Multinuclear Magnetic Resonance Studies. Part 4.[1] Tetra-alkyldiphosphines with Bulky Substituents †

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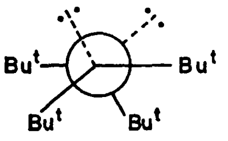
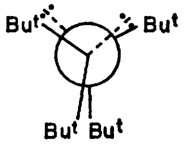
Phosphorus-31 and carbon-13 n.m.r. spectra have been obtained for three new tetra-alkyldiphosphines with bulky substituents: $(Bu^tPr^iP)_2$ (1), $(Bu^tEtP)_2$ (2), and $(Pr^iEtP)_2$ (3). The spectra are assigned and the n.m.r. parameters are compared to those for anologous compounds with lighter alkyl substituents. Molecular conformations are deduced and the effects of inversion at phosphorus discussed.

DIPHOSPHINES are of interest to the structural chemist from a number of aspects. They have all the conformational possibilities of ethanes, and interconversion between the various forms can occur by internal rotation about the P–P bond. In discussions of their structure, the lone pairs may be treated as pseudo-substituents, but inversion at phosphorus is an additional feature that needs to be considered. Usually it is assumed that, as with ethane derivatives, the stable conformations are staggered. A Raman study [2] of P_2Me_4 shows it to be essentially *trans* in the solid, but a mixture of *trans* and *gauche* forms in the liquid. However, a recent *X*-ray study [3] of tetracyclohexyldiphosphine indicates that the molecule is close to the semi-eclipsed form in the solid, and microwave studies [4] show a dihedral angle of 74° for gaseous P_2H_4. Photoelectron spectroscopy [5,6] and electron diffraction [7] have also been used to study the structure of diphosphines without electronegative substituents, and recently n.m.r. spectroscopy has been able to provide detailed information of the solution state. Thus low-temperature ^{13}C and ^1H n.m.r. spectra have shown [8,9] that $P_2Bu^t_4$ is not *trans* nor symmetrically eclipsed, since two types of Bu^t group are observed. These observations were interpreted [8,9] in terms of the *gauche* conformation (I) although even large deviations towards the semi-eclipsed form (II) cannot be excluded.



(I)



(II)

Of course there is no reason to expect that the projection of the CPC angle on to a plane perpendicular to the P–P bond should be 120°; in the case of solid $P_2(C_6H_{11})_4$ it is reported [3] to be 108°, although presumably it is likely to be higher for $P_2Bu^t_4$. Measurements of $N(PC) = |^1J(PC) + {}^2J(PPC)|$ have indicated [10] that N(PC) is characteristically near zero for alkyl groups *gauche* to the lone pair on the remote phosphorus, but substantial (15—50 Hz) for *trans* groups, subject to a reasonable assumption [10,11] regarding the preferred conformation of compounds of the type $(R^1R^2P)_2$. The possible influence of *trans* conformers on discussions of N(PC) is, however, problematical.

The n.m.r. parameters for diphosphines are themselves of considerable interest [for instance the variation of N(PC) referred to above, and the large variation of J(PP) and δ(P) with the nature of the substituents [12,13]]. A considerable body of data has appeared in the literature [12,13] for diphosphines of the types P_2R_4, $(R^1R^2P)_2$, $R^1_2PPR^2_2$, and $R^1R^2PPR^3_2$ (R,R^1, R^2, and R^3 = Me, Et, Pr^i, or Bu^t) although several of the compounds with the more bulky ligands have never been investigated by n.m.r. Since some of the results [12,13] for $P_2Bu^t_4$ and $Me_2PPBu^t_2$ appeared somewhat anomalous, it was decided to prepare and examine $(Bu^tPr^iP)_2$ (1), $(Bu^tEtP)_2$ (2), and $(Pr^iEtP)_2$ (3), which have not, to our knowledge, been studied previously. We report the n.m.r. data herein.

There are two special features of such compounds that deserve mention. First, they may exist in either *racemic* or *meso* forms; the relevant ideal staggered conformations (excluding mirror images) are shown in structures (III) and (IV). Secondly, the isopropyl groups in $(Pr^iEtP)_2$ and $(Bu^tPr^iP)_2$ are in a prochiral situation; the two methyl groups of a given isopropyl are chemically non-equivalent and give anisochronous ^{13}C (or ^1H) resonances when ^{31}P inversion is slow on the n.m.r. time scale.

Rapid ^{31}P inversion causes both *racemic* $\rightleftharpoons$ *meso* interconversion and interchange of the two anisochronous methyl groups for a given isopropyl group. Such ^{31}P inversion has been shown [12] to be slow on the n.m.r. time scale at ambient probe temperature for $P_2Pr^i_4$ and for $(Pr^iMeP)_2$, but in the former case the separate ^{13}C methyl-group n.m.r. signals coalesced above *ca.* 75 °C. However, internal rotation about the P–P bond is thought [12] to be rapid on the n.m.r. time scale above *ca.* −100 °C for all tetra-alkyldiphosphines so far studied except $P_2Bu^t_4$.

