Phosphorus-31 and Carbon-13 Nuclear Magnetic Resonance Studies of Unsymmetrical Tetra-alkyldiphosphanes $R^1R^2PPMe_2$ and $R^1R^2PPEt_2$

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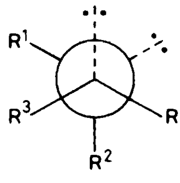
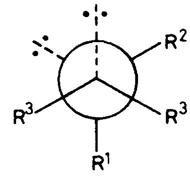
A series of unsymmetrical tetra-alkyldiphosphanes of general formulae $R^1R^2PPMe_2$ and $R^1R^2PPEt_2$ (with R^1, R^2 = Me, Et, Pr^i, Bu^t) have been obtained by scrambling reactions between the corresponding symmetrical diphosphanes in CH_2Cl_2 solution and have been studied by n.m.r. spectroscopy *in situ*. Values of ^{31}P and ^{13}C chemical shifts, together with (P,P) and (P,C) coupling constants, are reported and discussed in relation to substituent effects and conformation. The parameter $^1J_{PC} + {}^2J_{PC}$ is shown to be a good predictor of the preferred rotamer, and it is concluded that $^1J_{PC}$ and $^2J_{PC}$ must be opposite in sign.

The formation of unsymmetrical tetra-alkyldiphosphanes by mixing two symmetrical tetra-alkyldiphosphanes in dichloromethane was first observed by McFarlane and McFarlane.[1] N.m.r. data for several unsymmetrical tetra-alkyldiphosphanes were obtained by such scrambling reactions and reported in previous studies.[2,3] However, the compounds obtained by such mixing were found to be unstable, so, because of the low natural abundance of the ^{13}C nucleus, only ^{31}P n.m.r. spectra were studied in most cases. On the other hand, Ph_2PPEt_2 and Bu^{t}MePPEt$_2$ were found to be relatively stable, and both ^{13}C and ^{31}P n.m.r. data for these two compounds were obtained and reported.[2] The present paper describes ^{31}P and ^{13}C (whenever possible) n.m.r. data of some additional unsymmetrical tetra-alkyldiphosphanes of formula $R^1R^2P_aP_bR^3_2$ (**I**), with R^3 being either Me or Et. These compounds were formed by mixing the symmetric tetra-alkyldiphosphanes $(R^1R^2P)_2$ with Me_4P_2 or Et_4P_2. When $R^1 \neq R^2$ the molecules (**I**) contain a chiral centre (R^1R^2P), and idealised staggered conformations are shown below, although these are unlikely to be realistic.[4,5] The second phosphorus (PR^3_2) is prochiral. In such a case, provided rotation about the P–P bond is rapid on the n.m.r. time-scale, the proton-noise-decoupled ^{31}P spectrum should consist of a single set of four lines in an AB spin pattern. However, the two *gauche* forms (**Ia**) and (**Ib**) are non-equivalent. When $R^1 = R^2$ the two *gauche* forms are equivalent and the molecule possesses neither chiral nor prochiral centres.



(Ia)



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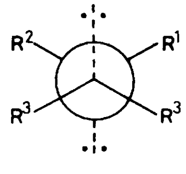

(Ic)

Results

The phosphorus-31 n.m.r. spectra of a number of unsymmetrical tetra-alkyldiphosphanes of the type $R^1R^2P_aP_bR^3_2$ were recorded under conditions of proton-noise decoupling at a number of temperatures. The data obtained are given in Table 1. Previously reported data on similar compounds are also included for convenience. In all cases, as expected, the $^{31}P-\{^1H\}$ spectra show an AB spin pattern. On the other hand carbon-13 in such a compound forms the X part of an ABX spin system, which will give four (or, in principle, six) lines due to coupling to the two non-equivalent phosphorus nuclei. In general $|\nu_A - \nu_B|$ is substantially greater than $|J_{AB}|$, so corrections to the ^{13}C splittings have not been made when values of J_{PC} are quoted. The $^{13}C-\{^1H\}$ spectrum of Bu^{t}Pr^{i}PPMe$_2$ is shown in Figure 1 as an example. The carbon-13 chemical shifts and (P, C) coupling constants for six of the unsymmetrical compounds studied are given in Table 2. It should be remarked that $^1J_{PC}$ and $^2J_{PC}$ for α carbons are indistinguishable in the absence of triple resonance experiments. Similarly, $^2J_{PC}$ and $^3J_{PC}$ for the β carbons cannot be distinguished. The value of N_{PC}, which is the sum of $^1J_{PC}$ and $^2J_{PC}$ coupling constants for α carbons or the sum of $^2J_{PC}$ and $^3J_{PC}$ couplings for β carbons, is obtained directly from ABX-type spectra. It clearly depends on the relative signs of the relevant coupling constants. However, no attempts were made to determine the signs of the coupling constants directly.

