta MeEt$	−50	204.4	−29.73	−52.30
$Et_2P_\alpha P_\beta Ph_2$	*ca.* 36	205.5	−28.40	−20.30
	−70	214.5	*c*	*c*
$Et_2P_\alpha P_\beta MeBu^t$	*ca.* 36	232.7	−38.14	−19.19
$MeEtP_\alpha P_\beta Ph_2$	*ca.* 36	202.4	−45.67	−15.47

[a] Values of $^1J(PP)$ are thought to be accurate to ±0.5 Hz, except where stated. The estimated error for δ(P) is ±0.05 p.p.m., excluding medium effects. [b] Reported as 318 Hz in ref. 4. [c] Not obtained.

P_2Me_4 and P_2Et_4, were mixed the ^{31}P linewidths of the resulting AB spectra of the unsymmetrical diphosphanes and the signals due to the reactants were of the order of 100 Hz at ambient probe temperature. At −50 °C, however, all the signals sharpened, but after 2 weeks the lines had broadened again, even at low temperature, and no distinct lineshapes could be seen. The mixed diphosphane formed between P_2Me_4 and $(Bu^tMeP)_2$ was also subject to such effects, and a rapid increase in the ^{31}P linewidth was seen. After 2 weeks only a broad bandshape from excess of P_2Me_4 and a sharp signal from $(Bu^tMeP)_2$ remained. The effects of time and temperature on the ^{31}P spectra of the system are illustrated in Figures 2 and 3. Similarly, the ^{31}P spectrum of $Me_2PPPr^i_2$ was recorded at ambient probe temperature, but after 2 weeks all the resonances, except that of $P_2Pr^i_4$ had increased in linewidth. The four lines of the AB spectrum had unequal linewidths, those associated with transitions in the PMe_2 part being broader than the lines of the PPr^i_2 part.

TABLE 2

Carbon-13 n.m.r. data [a] for (A) Et_2PPPh_2 and (B) $Bu^tMePPEt_2$

Molecule (A)

Resonance [b]	$\|J(PC)\|$ [c]/Hz (at 36 °C, 2.5 h after preparation)	$\|J(PC)'\|$ [c]/Hz (at 36 °C, 2.5 h after preparation)	δ(C)/p.p.m. (at 36 °C, 2.5 h after preparation)	$\|J(PC)\|$ [c]/Hz (at −70 °C, 3 weeks after preparation)	$\|J(PC)'\|$ [c]/Hz (at −70 °C, 3 weeks after preparation)	δ(C)/p.p.m. (at −70 °C, 3 weeks after preparation)
α-CH_2				9.7	16.0	16.98
β-CH_3				7.0	12.5	11.62
C^1	4 ±1	17 ±1	135.57	4.6	17.6	136.01
C^2	8.5	17.5	134.42	8.0	17.5	134.55
C^3	6.3	<1	128.65	6.5	<1	129.02
C^4	<1	<1	128.91	<1	<1	129.12

Molecule (B)

Resonance [d]	$\|N(PC)\|$/Hz	$\|J(PC)\|$ [c]/Hz	$\|J(PC)'\|$ [c]/Hz	δ(C)/p.p.m.
CH_3	26.3 or 29.7	1.7	28	2.95
$(\mathbf{C}H_3)C$		6.3	*e*	*ca.* 29.0
$\mathbf{C}H_3CH_2$	*ca.* 8 or 28.0	18 ±1	10 ±1	11.37
$CH_3\mathbf{C}H_2$ (g)	*ca.* 0	*ca.* ±6	*ca.* ±6	14.43
(t)	*ca.* 30	*ca.* ±12	*ca.* ±18	17.37

[a] Errors in coupling constants are ±0.5 Hz except where stated; in chemical shifts the errors are ±0.05 p.p.m. [b] C^1, C^2, *etc.*, refer to the phenyl group. [c] J(PC) and J(PC)′ are the two (P,C) coupling constants for a given ^{13}C. The assignment to long- and short-range interactions is ambiguous. [d] At −70 °C. [e] Not observed (see text).