Proton-decoupled ^{13}C and ^{31}P n.m.r. spectra of the simple symmetrical tetra-alkyldiphosphines are usually easy to assign and interpret.[12] However, the proton spectra are not so readily analysed because of the

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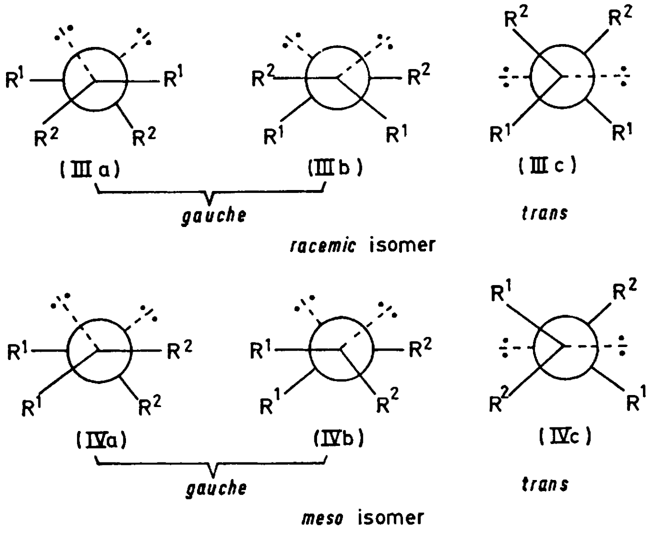
† Systematic names for the compounds studied are 1,2-di-isopropyl-1,2-di-t-butyldiphosphane (1), 1,2-diethyl-1,2-di-t-butyldiphosphane (2), and 1,2-diethyl-1,2-di-isopropyldiphosphane (3).

symmetry;[14,15] therefore the information to be obtained may be rather limited. In fact, the ^{13}C spectra are in principle[12] second order, forming the X parts of ABX spin systems with $\nu_A \approx \nu_B$, but in practice deceptively simple triplets are normally observed, which yield only chemical shifts and the sum of the two relevant (P,C) coupling constants, N(PC).



RESULTS

The ^{31}P-{^1H} spectra of the three compounds show immediately that $(Bu^tPr^iP)_2$ and $(Bu^tEtP)_2$ exist predominantly in one isomeric form, presumed to be *racemic*, since only one signal can be found. The alternative hypothesis, that ^{31}P inversion is rapid, was discounted by variable-temperature experiments, and [in the case of (1)] by observation of methyl anisochronicity in the ^{13}C spectrum. The conclusion is consistent with previous work[12] on $(Bu^tMeP)_2$, which was also found to exist essentially only in the *racemic* form. In contrast, two ^{31}P-{^1H} signals were found for $(Pr^iEtP)_2$ with an intensity ratio of *ca.* 2 : 1 (from measurement of peak heights). It is concluded that both stereoisomers are present, the *racemic* being favoured, as found previously[12] for $(EtMeP)_2$ and $(Pr^iMeP)_2$. It appears then, that the *meso* isomer of $(R^1R^2P)_2$ (R^1,R^2 = Me, Et, Pr^i, or Bu^t) is only too low in population to be detected by n.m.r. when one of the alkyl groups is Bu^t. The two ^{31}P signals for $(Pr^iEtP)_2$ broaden as the temperature is raised and ^{31}P inversion becomes more rapid. At the highest temperature we used (161 °C), the spectrum was just short of coalescence, implying $\Delta G^{\ddagger} \approx 86$ kJ mol^{-1}.

TABLE 1

Phosphorus-31 chemical shifts for tetra-alkyldiphosphines $(R^1R^2P)_2$

R^1R^2	Me_2	*rac*-MeEt	*meso*-MeEt	*rac*-$MePr^i$	*meso*-$MePr^i$	*rac*-$MeBu^t$	
δ(P)/p.p.m.	−57.86 [a]	−46.43 [b]	−44.59 [b]	−38.35 [b]	−31.31 [b]	−30.20 [b]	
$10^2[\Delta\delta(P)](\Delta T)^{-1}$/p.p.m. K^{-1}	0.6	2.6	2.4	3.7	3.2	3.2	
R^1R^2	Et_2	*rac*-$EtPr^i$	*meso*-$EtPr^i$	*rac*-$EtBu^t$	Pr^i_2	*rac*-Pr^iBu^t	Bu^t_2
δ(P)/p.p.m.	−31.92 [b]	−21.40 [c]	−17.12 [c]	−6.03 [c]	−10.64 [b]	15.12 [c]	40.96 [b]
$10^2[\Delta\delta(P)](\Delta T)^{-1}$/p.p.m. K^{-1}	4.7	6.3	5.0	3.9	8.9	6.6	5.2

[a] In toluene + C_6D_6 at 36 °C (refs. 12 and S. Aime and R. K. Harris, *J. Magn. Reson.*, 1974, **13**, 236 give −57.58 p.p.m.). [b] At 40 °C. The measurements were taken for the same samples used in the earlier study[12] and the data are consistent with the earlier (36 °C) results. [c] At 36 °C.

The ^{31}P chemical shifts for (1)—(3) are given in Table 1. These shifts were found to vary substantially with temperature, in a roughly linear fashion over the range studied, the rate of change is given in Table 1. We have also measured the effect of temperature on the ^{31}P chemical shifts of other tetra-alkyldiphosphines (see Figure 1 and Table 1). These variable-temperature experiments were carried out using an internal ^2H lock, but checks using an external ^{19}F lock showed little difference in $\Delta\delta(P)/\Delta T$ so that the temperature variation is genuinely that of δ(P) and not that of δ(H) for the lock.

The ^{31}P shift for P_2Me_4 is not very sensitive to dilution in benzene: we have measured (using ^2H internal lock) δ(P) = −57.74 and −57.77 p.p.m. for *ca.* 5 and 50% v/v solutions respectively. The values of δ(P) for the two isomers of $(Pr^iEtP)_2$, measured using ^{19}F external lock, are unchanged (to within a few Hz) in going from the neat liquid to a solution in benzene.