Assignments of ^{13}C n.m.r. spectra were carried out using low-power noise decoupling to distinguish quaternary and methylene carbons from CH and CH_3, followed by consideration of data[6–8] for symmetrical compounds. Details are given in ref. 9. It is assumed[1–3,6–10] that molecules exist preferentially in *gauche* forms with the more bulky substituent (R^1 or R^2) *gauche* to the lone pair on the PR^3_2 phosphorus.

As the temperature decreased, both P_a and P_b became more shielded in all cases measured, though with considerable variations in the rate of change. These effects are included in Table 1.

Discussion

Phosphorus Chemical Shifts.—Previous studies[3] on unsymmetrical tetra-alkyldiphosphanes of the type $R^1R^2P_aP_bMeEt$ revealed that increasing the total number of methyl groups β to P_a for the substituents R^1 and R^2, n_β, results in an increase in $\delta(P_a)$, the 'β-shielding effect', and a decrease in $\delta(P_b)$ by the well known 'γ-deshielding effect'. The latter effect was first observed for ^{13}C by Grant and Paul.[11] The phosphorus chemical shifts for the unsymmetrical compounds of general formulae $R^1R^2P_aP_bMe_2$ and $R^1R^2P_aP_bEt_2$ listed in Table 1 show the same pattern of change with n_β (see Figure 2). This plot shows a linear increase in β shielding with n_β except for Bu$^t_2$PPMe$_2$ which behaves anomalously. Such anomalous behaviour is always observed[3] for tetra-alkyldiphosphanes containing the Bu$^t_2$P moiety, and presumably a special geometry results from steric interaction between the two Bu^t groups. It may be noted that for predicting ^{13}C chemical shifts of alkanes it is necessary to use variable values for the β effect depending on the number of β carbons bonded to the same α carbon, such that reduced β effects are expected from Bu^t substituents.

Table 1. Phosphorus-31 n.m.r. data for the unsymmetrical tetra-alkyldiphosphanes $R^1R^2P_aP_bR^3_2$

R^1R^2	R^3	θ_c/°C	$\lvert J(P_aP_b)\rvert$/Hz	$\delta(P_a)$/p.p.m.	$\delta(P_b)$/p.p.m.	$\Delta\delta(P_a)/\Delta T$ (p.p.m. °C^{-1})	$\Delta\delta(P_b)/\Delta T$ (p.p.m. °C^{-1})	n[a]
(**1**) Bu^t_2	Me	36	320	38.46	−62.33	—	—	6
		−30[b]	327.3	32.62	−62.82			
(**2**) Bu^tPr^i	Me	36	231	32.75	−72.07	0.027	0.026	5
		−5	225	31.31	−73.30			
		−32	222	29.95	−74.04			
		−52	218	29.95	−74.54			
		−83	214	29.71	−75.32			
(**3**) Bu^tEt	Me	38	229	12.07	−71.09	0.014	0.065	4
		−18	230	8.27	−72.09			
		−32	230	7.47	−72.26			
		−50	230	6.58	−72.46			
		−65	233	5.11	−72.60			
		−87	233	4.05	−72.86			
(**4**) Bu^tMe	Me	36[b]	205 (±5)	−5.53	−74.02	—	—	3
		−72[c]	200	−9.03	−74.98			
(**5**) Pr^i_2	Me	36[b]	238.5	11.18	−74.78	—	—	4
(**6**) Pr^iEt	Me	36	204	−3.14	−70.13	0.021	0.030	3
		10	203	−3.86	−70.50			
		−10	201	−4.86	−71.21			
		−20	201	−4.90	−71.22			
		−78	195	−6.52	−72.45			
(**7**) Et_2	Me	−50[b]	191.5	−22.99	−67.63	—	—	2
(**8**) Bu^tPr^i	Et	36	286	15.51	−33.06			7
(**9**) Bu^tMe	Et	36[b]	232.7	−19.19	−38.14	—	—	5
(**10**) Pr^i_2	Et	36	272	0.01	−40.41	0.071	0.063	6
		−72	284	−6.27	−47.55			
		−80	288	−7.70	−48.97			
(**11**) Pr^iEt	Et	36	236	−16.27	−35.39	—	—	5
		−80	235	−22.45	−40.68			
(**12**) EtMe	Et	−50[b]	204.4	−52.30	−29.73	—	—	3

[a] The number of methyl groups β to a phosphorus atom. [b] Data quoted from ref. 2. [c] Solvent: $CHCl_3$.