Not all the unsymmetrical diphosphanes were formed immediately. After mixing a large excess of $(EtMeP)_2$ and P_2Ph_4 there was no immediate indication of the mixed diphosphane, but after 3 h the AB quartet emerged and the P_2Ph_4 resonance had disappeared. The product of mixing P_2Me_4 and $P_2Bu^t_4$ was even slower in appearing in the ^{31}P spectrum. After 10 h very weak signals from $Me_2PPBu^t_2$ were seen, and 40 h after mixing the doublet of doublets was clearly visible. At this stage, none of the resonances showed linewidth increases (at ambient probe temperature). After 2 weeks no signal from $P_2Bu^t_4$ remained (at −30 °C), indicating that it had all been used to form the mixed compound. ^1J(PP) has since been reported [4] for $Me_2PPBu^t_2$ at ambient temperature, but no details of the preparation or stability were given.

The mixed diphosphane Et_2PPPh_2 has been prepared previously.[5] The n.m.r. spectrum was reported to be four lines, but the compound decomposed rapidly and no value of ^1J(PP) was given. The phosphorus spectrum of the sample prepared here was recorded within 30 min of mixing, and at intervals later. The linewidths increased with time, although not equally; after 3 weeks the low-frequency AB lines, associated with PEt_2 transitions, were broader ($\Delta\nu_{\frac{1}{2}}$ 20 Hz) than the high-frequency lines ($\Delta\nu_{\frac{1}{2}}$ 12 Hz). After 3 months the linewidths were 100 and 70 Hz respectively.

The ^{13}C spectrum of this compound was also recorded, but at ambient probe temperature the broad band from P_2Et_4 overlapped any signals from the mixed compound. In the aromatic region all the carbon resonances were separately detectable. After 3 weeks these signals had broadened at ambient probe temperature, but at −70 °C the spectrum clearly showed coupling to two non-equivalent phosphorus nuclei. The ^{13}C parameters obtained are given in Table 2.

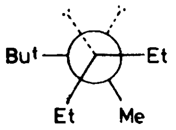
The ^{31}P AB quartet of the unsymmetrical compound formed by mixing P_2Et_4 and $(Bu^tMeP)_2$ also broadened with time so that linewidths after 2 weeks were *ca.* 30 Hz. There still remained some unchanged P_2Et_4, with a linewidth of *ca.* 100 Hz, and a sharp signal from unchanged $(Bu^tMeP)_2$. The ^{13}C spectrum recorded at this time showed broad lines in the ethyl region, but well resolved peaks from excess of $(Bu^tMeP)_2$. At −70 °C all the resonances were sharp, but the spectrum was quite complex. However, assignments to $Bu^tMePPEt_2$, P_2Et_4, and $(Bu^tMeP)_2$ could be made.

In all the reactions to form a mixed diphosphane at least one of the diphosphanes showed changes in its n.m.r. spectrum when dissolved alone in dichloromethane. Combining P_2Et_4 and $P_2Bu^t_4$, however, did not result in any unsymmetrical compound. Mixing two diphosphanes which were unaffected by dichloromethane, such as P_2Ph_4 and $P_2Bu^t_4$, or P_2Ph_4 and $(Bu^tMeP)_2$ did not cause any change in the ^{31}P spectrum at ambient temperature.