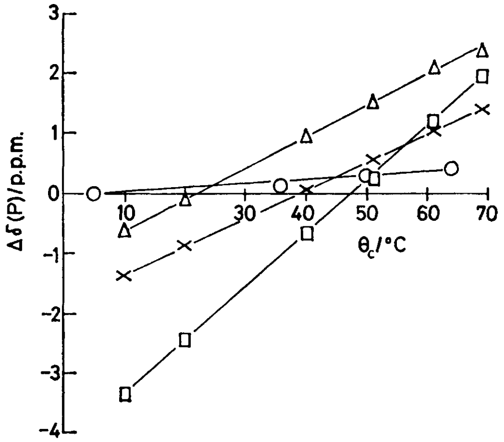


FIGURE 1 Effect of temperature on δ(P) for compounds of the type P_2R_4: (○), P_2Me_4; (×), P_2Et_4; (□), $P_2Pr^i_4$; and (△) $P_2Bu^t_4$. For convenience the shifts have been referenced to the following values of δ(P)/p.p.m.: −58.0 (P_2Me_4), −32.0 (P_2Et_4), −10.0 ($P_2Pr^i_4$), and +40.0 ($P_2Bu^t_4$)

The ^{13}C spectra are, of course, somewhat more complicated than the ^{31}P spectra, but in practice they can be readily interpreted. Analysis is simplified by the fact that, for the tetra-alkyldiphosphines of type $(R^1R^2P)_2$ (R^1,R^2 = Me, Et, Pr^i, or Bu^t) the ^{13}C chemical-shift ranges of the different alkyl groups do not overlap. They occur as shown below.

Group	Me	Et (α- and β-C)	Pr^i (α- and β-C)	Bu^t (α- and β-C)
δ(C)/p.p.m.	2—11	11—20	21—26	28—36

The quaternary and CH_2 carbon resonances may be readily distinguished from each other and from the CH and CH_3

resonances by low-power noise decoupling. Under such conditions, the CH and CH_3 resonances are broadened and appear with poor signal-to-noise ratio. The quaternary carbon signals remain sharp and have the same intensity as under high-power noise decoupling because only small (long-range) (C,H) couplings have to be removed. The CH_2 resonances also appear sharp but with only *ca.* $\frac{1}{4}$ the intensity obtained under high-power decoupling. The CH_2 effect, which is very marked, is shown in Figure 2. It does not appear to have been extensively used in other publications, although it has been noted for corresponding off-resonance experiments.[16] It arises from the fact that for the CH_2 protons (unless they are markedly non-equivalent) the singlet state (in composite particle notation) acts as if it were non-magnetic. Thus, ^{13}C signals from such CH_2 groups ($\frac{1}{4}$ of the total) do not require proton decoupling except to remove long-range (C,H) coupling effects.

The ^{13}C signals obtained under proton-noise-decoupling conditions are all triplets due to deceptively simple coupling [12] to the two phosphorus nuclei (although in some cases the relevant splitting is very small). The splittings yield values for $N(PC)$, *i.e.* $|^1J(PC) + ^2J(PPC)|$ for the α carbons and $|^2J(PCC) + ^3J(PPCC)|$ for the β carbons. The values of $N(PC)$ (α-C) were used to determine the assignment of the stereoisomers as described previously.[10,12] In the case of compounds (1) and (2) such measurements showed that only the *racemic* isomer is present, while for (3) they indicated that the favoured isomer was *racemic* (intensity considerations then allowed the β-C peaks to be assigned unambiguously to the *racemic* and *meso* forms).

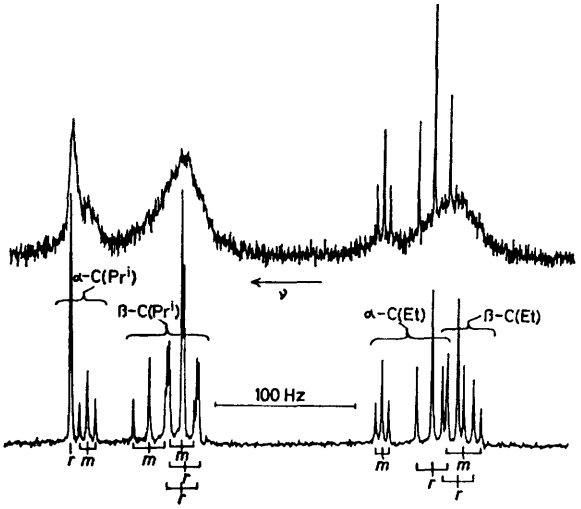


FIGURE 2 25 MHz ^{13}C-$\{^1H\}$ spectra of $(Pr^iEtP)_2$ at ambient probe temperature. The lower trace shows the effect of high-power noise decoupling, and gives the peak assignments (*r* = *racemic* isomer, *m* = *meso* isomer). The upper spectrum was recorded under conditions of low-power noise decoupling; only the CH_2 peaks remain sharp (see the text). For the lower and upper spectra, 500 and 750 transients, respectively, were co-added before Fourier transformation

The ^{13}C spectrum of compound (3), with the resonances assigned, is shown in Figure 2, and the ^{13}C chemical shifts, together with data on $N(PC)$, for the three compounds studied are given in Table 2. For compound (3) the β-C atoms of the isopropyl groups (for each stereoisomer) are anisochronous at ambient probe temperature, as mentioned above. However, for *rac*-$(Bu^tPr^iP)_2$ the temperature must be lowered to observe two *sharp* triplets for the isopropyl β carbons; the signals were found to coalesce at *ca.* 40 °C (leading to $\Delta G^{\ddagger} \approx 65$ kJ mol^{-1}) and a single sharp triplet is observed above 80 °C. The barrier may be compared to that for $(Pr^iEtP)_2$ (86 kJ mol^{-1}, see above) and for $P_2Pr^i_4$ (75 kJ mol^{-1}, derived from ^{13}C work [12]). It is clear that increasing the bulk of the alkyl groups attached to phosphorus in diphosphines lowers the barrier to phosphorus inversion (although this was not obvious in earlier work [17]) since the other factors of importance (substituent electronegativity and π-bonding ability) do not vary appreciably for the tetra-alkyldiphosphines. Presumably substituent bulk destabilises the ground state and increases the CPP and CPC angles.