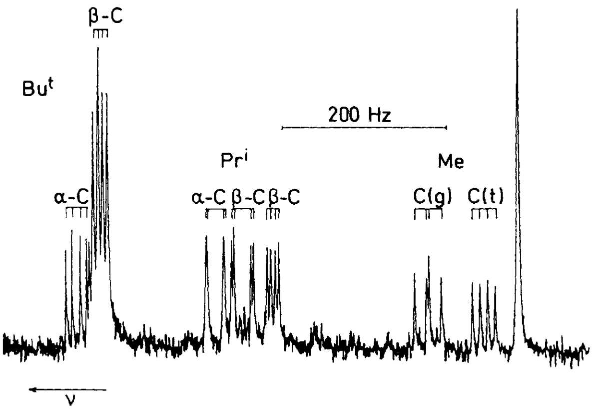

Figure 1. $^{13}C-\{^1H\}$ N.m.r. spectrum of $Bu^tPr^iPPMe_2$ at −80 °C. The intense peak at low frequency arises from Me_4P_2

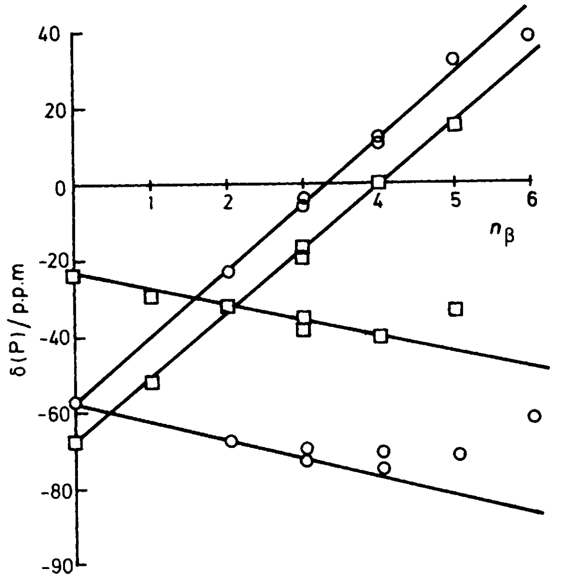

Figure 2. Plot of ^{31}P chemical shifts for the two phosphorus nuclei of tetra-alkyldiphosphanes $R^1R^2P_aP_bMe_2$ (○) and $R^1R^2P_aP_bEt_2$ (□) against the number of β-methyl groups, n_β, for the R^1R^2P moiety. The upper lines, for P_a, illustrate the β effect whereas the lower lines, for P_b, show the influence of γ shielding

There are 55 possible compounds (excluding stereoisomers) of the type $R^1R^2PPR^3R^4$ with R^1, R^2, R^3, R^4 = Me, Et, Pr^i, Bu^t. The ^{31}P chemical shifts are now known for 27 of them, including all 10 symmetrical species $(R^1R^2P)_2$. Consequently many measures of the β and γ effects are now available, though the matter is complicated by variations of δ_P with temperature. Comparison of shifts for individual pairs of molecules shows that the γ effect varies from 0.2 to −8.6 p.p.m. per methyl substituent, whereas the β effect shows a somewhat narrower range, from 13.6 to 18.2 p.p.m. The sum β + γ is distinctly more variable than the difference β − γ.

Clearly, values of β and γ are affected by (*i*) substituent electronic effects, (*ii*) geometry variations, and (*iii*) conformational variations. It is difficult to disentangle these influences, but (*ii*) and (*iii*) are likely to be maximised for the bulkiest substituents, such as tend to give 'anomalous' values of β and γ.

Table 2. Carbon-13 n.m.r. data for the unsymmetrical tetra-alkyldiphosphanes $R^1R^2P_aP_bR^3_2$ below −60 °C