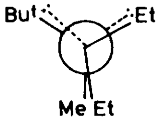
DISCUSSION

(*a*) *The Chemical Processes.*—At the present time we are unable to offer any precise explanation for the effect of dichloromethane on diphosphanes. The polymerization suggested by McFarlane [1] does not fully account for the results we obtained with P_2Et_4, and it seems more likely that cleavage of the P–P bond followed by exchange of the PR^1R^2 group occurs. This can result in an apparent decoupling of both ^{31}P nuclei from the ^{13}C or ^1H of a symmetrical diphosphane (see ref. 10), as can rapid relaxation of ^{31}P (*e.g.* induced by paramagnetic sites). We are currently carrying out more work in order to clarify this aspect. However, it is clear that the processes at work are solvent-assisted, since they occur for dichloromethane (and chloroform) solutions but not for benzene or toluene solutions. Moreover the n.m.r. broadening phenomena observed for P_2Me_4, P_2Et_4, and $(EtMeP)_2$ as individual species in solution in CH_2Cl_2 are presumably closely related to the occurrence of scrambling reactions. In all cases for CH_2Cl_2 solutions, further reactions, often resulting in complete decomposition of the diphosphanes, occur when samples are left for long periods of time at refrigerator temperature (*ca.* 4 °C), the time scale for these effects varying from hours to months.

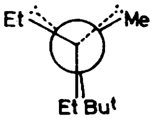
(*b*) *The Structure of* $Et_2PPMeBu^t$.—To interpret the ^{13}C spectrum of $Et_2PPMeBu^t$ a structure (I) with *gauche* lone pairs on phosphorus may be assumed,[4,11,12] with the Bu^t group in a position of least crowding.



(I)



(II)



(III)

The methyl carbon resonance of $Et_2PP\mathit{Me}Bu^t$ is shifted 8 Hz to high frequency of the signal in $(Bu^tMeP)_2$. The sum of the one- and two-bond couplings, $|N(PC)|$, is 26 or 30 Hz depending on the relative signs of $^1J(PC)$ and $^2J(PC)$. These values are in the region expected for a methyl carbon *trans* to the lone pair.[11]

The ethyl groups in structure (I) are non-equivalent, and the CH_2 group *gauche* to the lone pair (g) is expected to have a very small value of $|N(PC)|$ [$= |^1J(PC) + {}^2J(PPC)|$ for α-carbons] and, by analogy with $(Bu^t{}_2P)_2$ at low temperatures,[12] this should resonate to low frequency of the *trans* CH_2 group. Two sets of signals were assigned for the α-carbon of the ethyl group, one a doublet of doublets and the other a triplet]suggesting $|^1J(PC)|$ and $|^2J(PC)|$ are nearly equal]. The signs of $^1J(PC)$ and $^2J(PC)$ for $Et_2PPMeBu^t$ are unknown, and $|N(PC)|$ for CH_2(t) could be 6 or 30 Hz. Previous results, however,[11] suggest that $|N(PC)| = 30$ Hz (for an α-carbon *trans* to the lone pair) is the more reasonable, implying that $^1J(PC)$ and $^2J(PC)$ have the same sign. $|N(PC)|$ for the triplet could be 6 ± 6 Hz, and since the near-zero value is expected for a carbon *gauche* to the lone pair, $^1J(PC)$ and $^2J(PC)$ must have opposite signs.

Reported signs for $^1J(^{31}P^{III}-^{13}C)$ are all negative,[13] except the value of +0.6 Hz for a compound with a four-membered ring.[14] Most values of $^2J(^{31}P^{III}-^{13}C)$ are positive, although some exceptions have been reported.[13,15,16] Both ^1J and ^2J are known to vary considerably, even when the same phosphorus nucleus is involved.[13-17] Dutasta and Robert [17] report that, for PBu^tCl_2, $^2J(PCC)$ is ~0 for Me *trans* to the phosphorus lone pair and 31.5 Hz for the *gauche* Me. For PPh(Cl)-(NMe_2) the two values of $^2J(PNC)$ were found [16] to be +33.9 and −11.4 Hz for the *gauche* and *trans* methyl groups respectively, and the corresponding values [16] for $PPh(NMe_2)(OMe)$ were +40 and −7 Hz.

Non-equivalence of the CH_3 signals in the ethyl groups may also be expected, but only one doublet of doublets could be seen. The difference in the chemical shifts of β-carbons between *trans* and *gauche* orientations must therefore be very small, or some signals must be obscured by the methyl peaks of P_2Et_4.