DISCUSSION

The data of Tables 1 and 2 will be discussed in terms of the conformations (IIIa)—(IIIc) and (IVa)—(IVc), together with the corresponding forms for $R^1 = R^2$. However, these are idealised forms, subject to several types of distortion (*e.g.* towards semi-eclipsed forms) as mentioned in the introduction. We shall assume, following McFarlane and McFarlane,[11] that if R^2 is more bulky than R^1, form (IIIb) is preferred over form (IIIa), but there is as yet no definitive proof on this point.

TABLE 2

Carbon-13 n.m.r. parameters for tetra-alkyldiphosphines *

		α-carbons		β-carbons	
Molecule	Group	δ(C)/ p.p.m.	$N(PC)$/ Hz	δ(C)/ p.p.m.	$N(PC)$/ Hz
$(Bu^tPr^iP)_2$	Pr^i	23.56	34.5	25.92 24.31	26.8 9.7
	Bu^t	31.34	4.3	31.78	22.0
$(Bu^tEtP)_2$	Et	12.26	31.1	14.93	26.5
	Bu^t	29.13	1.1	29.69	21.3
rac-$(Pr^iEtP)_2$	Et	14.34	22.0	13.60	22.2
	Pr^i	24.57	<2	21.43 21.37	21.1 21.2
meso-$(Pr^iEtP)_2$	Et	15.75	9.4	13.44	24.5
	Pr^i	24.11	11.1	22.35 21.43	23.2 17.0

* Data given are for ambient probe temperature (*ca.* 36 °C), except for $(Bu^tPr^iP)_2$, at $T = 1$ °C.

Phosphorus-31 *Chemical Shifts*.—The pattern of shifts for compounds of the type $(R^1R^2P)_2$ is displayed in Figure 3 as a function of the total number, *n*, of methyl groups β to either phosphorus. For compounds without Bu^t there is a linear relationship (line A on Figure 3) between δ(P) and *n*, as might be expected if there are no effects from large geometry distortions or changes in conformer populations. The slope of this graph (5.92 p.p.m.) is, in that case, $\frac{1}{2}(\beta + \gamma)$, where β and γ are the effects of replacement of H by Me two and three bonds removed from the probe nucleus respectively.[13] However, compounds containing Bu^t show departures from line A, as has been noted previously [13] for $P_2Bu^t_4$ (and, in a corresponding situation,[13] for $Me_2PPBu^t_2$). Matters are complicated because *meso* stereoisomers of $(RBu^tP)_2$ have not been detected. It would be anticipated that *meso* forms would behave similarly to compounds P_2R_4 because the *gauche* rotamers (IVa) and (IVb) are equivalent, whereas conformational bias for *racemic* forms should lead to deviations. Some justification for this situation is evident in Figure 3. Moreover the value of $\Delta = \delta(P)(meso) - \delta(P)(rac)$ would be expected to increase as the difference in bulk between R^1 and R^2 increases. The data for $(EtMeP)_2$ ($\Delta = 1.8$ p.p.m.), $(Pr^iEtP)_2$ ($\Delta = 4.3$ p.p.m.), and $(Pr^iMeP)_2$ ($\Delta = 7.0$ p.p.m.) bear this out. Thus a large value of Δ is expected for $(Bu^tMeP)_2$, and it may be that the value $\frac{1}{2}[\delta(P)(meso) + \delta(P)(rac)]$ or, perhaps more likely,* $\delta(P)(meso)$ itself for this compound may fall on the line A in Figure 3. The point for $(Bu^tEtP)_2$ does fall on line A, but this is probably fortuitous since only the *racemic* compound is known. The point for *rac*-$(Bu^tPr^iP)_2$ falls off line A, as already also noted for $P_2Bu^t_4$. In fact points for compounds of the type *rac*-$(RBu^tP)_2$ plus $P_2Bu^t_4$ fall on a second line, B, in Figure 3, of greater slope than line A. Presumably the *meso* isomers of $(RBu^tP)_2$ plus $P_2Bu^t_4$ would fall on a third line of slope intermediate between those of A and B. Clearly the deviations of the t-butyl compounds from line A are not due to a difference in γ effect for the final Me substituent arising from a different orientation [18] (γ_{trans}, say, differing from γ_{gauche}), since in that case a constant deviation would be expected, rather than a change in slope. Therefore, we believe that the t-butyl compounds $(RBu^tP)_2$ show a progressive geometric distortion as the size of R increases. However, the normal β-deshielding effect, which operates for the smaller substituents, has been attributed [19] to changes in hybridisation (increase in *s* character of the P–C bonds as the substituent bulk increases) consequent upon changes in the CPC bond angles.