R^1R^2	R^3	θ_C/°C	Resonance	$\lvert J_{PC}\rvert$[a]/Hz	$\lvert J'_{PC}\rvert$[b]/Hz	$\lvert N_{PC}\rvert$[c]/Hz	Position[d]	δ_C/p.p.m.
Bu^t_2	Me	−80	$Bu^t(\alpha)$	5.2	25.0	30.2 or *19.8*	a	35.33
			$Bu^t(\beta)$	5.3	12.4	*17.7* or 7.1		31.80
			Me	10.1	17.0	27.1 or *6.9*	a	12.65
Bu^tPr^i	Me	−75	$Bu^t(\alpha)$	7.8	18.0	25.8 or *10.2*	g	31.49
			$Bu^t(\beta)$	6.2	11.8	*18.0* or 5.6		30.31
			$Pr^i(\alpha)$	3.0	24.1	27.1 or *21.1*	t	23.29
			$Pr^i(\beta)$	0.5	21.4	21.9 or 20.9		24.62
			$Pr^i(\beta)$	4.4	10.0	*14.4* or 5.6		21.78
			Me	15.0[e]	17.9[e]	32.9 or *2.9*	g	14.13
			Me	9.5	19.0	28.5 or *9.5*	t	11.43
Bu^tEt	Me	−70	$Bu^t(\alpha)$	8.8[e]	11.8[e]	20.6 or *3.0*	g	30.00
			$Bu^t(\beta)$	7.4	11.2	*18.6* or 3.8		29.20
			Et(α)	3.1	24.2	27.3 or *21.1*	t	13.00
			Et(β)	0.0	21.8	21.8		14.42
			Me	19.6	11.9	31.5 or *7.7*[f]	g	13.84
			Me	4.0	22.6	26.6 or *18.6*	t	9.32
Pr^iEt	Me	−70	$Pr^i(\alpha)$	10.5[e]	13.4[e]	23.9 or *2.9*	g	23.32
			$Pr^i(\beta)$	7.5	11.8	*19.3* or 4.3		21.00
			$Pr^i(\beta)$	7.4	12.2	*19.6* or 4.8		20.99
			Et(α)	6.5	20.5	27.0 or *14.0*	t	14.14
			Et(β)	5.3	11.5	*16.8* or 6.2		12.02
			Me	15.0[e]	16.5[e]	31.5 or *1.5*	g	12.52
			Me	8.4	18.8	27.2 or *10.4*	t	10.33
Et_2	Me	−70	Et(α)	10.1	16.7	26.8 or *6.6*	a	16.30
			Et(β)	6.7	12.2	*18.9* or 5.5		11.96
			Me	11.9	18.1	30.0 or *6.2*	a	10.82
Pr^i_2	Et	−85	$Pr^i(\alpha)$[g]	5.5	17.0	22.5 or *11.5*	a	21.84
			$Pr^i(\beta)$	0.0	18.5	18.5		21.71
			$Pr^i(\beta)$[g]	4.8	14.1	*18.9* or 9.3		21.33
			Et(α)	8.5	15.1	23.6 or *6.6*	a	17.10
			Et(β)	5.5	17.3	*22.8* or 11.8		12.78

[a] For α carbons, this value is assumed to be $^2J_{PC}$. [b] For α carbons, this value is assumed to be $^1J_{PC}$. [c] The preferred value is in italics. [d] Preference: g ≡ *gauche* and t ≡ *trans* to the lone pair; a = average. [e] These assignments may be interchanged (and consequently the preferred value of N_{PC} changed in sign). [f] Believed to be of opposite sign to the other values of N_{PC} for α carbons. [g] These assignments may be interchanged.

Phosphorus–Phosphorus Coupling Constants.—In the case of tetra-alkyldiphosphanes, the electronegativity of the substituents varies very little. Thus the factors that would influence the stability of the conformers are the orientation of the lone pairs and the bulk of the substituents. In general, as previously observed for symmetrical[7] and unsymmetrical[2,3] tetra-alkyldiphosphanes, $^1J_{PP}$ decreases (assuming it is negative) with the total number of β methyls, *n* (Figure 3). Inconsistent change in $^1J_{PP}$ is observed with decreasing temperature (Table 1): there is an increase in $^1J_{PP}$ (*i.e.* it becomes less negative) for $Bu^tPr^iPPMe_2$, $Bu^tMePPMe_2$, $Pr^iEtPPMe_2$, and $Pr^iEtPPEt_2$ (though by only 1 Hz in the last case), but a decrease in $^1J_{PP}$ (*i.e.* it becomes more negative) for $Bu^tEtPPMe_2$ and $Pr^i_2PPEt_2$. The variations are roughly linear with temperature. The value of $^1J_{PP}$ for $Bu^t_2PPMe_2$ and Et_2PPPh_2 has been reported[6,8,9,12] to decrease while that of $Bu^t_4P_2$ and Me_4P_2 increases at low temperature. Clearly, with such variable behaviour it is not easy to explain the effects on J_{PP} of temperature change in terms of changes in conformer populations. Indeed, since calculations[9] suggest J_{PP} is positive when the phosphorus lone pairs are *trans* yet n.m.r. spectroscopy shows[6] the stable form of $Bu^t_4P_2$ is *gauche*, the fact that $|J_{PP}|$ *decreases* for this compound as the temperature is lowered cannot be reconciled with a simple model in which conformer populations have a dominating effect.