The resonances from the methyl carbons of the Bu^t group of the unsymmetrical molecule are very close to those from $(Bu^tMeP)_2$ and only one doublet, $|J(PC)|$ 6.3 Hz, was observed for the $(CH_3)_3$ carbons of the unsymmetrical compound. It is, however, possible to predict a value for the coupling to the second phosphorus, by assuming that $|N(PC)|$ is similar to that for the β-carbons in $(Bu^tMeP)_2$ and $P_2Bu^t{}_4$ (21.4 and 21.2 Hz respectively). Such a procedure suggests that the second coupling constant may be 15 or 27 Hz, depending on the relative signs of $^2J(PC)$ and $^3J(PC)$. If the former value is correct, the second doublet would indeed lie below the $(CH_3)_3$ region of the spectrum of the parent molecule $(Bu^tMeP)_2$. This implies that $^2J(PC)$ and $^3J(PC)$ for carbons *gauche* to the lone pair have the same sign. No signal from the t-butyl quaternary carbon of the unsymmetrical molecule was detected.

Recently, *X*-ray evidence has shown [18] that, in the solid state, tetracyclohexyldiphosphane, $P_2(C_6H_{11})_4$, adopts a conformation that is approximately semieclipsed rather than staggered, with CPC angles closed down to *ca.* 103°. Such a conformation for $Et_2PPMeBu^t$ would be as in (II) or (III). If repulsion of bonded groups is important (II) would be preferred over (III). The above discussion would still be relevant except that the references to *gauche* and *trans* orientations to the lone pair should be replaced by dihedral angles of *ca.* 0 and *ca.* 120° respectively. Similar changes should be read into related work [9,11,12] and into the discussion of $^1J(PP)$ below. It does not appear currently possible to state whether a semieclipsed conformation is general for diphosphanes or whether such a conformation is retained in the solution state.

(*c*) *Phosphorus Chemical Shifts*.—The ^{31}P chemical shifts (Table 1) follow a regular pattern. The substitutions $Me \longrightarrow Et \longrightarrow Pr^i \longrightarrow Bu^t$ increase the number of methyl groups β to the adjacent phosphorus atom. Such methyl groups are in the γ position relative to the more distant phosphorus, which should therefore be increasingly shielded by the well known (although not properly understood) 'γ effect.' The data of Table 1 may be compared to literature values of δ(P) for symmetrical tetra-alkyldiphosphanes; such a comparison (Table 3) shows that the average shift per additional γ-carbon lies between −4.30 and −6.83 p.p.m., with three exceptions. One of these is presumably due to the fact that the *meso* isomer of $(Bu^tMeP)_2$ is unknown, and the high γ effect of −8.58 p.p.m. is based on the shift for the *racemic* isomer alone (the γ effect for the *meso* isomer would be expected to be smaller, see below). The other two anomalous results both refer to the compound $Me_2PPBu^t{}_2$. The value of δ(P) for the PMe_2 moiety of this compound actually lies between that for Me_2PPMe_2

TABLE 3

Measures of the γ-shielding effect of methyl groups on ^{31}P in tetra-alkyldiphosphanes

Observed group	Group changed, X	$\Delta\delta(P)$/ p.p.m.	Δn_γ [a]	$\Delta\delta(P)/\Delta n_\gamma$ p.p.m.
$Me_2P{-}X$	$PMe_2 \longrightarrow PEt_2$	−10.05	2	−5.03
	$PMe_2 \longrightarrow PPr^i{}_2$	−17.20	4	−4.30
	$PMe_2 \longrightarrow PBu^t{}_2$	−4.66	6	−0.78 [b]
	$PMe_2 \longrightarrow PMeBu^t$	−16.44	3	−5.48
$Et_2P{-}X$	$PMe_2 \longrightarrow PMeEt$	−6.74	1	−6.74
	$PMe_2 \longrightarrow PEt_2$	−9.71	2	−4.86
	$PMe_2 \longrightarrow PMeBu^t$	−15.15	3	−5.05
$Pr^i{}_2P{-}X$	$PMe_2 \longrightarrow PPr^i{}_2$	−22.76	4	−5.69
$Bu^t{}_2P{-}X$	$PMe_2 \longrightarrow PBu^t{}_2$	−1.08	6	−0.18 [b]
$EtMeP{-}X$	$PMeEt$ [c] $\longrightarrow PEt_2$	−6.65	1	−6.65
$Bu^tMeP{-}X$	$PMe_2 \longrightarrow PEt_2$	−13.66	2	−6.83
	$PMe_2 \longrightarrow PMeBu^t$ [d]	−25.73 [e]	3	−8.58 [f]