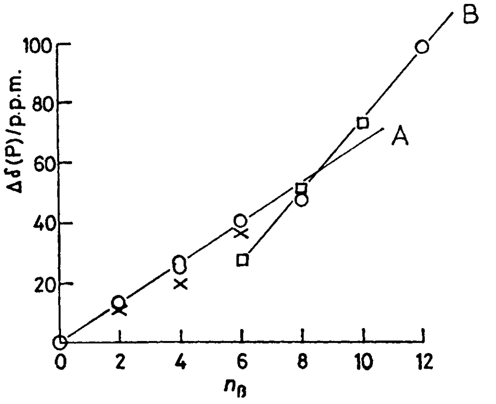


FIGURE 3 Plot of ^{31}P chemical shifts (with respect to the value for P_2Me_4) for tetra-alkyldiphosphines as a function of n_β, the total number of methyl groups β to phosphorus. (○), P_2R_4 and *meso*-$(R^1R^2P)_2$; (□), *rac*-$(RBu^tP)_2$; and (×), other *rac*-$(R^1R^2P)_2$ compounds. The lines A and B are referred to in the text

Figure 4 plots the rate of change of $\delta(P)$ with temperature against n_β. It can be seen that although there is a relatively wide scatter of points (possibly arising in part from concentration variations), there is a general tendency for $\Delta\delta(P)/\Delta T$ to increase as the substituents become larger, but the point for $P_2Bu^t_4$ is anomalously low, again possibly indicating geometrical distortion. Values for the other t-butyl compounds are also low. Temperature variation of $\delta(P)$ may partly arise from intermolecular interactions and partly from conformational averaging. From the latter point of view it is interesting to note that $\Delta\delta(P)/\Delta T$ is less for the *meso* isomers than for the *racemic* forms. According to Figure 3 this implies that $\delta(P)(rac)$ will approach $\delta(P)(meso)$ at high temperatures, suggesting that the populations of (IIIa) and (IIIb) are becoming closer. The large value of $\Delta\delta(P)/\Delta T$ for $P_2Pr^i_4$ implies that at high temperatures the point for this compound would fall closer to line A of Figure 3 than currently displayed.

Carbon-13 *Chemical Shifts*.—The values of $\delta(C)$ for symmetrical tetra-alkyldiphosphines $(R^1R^2P)_2$ are plotted in Figure 5. Several points of interest emerge. (*i*) For α-carbon atoms $\delta(C)(racemic)$ is always less than $\delta(C)(meso)$ for the *lighter* of the two substituents R^1 and R^2. This means that the plots for a given carbon in the *meso* and *racemic* forms cross at the point for the relevant compound of the type P_2R_4. Such an observation implies that groups *gauche* to a lone pair are less shielded than those in a *trans* position. However, there is no direct evidence on this point for diastereoisomeric t-butyl compounds, and a contrary situation (*i.e.* $\sigma_{gauche} > \sigma_{trans}$) is found [8] at low temperatures for $P_2Bu^t_4$ (an assignment of the α-carbon signals may be deduced from refs. 8 and 10). Again, therefore, the bulky t-butyl groups appear to be causing departures from ' normal ' behaviour.

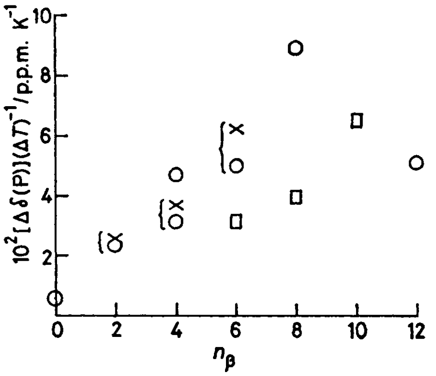


FIGURE 4 Temperature variation of $\delta(P)$ for tetra-alkyldiphosphines as a function of n_β, the total number of methyl groups β to phosphorus. For meanings of symbols see Figure 3

(*ii*) The difference $|\delta(C)(meso) - \delta(C)(racemic)|$ for the α-carbons increases as the bulk of the substituents R^1 and R^2 differs increasingly. This would be expected, either on the basis of variations in conformational biassing or of geometry distortions. The smooth crossover discussed under (*i*) above tends to suggest that conformational changes are the more likely origin of the observations, although this is not entirely in accord with the results for $N(PC)$ discussed below.

(*iii*) For methyl carbons in $(RMeP)_2$ compounds,

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*A previous paper [13] estimated $\delta(P)$ (*meso*) for this compound to be −14.6 p.p.m., on the assumption that $\frac{1}{2}[\delta(P)(meso) + \delta(P)(rac)]$ should lie on a line analogous to A. We now believe this is not necessarily so, and that $\delta(P)$ (*meso*) may be nearer to −19 p.p.m.

δ(C) decreases smoothly as the bulk of R increases. Such a change represents a $\gamma + \delta$ effect of substitution of H by Me provided the situation is not affected by conformational variations. It is best to compare *meso* compounds with the symmetrical $\mathrm{P_2Me_4}$ since the conformational situation is similar, and these give on average $\gamma + \delta = -2.4$ p.p.m., presumably because of the usual γ-shielding effect.[12] (Variations in the population of *trans* rotamers may however, complicate the interpretation.) There is a similar variation for the α-carbon of ethyl groups and of isopropyl groups with the exception of *rac*-$(\mathrm{Bu^tPr^iP})_2$. The α-carbon of t-butyl groups in $(\mathrm{RBu^tP})_2$ compounds (only the *rac* isomers are known) is, however, consistently *deshielded* as the bulk of R increases, another example of the anomalous behaviour of the compounds with bulky substituents. The *racemic* forms show *larger* values of $|\gamma + \delta|$ than the *meso* isomers for Me, Et, and $\mathrm{Pr^i}$ groups, omitting *rac*-$(\mathrm{Bu^tPr^iP})_2$, so the reversal of the slope in the *rac*-$(\mathrm{RBu^tP})_2$ series is all the more anomalous.