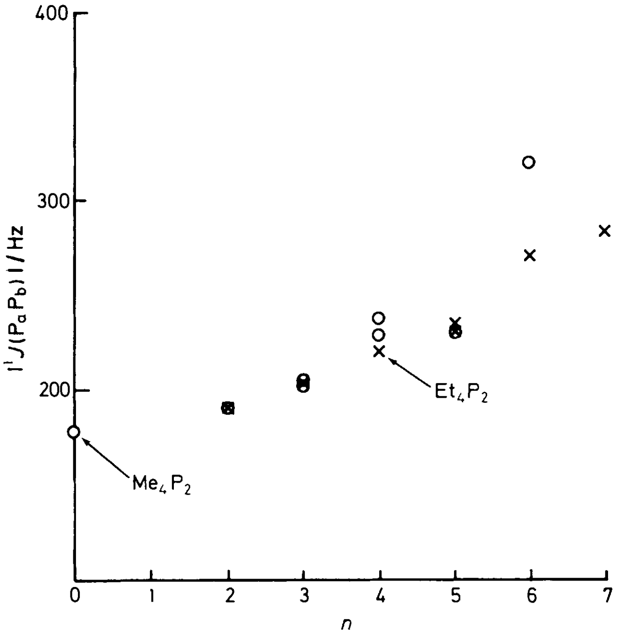

Figure 3. A plot of $|^1J(P_aP_b)|$ with the total number of β-methyl groups, *n*, for tetra-alkyldiphosphanes: (○) $R^1R^2P_aP_bMe_2$; (×) $R^1R^2P_aP_bEt_2$. The values of $^1J_{PP}$ for Me_4P_2 and Et_4P_2 are included (ref. 9)

Carbon–Phosphorus Coupling Constants.—The magnitudes and signs of (P, C) spin–spin coupling constants are found in general to depend on: (*i*) the valency of the phosphorus atom,

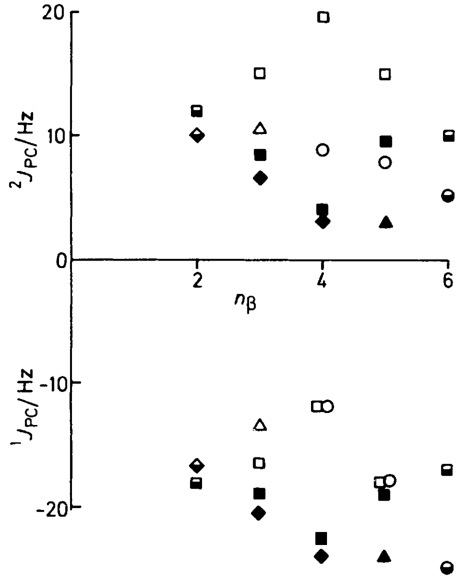

Figure 4. Plot of $^1J_{PC}$ (presumed to be negative) and $^2J_{PC}$ (presumed to be positive) for the α-carbon nuclei of tetra-alkyldiphosphanes $R^1R^2PPMe_2$ (using the data in Table 2 with the preferred assignments) against the number of β-methyl groups, n_β. The symbols □, ◇, △, and ○ are for Me, Et, Pr^i, and Bu^t groups respectively. The filled symbols indicate a preference for the group being *trans* to the lone pair, whereas empty symbols are for a *gauche* preference

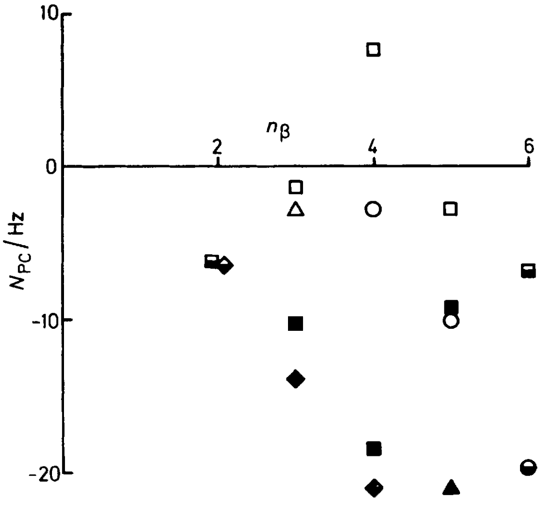

Figure 5. Plot of N_{PC} *vs.* n_β for the tetra-alkyldiphosphanes. The symbols are as for Figure 4