[a] The change in the number of γ-methyl groups corresponding to the change in $\delta(P)$ given in the previous column. [b] Anomalous values (see text). [c] The average shift for the *meso* and *rac* isomers is used. [d] The shift for the *rac* isomer is used. [e] The value corrected so as to relate to the average shift of *meso*- and *rac*-$(Bu^tMeP)_2$ is −17.42 p.p.m. (see text). [f] The corrected value is −5.81 p.p.m. (see text).

and that for Me_2PPEt_2. Presumably, special considerations of stereochemistry, resulting from steric interactions, counteract the γ effect on this case. It should also be remarked that solvent and temperature effects may well contribute to anomalies and variations. The data for the symmetrical compounds were given for benzene solutions, whereas the shifts in Table 1 are for solutions in CH_2Cl_2–CD_2Cl_2. A pronounced effect of temperature on $\delta(P)$ is found for $Me_2PPBu^t{}_2$. These influences can be partially discounted by taking the internal chemical-shift differences of the unsymmetrical compounds as a function of the difference in the number of β-methyl groups for the two parts of the molecules. Such a plot, shown in Figure 4, accounts for β- as well as γ-substituent effects. The plot is remarkably linear, with the single exception of $Me_2PPBu^t{}_2$, confirming the anomalous nature of this compound. The shift differences between the corresponding symmetrical compounds may be plotted in a similar fashion. Those involving Me_2PPMe_2 only (the remaining information being redundant) are plotted in Figure 4. The value of $\delta(P)$ for $(Bu^tMeP)_2$ needs to be corrected by 8.3 p.p.m. to bring it into line with the others. This is to account for the fact that only the shift for the *rac* isomer is known [for $(EtMeP)_2$ and $(Pr^iMeP)_2$ the average shift for the *rac* and *meso* isomers has been used for Figure 4]. We are thus predicting that the shift for *meso*-$(Bu^tMeP)_2$ is *ca.* $\delta(P) = -14.6$ p.p.m., giving a corrected mean γ effect of −5.81 p.p.m. for Table 3, in line with the other values, in place of the anomalous value of −8.58 p.p.m. The points for the symmetrical compounds in Figure 4 fall on a straight line passing through zero, except for the one for $(Bu^t{}_2P)_2$. There is therefore an anomaly in the shift of $(Bu^t{}_2P)_2$, to the extent of *ca.* 28 p.p.m. The anomaly in the shift difference for $Me_2PPBu^t{}_2$ appears to be the same, within reasonable error. Thus the problem arises from the presence of a single $PBu^t{}_2$ group, not from the interaction between two such groups. However, the shift anomaly for $Me_2PPBu^t{}_2$ is substantially greater for the PMe_2 than for the $PBu^t{}_2$ moiety, *i.e.* the long-range shift influence of the (presumed) geometry change at $PBu^t{}_2$ is greater than the short-range shift influence. This fact accounts for the apparent opposite signs of the anomalies in Figure 4. The difference in the gradients for the symmetrical and unsymmetrical compounds in Figure 4 is 2γ; measurement shows this to give $\gamma = -5.4$ p.p.m. The average value of γ from Table 3 (excluding the two anomalous values but including the corrected last value) is $\gamma = -5.6$ p.p.m. The γ-shielding effect is frequently found to derive from *gauche* interactions only. However, in the present case the smoothness of the chemical-shift changes argues for an effect regardless of conformation (or, alternatively, there may be no preferred conformation for the methyl groups, which seems unlikely).