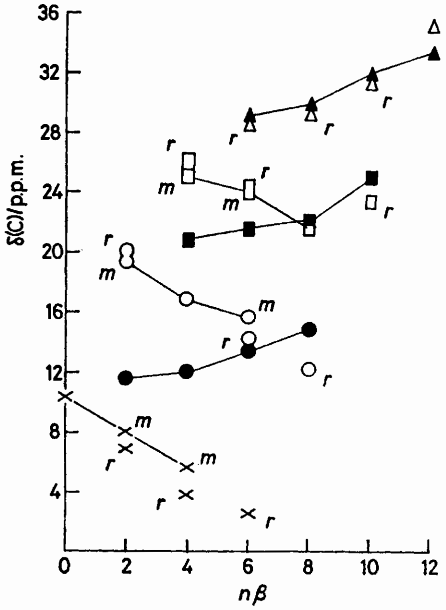

FIGURE 5 Carbon-13 chemical shifts for tetra-alkyldiphosphines as a function of n_β, the total number of methyl groups β to phosphorus. *Racemic* (*r*) and *meso* (*m*) results are distinguished only for α carbons. The two anisochronous β methyls for isopropyl groups are not distinguished. Solid lines link results for α carbons of *meso*-$(\mathrm{R^1R^2P})_2$ and $\mathrm{P_2R_4}$, and also β carbons. (○), α-Et; (□), α-$\mathrm{Pr^i}$; (△), α-$\mathrm{Bu^t}$; (×), Me; (●), β-Et; (■), β-$\mathrm{Pr^i}$; (▲), β-$\mathrm{Bu^t}$

(*iv*) The β-carbon ($\mathrm{CH_3}$) of the ethyl groups in $(\mathrm{REtP})_2$ has a steadily increasing value of δ(C) as the bulk of R increases. This represents the effect at a δ position (*via* one phosphorus atom) of progressive substitution of H by Me, and it is *ca.* 1.1 p.p.m. per replacement. The shift difference between *racemic* and *meso* forms appears to be small. Similar replacement effects may be noted on the β-carbon chemical shifts for $\mathrm{Pr^i}$ and $\mathrm{Bu^t}$ groups, and the more bulky groups do not appear to introduce any substantial anomaly. If a similar δ effect (but *via* two phosphorus atoms) occurs for the α-carbons, then the normal γ effect of the Me for H replacement, mentioned in (*iii*) above, must be *ca.* -3.5 p.p.m. The low-temperature measurements[8] on $\mathrm{P_2Bu^t_4}$ showed that there is a relatively small difference (1.36 p.p.m.) between δ(C) for β-carbons in $\mathrm{Bu^t}$ groups *gauche* and *trans* to the lone pair.

(*v*) The anisochronicity between the β-methyl carbons of an isopropyl group decreases from *meso*-$(\mathrm{Pr^iMeP})_2$ to *meso*-$(\mathrm{Pr^iEtP})_2$ to $\mathrm{P_2Pr^i_4}$ [$\Delta\delta(\mathrm{C}) = 1.39$, 0.92, and 0.64 p.p.m. respectively], as might be expected. For the *racemic* isomers of $(\mathrm{RPr^iP})_2$ the values are $\Delta\delta(\mathrm{C}) = 0.53$, 0.06, and 1.61 p.p.m. for R = Me, Et, or $\mathrm{Bu^t}$ respectively; the large value for $(\mathrm{Bu^tPr^i})_2$ may be related to the preferred position of $\mathrm{Pr^i}$ *trans* to a lone pair in this compound (in contrast to the other two).

(*P,C*) *Coupling Constants.*—In general, values of *N*(PC) for α-carbons follow the pattern suggested earlier,[10,12] assuming reasonable conformational biassing.[10,11] Thus, for the three compounds (1)—(3) in the *racemic* form, the lighter alkyl substituent has a large value of *N*(PC), corresponding to a position *trans* to the lone pair [$\mathrm{R^2}$ in (IIIa)] whereas the heavier substituent has a small value of *N*(PC) since it is preferentially *gauche* to the lone pair [$\mathrm{R^1}$ in (IIIa)]. Both alkyl groups have intermediate *N*(PC) values for α-carbons in the *meso* form since rotamers (IVa) and (IVb) are equivalent.

TABLE 3

Classification of data for *N*(PC) [a] of α-carbon nuclei in tetra-alkyldiphosphines $(\mathrm{R^1R^2P})_2$

Group observed	Me	Me	Me	Me	Et	Et	Et	Et
$\mathrm{R^1R^2}$	$\mathrm{Me_2}$	MeEt	$\mathrm{MePr^i}$	$\mathrm{MeBu^t}$	MeEt [b]	$\mathrm{Et_2}$	$\mathrm{EtPr^i}$	$\mathrm{EtBu^t}$
trans to lone pair [c]		15.6 [b]	25.5 [b]	33.7 [b]			22.0	31.1
gauche to lone pair [c]					<2 [b]			
Average [d]	8.6 [e]	9.3 [b]	9.7 [b]		6.5 [b]	8.5 [b]	9.4	
Group observed	$\mathrm{Pr^i}$	$\mathrm{Pr^i}$	$\mathrm{Pr^i}$	$\mathrm{Pr^i}$	$\mathrm{Bu^t}$	$\mathrm{Bu^t}$	$\mathrm{Bu^t}$	$\mathrm{Bu^t}$
$\mathrm{R^1R^2}$	$\mathrm{MePr^i}$	$\mathrm{EtPr^i}$	$\mathrm{Pr^i_2}$	$\mathrm{Pr^iBu^t}$	$\mathrm{MeBu^t}$	$\mathrm{EtBu^t}$	$\mathrm{Pr^iBu^t}$	$\mathrm{Bu^t_2}$
trans to lone pair [c]				34.5 [f]				45.5 [g]
gauche to lone pair [c]	<1.0 [b]	<2			0.8 [b]	1.1 [h]	4.3 [f]	<1 [g]
Average [d]	9.3 [b]	11.1	12.0 [b]					24 [b]