(*ii*) the orientation of carbon to the lone-pair electrons, (*iii*) the number of the bonds through which coupling occurs, and (*iv*) the hybridisation of carbon. The sign of $^1J_{PC}$ for phosphorus(III) compounds is normally negative, but $^2J_{PC}$ couplings *through carbon* are positive.[13–15] However, $^1J_{PC}$ and $^2J_{PC}$ may be similar in magnitude. In studies of symmetric tetra-alkyldiphosphanes of the type $(R^1R^2P)_2$ only the value of $|N_{PC}| = |J_{PC} + J'_{PC}|$ can be measured directly from the ^{13}C spectra. Low $|N_{PC}|$ values were obtained[6,7,8,16] for α carbons *gauche* to a lone pair of electrons. This is presumed to be due to the near cancellation of $^1J_{PC}$ and $^2J_{PC}$. However, $|N_{PC}|$ values for α carbons *trans* to a lone pair of electrons are large.

The magnitudes of the (P, C) coupling constants for unsymmetrical diphosphanes may be readily derived *separately* from the ^{13}C n.m.r. spectra, and those obtained for the α carbons of the compounds studied here are given in Table 2. Of course, there is *a priori* complete ambiguity both as to the sign and as to the assignment (to $^1J_{PC}$ and $^2J_{PC}$) of the couplings. Our conclusions are based on consideration of the total body of results, including those published previously for N_{PC}. We have *assumed* that in general $|^1J_{PC}| > |^2J_{PPC}|$ (though usually the opposite is true for $^1J_{PC}$ and $^2J_{PCC}$ in alkylphosphines), and that the signs of the coupling constants are as discussed above. In the case of Me_4P_2, N_{PC} has been proved to be negative.[17] We also assume that bulky alkyl groups prefer to be *gauche* to the corresponding lone pair. For the purposes of discussion the existence of conformations with *trans* lone pairs will be ignored, as will deviations from staggered geometry.

The compounds we have studied fall into two categories. For those of the type $R^1{}_2PPR^2{}_2$ the results for J_{PC} represent averages of *gauche* and *trans* orientations with respect to the relevant lone pair, since conformational interchange between equivalent conformations with *gauche* lone pairs is rapid on the n.m.r. time-scale even at low temperature. The value of $^1J_{PC}$ is -15 to -18 Hz for Me and Et, but is lower (more negative) for Bu^t. For $^2J_{PC}$ the range is $+8$ to $+12$ Hz for Me and Et, but is again lower for Bu^t. The corresponding values of N_{PC} are in line with those reported previously[8] for compounds of the type $(R^1R^2P)_2$, but one can now see that the reason for a large $|N_{PC}|$ for Bu^t lies in changes for *both* $^1J_{PC}$ and $^2J_{PC}$ compared to Me. The other feature that emerges clearly from these results is that the coupling constants involving Me (and, by extrapolation, those for the other alkyl groups) are relatively unaffected by substitution of more bulky groups at the β phosphorus. This conclusion is crucial to the rationalisation of the complete set of data.

Conformational biassing for compounds of the type $R^1R^2PPR^3{}_2$, where $R^1 \neq R^2$, causes the R^3 groups themselves to be inequivalent, giving a spread of $^1J_{PC}$ and $^2J_{PC}$ about the mean values anticipated from the results from $R^1{}_2PPR^2{}_2$. This fact allows choices to be made for assignments of the coupling constants. The preferred assignments are shown in Table 2 and the conformational effects are highlighted in Figures 4 and 5. The plots show several features of interest. (*i*) The values for Me averaged over the two orientations are sensibly constant, as foreshadowed above. Thus, for $|N_{PC}|$, the results (including those for $R^1R^2PPR^3{}_2$) are 6.9, 6.2, 5.5, 6.0, and 6.2 Hz, compared to 7.3 Hz for Me_4P_2 at -63 °C.[8] (*ii*) Biassing of the conformational equilibrium between the *gauche* forms is incomplete and is largest for Bu^{t}EtPPMe$_2$, as would be expected. (*iii*) The more bulky alkyl group prefers to be *gauche* to the relevant lone pair. In particular $|N_{PC}|$ for the α carbon of the isopropyl group is less than the average for Pr^{i}EtPPMe$_2$ but is more than the average for Bu^{t}Pr^{i}PPMe$_2$. (*iv*) No value of $^1J_{PC}$ is positive and no value of $^2J_{PC}$ is negative. (*v*) However, $|^1J_{PC}| < |^2J_{PC}|$ for the preferentially *gauche* methyl carbon of Bu^{t}EtPPMe$_2$, giving rise to a positive value of N_{PC}. This may also be true in other cases, though these are not then our preferred assignments. It may be noted that earlier data suggested[8] a variation in sign for N_{PC} for *gauche* methyl carbons, but only indirectly (the *trans* value being more than twice related averaged results). Moreover, the average value of N_{PC} for the two methyl carbons of Bu^{t}EtPPMe$_2$ is -5.5 Hz, which is in good agreement, both as to magnitude and as to sign, with that reported[17] for Me_2PPMe_2. (*vi*) It may now be clearly seen that $|^1J_{PC}$ (*trans*)$| > |^1J_{PC}$ (*gauche*)$|$ but $|^2J_{PC}$ (*trans*)$| < |^2J_{PC}$ (*gauche*)$|$. Thus variations in *both* coupling constants lead to the pronounced orientation dependence of N_{PC}.