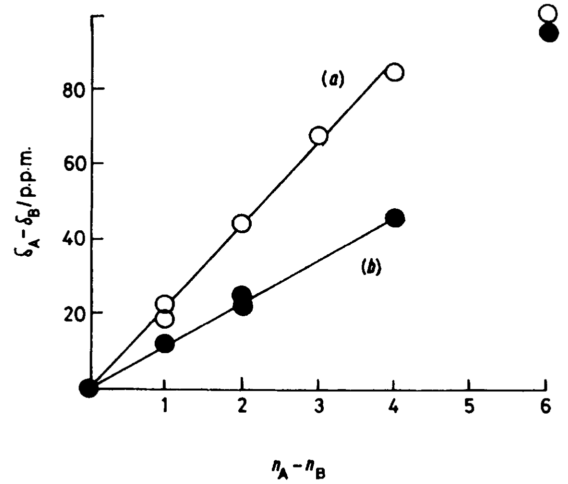


FIGURE 4 Plots of $\delta(P)$ against n, the number of methyl groups β to the relevant ^{31}P: (*a*) $\delta[P(A)] - \delta[P(B)]$ against $n_A - n_B$ for unsymmetrical diphosphanes of the type $R^1R^2P_AP_BR^3R^4$; (*b*) the same plot for symmetrical diphosphanes of the types $(R^1R^2P_A)_2$ and $(Me_2P_B)_2$

The average of the two gradients in Figure 4 gives the β effect of a methyl group on the ^{31}P chemical shift, and this is found to be $\beta = 17$ p.p.m. According to Gorenstein,[19] γ-*gauche* interactions also affect the shifts of the intervening atoms, but if this occurs for our compounds the effect would be subsumed into the β shift.

The nature of the above discussion implies that, since γ is negative, the shift difference between the non-equivalent ^{31}P nuclei in $R^1R^2PPR^3R^4$ will always be greater than that between $(R^1R^2P)_2$ and $(R^3R^4P)_2$ for compounds that behave as expected. This is indeed the case (it is also true, although only just so, for the anomalous system $Me_2PPBu^t{}_2$). However, this situation does not hold (indeed, the reverse is true) for the compounds containing the PPh_2 group; other factors (*e.g.* changes in electronic structure) would be expected to be involved here. Nevertheless, the ^{31}P shift for the PPh_2 group shows the normal γ effect (−4.83 p.p.m.) of changing the other moiety from PMeEt to PEt_2.

(*d*) *Phosphorus–Phosphorus Coupling Constants.*—Values of ^1J(PP) for the mixed diphosphanes show the same decrease [assuming ^1J(PP) is negative] with substituent bulk as the symmetrical diphosphanes. The total number of β-methyl groups, *n*, may be taken as a measure of the steric crowding around the phosphorus atoms, and there is a clear correlation between *n* and ^1J(PP) (Figure 5).

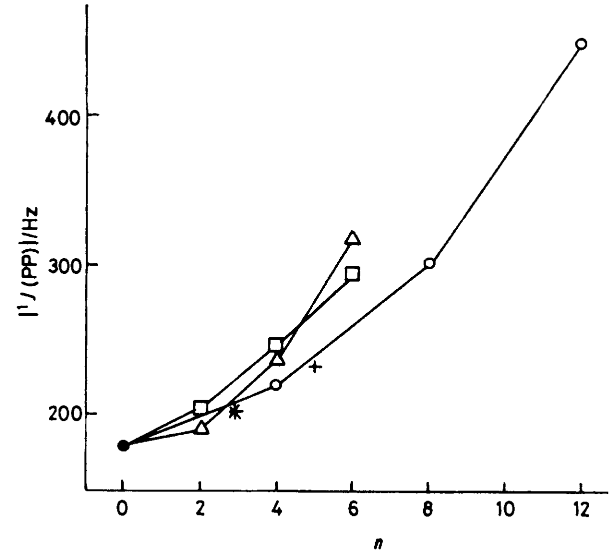


FIGURE 5 Plot of ^1J(PP) against *n*, the total number of β-methyl groups, for a series of tetra-alkyl-substituted diphosphanes: (●) $(Me_2P)_2$; (○) $(R_2P)_2$; (□) $(RMeP)_2$; (△) Me_2PPR_2; (+) Et_2PPEtR; (×) $Me_2PPMeBu^t$