[a] Defined as $|{}^1J(\mathrm{PC}) + {}^2J(\mathrm{PPC})|$ and given in Hz. [b] Data from ref. 10. [c] Given in Hz, assuming *racemic* form (IIIa) is the stable one when $\mathrm{R^1}$ is more bulky than $\mathrm{R^2}$, and ignoring possible contributions from *trans* rotamers. [d] For the symmetrical compounds $\mathrm{P_2R_4}$ or the *meso* isomers of $(\mathrm{R^1R^2P})_2$ with $\mathrm{R^1} \neq \mathrm{R^2}$. [e] F. J. Weigert and J. D. Roberts, *Inorg. Chem.*, 1973, **12**, 313. We find *N*(PC) for a solution of $\mathrm{P_2Me_4}$ in toluene varies from 7.3 Hz at -63 °C to 8.4 Hz at 104 °C. [f] For the neat liquid *N*(PC) ($\mathrm{Bu^t}$) varies consistently from 4.3 Hz at 0 °C to 8.4 Hz at 130 °C but *N*(PC) ($\mathrm{Pr^i}$) remains at 34 Hz within experimental error (±0.5 Hz). [g] Measured [8] at -55 °C. [h] For a solution in benzene *N*(PC) varies from 1.5 Hz at 7 °C to <1 Hz at 61 °C.

Table 3 sets out all the data for tetra-alkyldiphosphines. It is apparent that *N*(PC) for R^1 in the *trans* position of $(R^1R^2P)_2$ increases as the bulk of R^2 increases and as the bulk of R^1 itself increases (except for the comparison of $R^1 = Me$ with $R^1 = Et$). The 'average' value of *N*(PC) obtained from P_2R_4 and *meso* forms of $(R^1R^2P)_2$ varies similarly but to a lesser extent. These changes may be associated with varying amounts of the *trans* rotamers (IIIc) and (IVc), or with geometry changes caused by substituent bulk. In so far as Raman spectroscopic evidence shows [2] that liquid P_2Me_4 contains a considerable proportion of *trans* rotamer (in contrast to the deductions of McFarlane and McFarlane [11]), whereas n.m.r. spectra clearly show $P_2Bu^t_4$ is predominantly *gauche*, it is likely that the effect on *N*(PC) of conformational variations throughout the series of tetra-alkyldiphosphines may be considerable. Indeed, this hypothesis predicts lower values for *N*(PC) ('*trans*') for P_2Me_4 than for $P_2Bu^t_4$, as observed, since in the former case there will be a contribution from a *gauche* orientation of a carbon nucleus with respect to a lone pair arising from the *trans* conformer. The evidence for trends in *N*(PC) for the *gauche* position is less clear. Variable-temperature experiments in the range 0—130 °C for the α-carbon of Bu^t in *rac*-$(Bu^tPr^iP)_2$ show that *N*(PC) increases steadily with temperature, whereas for *rac*-$(Bu^tEtP)_2$ the opposite behaviour appears to occur in the region 7—61 °C, suggesting the signs of *N*(PC) (*gauche*) may be opposite in the two compounds. However *N*(PC) for the Pr^i α-carbon in *rac*-$(Bu^tPr^iP)_2$ does not appear to vary substantially with temperature. Again, the temperature variations of *N*(PC) may be associated with conformational changes, or possibly with intermolecular interactions. It is also possible, although unlikely, that for compounds (1) and (2) *racemic* $\rightleftharpoons$ *meso* exchange is fast with respect to the ^{13}C time scale at the temperatures studied and that there is a contribution to the observed *N*(PC) from a small population (varying with temperature) of the *meso* form. It may be noted that for P_2Me_4 in toluene |*N*(PC)| varies from 7.3 to 8.4 Hz in the temperature range −63 to 104 °C. This observation is consistent with an increasing amount of *gauche* conformer. (Raman evidence [2] suggests this form has a slightly higher free energy than the *trans* form when the statistical advantage of the former is discounted.)

The β-carbon nuclei do not, in most cases, show any substantial difference in *N*(PC) for the *meso* and *racemic* forms (see Table 4). For the ethyl group, |*N*(PC)| lies between 20 and 27 Hz, and for the t-butyl group the range is 19—22 Hz. However, the isopropyl group shows some oddities, associated with the non-equivalence of the β methyls. Thus, although nine of the relevant values of |*N*(PC)| lie between 18 and 27 Hz and are thus 'normal', the *meso* forms of $(Pr^iMeP)_2$ and $(Pr^iEtP)_2$ each show one low value (15.8 and 17.0 Hz respectively), and the *racemic* form of $(Bu^tPr^iP)_2$ has one very low value (9.7 Hz). Although the explanation presumably lies in the details of molecular conformation, we are unable to present any satisfactory reason for these oddities. However, the low-temperature data [8] for $P_2Bu^t_4$ show there is a substantial dependence of *N*(PC) for β-carbons on orientation with respect to the lone pair, since values of 21.2 and 15.6 Hz are reported, the lower value being due to the Bu^t group *trans* to the lone pair.