It should be stated that rejection of the alternative assignments for N_{PC} in Table 2 and evidence for the only partial biassing of *gauche* conformation populations is not overwhelming. The most convincing information on partial biassing comes from the results for the α carbon of Bu^t in $Bu^tPr^iPPMe_2$; the alternatives, namely (*a*) $N_{PC} = -25.8$ Hz or (*b*) $N_{PC} = +10.2$, are not feasible for a *gauche* orientation to the lone pair in this case, given[6] the values for $Bu^t_4P_2$.

Less information is available from the (P, C) coupling constants for the β carbons, but there are still some points of interest. The values of $|J_{PC}|$ and $|J'_{PC}|$ are remarkably constant, with ranges 4.4—7.5 and 10.0—12.4 Hz. We cannot be certain which of these ranges corresponds to $^2J_{PCC}$ and which to $^3J_{PPCC}$. In the case of alkylphosphines it has been shown[18] that $^2J_{PCC}$ lies between 11.6 and 28.3 Hz and is greater than $^3J_{PCCC}$ (which is sensibly constant, between 11.1 and 13.4 Hz) for any given compound. The ranges quoted above for the compounds studied here have two significant exceptions, *viz.* the Et group of $Bu^tEtPPMe_2$ and *one* of the methyl carbons for the isopropyl group of $Bu^tPr^iPPMe_2$, which have one very small coupling constant (magnitude <0.5 Hz) and one large one ($\approx$21—22 Hz). The anomalies are presumably occasioned because steric effects prevent the relevant methyl groups from occupying one of the available positions. Both $^2J_{PCC}$ and $^3J_{PPCC}$ are affected by orientation, perhaps with respect to *both* lone pairs. The N_{PC} data for β methyls do not vary very greatly, but the largest values ($\approx$22 Hz) are for the anomalous groups discussed above, and the lowest (14.4 Hz) is for the other methyl of Pr^i in $Bu^tPr^iPPMe_2$. One new fact emerges: $^2J_{PCC}$ and $^3J_{PPCC}$ must be of the same sign (presumed to be positive).

Carbon-13 *Chemical Shifts.*—The values of δ_C reported in Table 2 for unsymmetrical tetra-alkyldiphosphanes $R^1R^2PPMe_2$ show that the α and β carbons for the substituents R^1 and R^2 behave more or less as for the symmetrical diphosphanes, implying that the anomalous behaviour of tetra-alkyldiphosphanes with bulky substituents arises from the effect of the bulky groups on the same phosphorus as the carbon observed. The crossover of the α- and β-carbon resonances of the ethyl group from $Pr^iEtPPMe_2$ to $Bu^tEtPPMe_2$ is notable.

For the Me carbons in $R^1R^2PPMe_2$ the average δ_C values for the *gauche* and *trans* positions increase slightly but monotonically as the bulk of R^1 and R^2 increases. Such a change represents a 'δ effect' of H $\longrightarrow$ Me substitution, assuming that conformational changes have no appreciable effect, and has an average value of 0.6 p.p.m. This behaviour may be compared to that for the Me carbons in $(RMeP)_2$ compounds[7] for which δ_C is affected by both γ and δ carbons, with an average value of $\gamma + \delta = -2.4$ p.p.m.[8] With $\delta = 0.6$ p.p.m. this leaves $\gamma = -3.0$ p.p.m. for the γ-deshielding effect in the symmetrical diphosphanes $(R^1R^2P)_2$, compared to the normal value of *ca.* -3.5 p.p.m. (see ref. 8). It might be expected that the difference in δ_C for the two methyl carbons for compounds $R^1R^2PPMe_2$ with $R^1 \neq R^2$ should reflect conformational biassing. This is borne out in practice, since values (*gauche* minus *trans*) for $R^1R^2 \equiv Bu^tPr^i$, Bu^tEt, and Pr^iEt are 2.70, 4.52, and 2.19 p.p.m. respectively.