At low temperature the magnitudes of ^1J(PP) for $Me_2PPBu^t{}_2$ and Et_2PPPh_2 are increased, in contrast to the change for $P_2Bu^t{}_4$ recorded earlier.[4,12] Since the *gauche* isomer is expected to be the predominant form at low temperatures,[4,12] the change in ^1J(PP) is presumably associated with an increasing proportion of the *trans* isomer as the temperature increases. Robert and his co-workers [20] have calculated the changes in ^1J(PP) with dihedral angle for diphosphane, P_2H_4, and found that a more negative coupling constant was produced with the lone pairs *gauche*. McFarlane and McFarlane [4] had proposed earlier, however, that the more negative coupling constant was from the *trans* isomer. The evidence here for the mixed diphosphanes supports the prediction from the treatment in ref. 20. In symmetrical diphosphanes there must be influences other than changes in rotamer population dominating the change in ^1J(PP) with temperature.

One of us (E. M. N.) acknowledges receipt of a research studentship from the Northern Ireland Department of Education.

[8/956 *Received*, 22*nd May*, 1978]

REFERENCES

[1] H. C. E. McFarlane and W. McFarlane, *J.C.S. Chem. Comm.*, 1972, 1189.
[2] E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **12**, 457.
[3] L. Maier in 'Organic Phosphorus Compounds,' vol. 1, ed. G. M. Kosolapoff and L. Maier, Wiley–Interscience, New York, 1972, p. 289.
[4] H. C. E. McFarlane and W. McFarlane, *J.C.S. Chem. Comm.*, 1975, 582.
[5] K. Isslieb and K. Krech, *Chem. Ber.*, 1965, **98**, 1093.
[6] E. Fluck and K. Issleib, *Chem. Ber.*, 1965, **98**, 2674.
[7] R. G. Cavell and R. C. Dobbie, *J. Chem. Soc.* (*A*), 1968, 1406.
[8] R. K. Harris and B. J. Kimber, *J. Magn. Resonance*, 1975, **17**, 174.
[9] S. Aime, R. K. Harris, E. M. McVicker, and M. Fild, *J.C.S. Dalton*, 1976, 2144.
[10] J. P. Fackler, J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 1970, **92**, 3093.
[11] R. K. Harris, E. M. McVicker, and M. Fild, *J.C.S. Chem. Comm.*, 1975, **886**.
[12] S. Aime, R. K. Harris, E. M. McVicker, and M. Fild, *J.C.S. Chem. Comm.*, 1974, 426.
[13] G. Mavel, *Progr. N.M.R. Spectroscopy*, 1973, **B5**, 1.
[14] G. A. Gray, *J.C.S. Chem. Comm.*, 1974, 451; 1975, 304.
[15] S. Sorensen, R. S. Hansen, and H. J. Jakobsen, *J. Amer. Chem. Soc.*, 1972, **94**, 5900.
[16] M. P. Simonnin, R. M. Lequan, and F. W. Wehrli, *J.C.S. Chem. Comm.*, 1972, 1204.
[17] J. P. Dutasta and J. B. Robert, *J.C.S. Chem. Comm.*, 1975, 747.
[18] R. Richter, J. Kaiser, J. Sieler, H. Hartung, and C. Peter, *Acta Cryst.*, 1977, **B33**, 1887.
[19] D. G. Gorenstein, *J. Amer. Chem. Soc.*, 1977, **99**, 2254.
[20] J. P. Albrand, H. Faucher, D. Gagnaire, and J. B. Robert, *Chem. Phys. Letters*, 1976, **38**, 521.