TABLE 4

Data on *N*(PC) [a] for β-methyl carbon nuclei in tetra-alkyldiphosphines

Group observed	Et	Et	Et	Et	Bu^t	Bu^t	Bu^t	Bu^t
R^1R^2	MeEt	Et_2	$EtPr^i$	$EtBu^t$	$MeBu^t$	$EtBu^t$	Pr^iBu^t	Bu^t_2
racemic isomer	22.5 [b]		22.2	26.5	21.3 [b]	21.3	22.0	
meso isomer or P_2R_4	20.5 [b]	21.5 [b]	24.5					19 [b,c]
Group observed	Pr^i	Pr^i	Pr^i	Pr^i				
R^1R^2	$MePr^i$	$EtPr^i$	Pr^i_2	Pr^iBu^t				
racemic isomer [d]	24.2 [b] 22.0 [b]	21.1 21.2		26.8 [e] 9.7 [e]				
meso isomer or P_2R_4 [d]	22.0 [b] 15.8 [b]	23.2 17.0	18 [b] 20 [b]					

[a] Defined as $|^2J(PCC) + {}^3J(PPCC)|$ and given in Hz. [b] Ref. 12. [c] At −55 °C *N*(PC) (β–C) = 15.6 and 21.2 Hz for the high- and low-frequency signals respectively (hindered internal rotation slowed on the n.m.r. time scale).[8] [d] In each case *N*(PC) for the high frequency signal is given first. [e] The average value at 100 °C for the neat liquid is found to be 19.1 Hz (using ^{19}F external lock).

EXPERIMENTAL

Compounds (1)—(3) do not appear to have been reported following standard reaction sequence. Alkyldichlorophosphines PR^1Cl_2 ($R^1 = Et$ or Bu^t) were treated with the Grignard reagent MgR^2Cl ($R^2 = Pr^i$ or Bu^t) in a 1 : 1 molar ratio to yield the asymmetric phosphinous chlorides $PEtBu^tCl$, $PEtPr^iCl$, and PPr^iBu^tCl, respectively. The diphosphines were then prepared from the chlorides by dehalogenation with sodium in dioxan, and purified by repeated distillation. All operations were carried out under an atmosphere of dry oxygen-free nitrogen, since the diphosphines are readily oxidised by air. $(Bu^tEtP)_2$, b.p. 72 °C (0.5 mmHg) * (Found: P, 26.15. $C_{12}H_{28}P_2$ requires P, 26.45%); $(EtPr^iP)_2$, b.p. 57 °C (0.5 mmHg) (Found: P, 30.2. $C_{10}H_{24}P_2$ requires P, 30.05%); $(Pr^iBu^tP)_2$, b.p. 116 °C (4 mmHg) (Found: P, 23.1. $C_{14}H_{32}P_2$ requires P, 23.6%).

The n.m.r. samples of the diphosphines were prepared by dissolution in benzene, with C_6D_6 to provide a lock signal, using a dry-box under a nitrogen atmosphere. The concentrations were *ca.* 20, 25, and 30% by volume for (1),

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

(2), and (3) respectively. The solutions were placed in n.m.r. tubes (outside diameter 12 mm). The samples were then degassed by the freeze–pump–thaw method using liquid nitrogen. The samples were stored at −4 °C when the spectra were not being obtained.

The spectra were recorded using a Varian XL 100 spectrometer, in the Fourier-transform mode for carbon (25.14 MHz) and phosphorus (40.51 MHz). Both types of spectra were normally obtained under conditions of proton-noise decoupling, with a ^{2}H field–frequency lock. For certain variable-temperature experiments other medium conditions (*e.g.* neat liquid) were used, together with the ^{19}F external lock facility of the XL 100.

The chemical shifts are quoted with the positive frequency convention,[20,21] *i.e.* a positive sign 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,[22] using Ξ_P (85% H_3PO_4) = 40 480 720 Hz and Ξ_C ($SiMe_4$) = 25 145 004 Hz. The standardised lock frequency was Ξ_D (C_6D_6) = 15 350 721 Hz. The value of Ξ_P given above was used for consistency with previously reported data for diphosphines, so that all relative chemical shifts would be accurate. However, McFarlane[23] has reported Ξ_P (85% H_3PO_4) as 40 480 740 Hz, and we ourselves have measured this parameter to be 40 480 737 Hz.

It should be appreciated that no fundamental importance attaches to the precise value of Ξ for the reference compound, and our data can be adjusted, if required, to fit any future internationally agreed value for this parameter.

The spectrometer conditions were varied as required. Spectral widths (SW) were in the range 250—500 Hz, with acquisition times (T_{ac}) 4.0—8.0 s and pulse angles 35—45° for carbon and 50—65° for phosphorus. The number of transients co-added in the computer ranged from 250 to 500 for carbon and 10 to 50 for phosphorus.

The temperature was directly measured by a thermometer, placed in a n.m.r. tube containing methanol for low temperatures (<37 °C) and ethylene glycol for high temperatures (>37 °C). The quoted temperatures are probably accurate to ±2 °C. Ambient probe temperature is *ca.* 36—37 °C.

One of us (G. B.) thanks N.A.T.O. and C.N.R. (Rome) for the award of a research fellowship. Another of us (A. A. M. A.) thanks the University of Kuwait for a postgraduate studentship.

[9/224 *Received*, 12*th February*, 1979]

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