Experimental

All samples were prepared by mixing diphosphanes $(R^1R^2P)_2$ with Me_4P_2 or Et_4P_2 (as appropriate) in CH_2Cl_2 solution in n.m.r. tubes (outside diameter 12 mm) in a dry-box under nitrogen gas. The samples were then degassed by the freeze–pump–thaw technique and sealed. The solvent, CH_2Cl_2, was kept over molecular sieve for at least 3 months before use. The ^2H field/frequency lock for all samples was provided by CD_2Cl_2, except for the mixtures of Et_4P_2 with Me_4P_2 and $(Bu^tPr^iP)_2$ with Et_4P_2, where perdeuteriobenzene was used to provide the lock. In the cases where CD_2Cl_2 provided the field/frequency lock the two symmetrical diphosphanes in question were mixed directly together in a 12-mm n.m.r. tube. The mixture was then frozen using liquid nitrogen, after which the solvent, together with a smaller amount of CD_2Cl_2, was transferred to the sample under vacuum, and the tube was degassed and sealed. However, when C_6D_6 provided the lock signal only the CH_2Cl_2 was transferred to the frozen sample of the mixture of the diphosphanes with C_6D_6. For these mixtures, the temperature of the sample was not allowed to rise substantially above that where total melting occurred. The sample tube in question was then placed as soon as possible in the probe, which was present at low temperature (Table 2). The $^{13}C-\{^1H\}$ n.m.r. spectra were recorded first at low temperature and then the $^{31}P-\{^1H\}$ spectra. In between experiments the sample was kept frozen by keeping it immersed in liquid nitrogen.

In the case of tetra-alkyldiphosphanes with bulky substituents (*i.e.* with a Bu^t group) the unsymmetrical diphosphanes were formed only after raising the temperature of the sample. In such cases the sample was removed from the probe and was kept at ambient temperature for between 5 and 30 min (depending on the nature of the substituents). It was then replaced in the probe at low temperature.

The mixing of $Bu^t_4P_2$ with Me_4P_2 and $(Bu^tPr^iP)_2$ with Et_4P_2 was carried out as above and then CH_2Cl_2 was added (in the dry-box) at ambient temperature, after which the samples were degassed and sealed. For the former sample the $^{13}C-\{^1H\}$ n.m.r. spectrum obtained after a long time at 36 °C showed the signals for the unsymmetrical compound, then the $^{31}P-\{^1H\}$ spectrum was recorded at the same temperature. For the latter, however, only the $^{31}P-\{^1H\}$ n.m.r. spectrum was recorded at 36 °C, as soon as possible after mixing.

The existence of signals due to the parent diphosphanes did not, in general, impede the interpretation and assignment of the spectra from the unsymmetrical diphosphanes.

A positive sign for a chemical shift implies the sample resonates to high frequency of the reference ($SiMe_4$ and 85% H_3PO_4 for ^{13}C and ^{31}P respectively). The shifts were measured by the absolute frequency indirect method, described previously,[19] using $\Xi(H_3PO_4) = 40\,480\,720$ Hz and $\Xi(SiMe_4) = 25\,145\,004$ Hz for consistency.[8]

The spectra were recorded using a Varian XL 100 spectrometer in the Fourier-transform mode for carbon-13 (25.14 MHz) and phosphorus-31 (40.51 MHz), both under conditions of proton-noise decoupling. For phosphorus spectra, spectral widths of 10 kHz and acquisition times of 0.4 s (or 5 kHz and 0.8 s respectively) were used. The pulse duration corresponded to a flip angle of *ca.* 90°. Reasonable spectra were achieved from 1 000 transients co-added in the computer. However, at low temperature, spectra with a good signal-to-noise ratio could be obtained with 100 transients. The ^{13}C n.m.r. spectra were recorded with spectral widths of 1000 Hz and acquisition times of 3.0 or 4.0 s. The number of transients for spectra with a reasonable signal-to-noise ratio ranged from 3 000 to 5 000. The pulse angle corresponded to *ca.* 45°. The temperatures were directly measured by a thermometer inserted in an n.m.r. tube with MeOH and are accurate to ± 2 °C.

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