Intramolecular Motion in Tetra-t-butyldiphosphine

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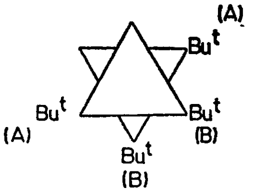
Summary ^{13}C and ^{1}H N.m.r. spectra of $Bu^t_2PPBu^t_2$ at temperatures well below ambient show that there are two distinct environments for the tertiary butyl groups on the n.m.r. time-scale, whereas ^{31}P spectra show there is only one type of phosphorus; this is attributed to the existence of the *gauche* isomer in preference to the *trans* and the two values of $|^1J_{PC} + {}^2J_{PPC}|$ differ markedly.

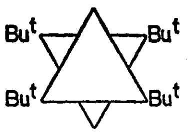
A NUMBER of intramolecular processes may occur for tetra-alkyldiphosphines, *viz.* (i) inversion at phosphorus,[1] (ii) hindered internal rotation about the P–P bond,[1] and (iii) hindered internal rotation about the C–P bonds.[2] Process (iii) is known to be rapid on the n.m.r. time-scale at room temperature, and (i) and/or (ii) must also be rapid since a single proton environment is observed for Me_2PPMe_2. There are, in addition, possible intermolecular processes of importance.[3]

We have observed n.m.r. spectra for tetra-t-butyldiphosphine (I), which must be highly sterically crowded. At room temperature the ^{1}H and $^{13}C-\{^{1}H\}$ spectra consist of one triplet each (these spectra are deceptively simple[4] as a result of a very large value of $|^1J_{PP}|$ which we believe to be *ca.* 450 Hz; the separation of the outer lines of each triplet gives the sum of the appropriate short- and long-range (P,C) coupling constants). Moreover the $^{31}P-\{^{1}H\}$ spectrum is a single line. Thus there is only one t-butyl environment on the n.m.r. timescale. However, as the system is cooled the ^{1}H and $^{13}C-\{^{1}H\}$ spectra broaden, and eventually more complex spectra are seen. The ^{1}H spectrum at low temperature (−55 °C) shows two equally intense triplets. The $^{13}C-\{^{1}H\}$ spectrum (Figure) shows there are two types of quaternary carbon and two types of methyl carbon; in each case the concentrations of the two types of carbon are equal.

We believe these results can only be explained as a result of both process (i) and process (ii) being slow on the n.m.r. time-scale at the appropriate temperature. [It is just possible that process (iii) is responsible for the observed effect, but it is unlikely that this would produce a 1 : 1 ratio[2] for the two types of environment.] It is also essential to assume that the *gauche*-form (Ia) is more stable than the *trans*-form (Ib). This is somewhat surprising since steric crowding appears from molecular models to be more marked for (Ia) than for (Ib). However, doubtless the molecular geometry does not have standard bond angles, and presumably a flattening of the ^{31}P environment or lengthening of the P–P bond would relieve steric strain to some extent. Also the lone pairs may play an important role. It is not entirely clear whether the process which averages environments (A) and (B) of (Ia) is inversion at phosphorus or internal rotation about the P–P bond but the latter is the more likely. Calculations using an approximate coalescence temperature of *ca.* −25 °C (for the ^{13}C resonances) show that the free energy of activation of the process in (I) is *ca.* 12 kcal mol^{-1}, which is higher than expected[2] for C–P internal rotation but much lower than expected[1] for inversion. Lambert *et al.*[1] found that the ^{1}H spectrum of tetramethyldiphosphine was unchanged down to −65 °C, so the effect of the t-butyl groups in (I) must be either to raise the barrier to P–P internal rotation or to stabilise (Ia).



(Ia)



(Ib)

The n.m.r. parameters at low temperature (Table) are of some interest since the coupling constants differ for the two environments (A) and (B). This is particularly marked for $|{}^1J_{PC} + {}^2J_{PPC}|$—one of the values is so small that it cannot be resolved. It is not known whether the low value of $|{}^1J_{PC} + {}^2J_{PPC}|$ is associated with environment (A) or with (B). The anomalies in $|{}^1\mathrm{J}_{PC} + {}^2J_{PPC}|$ may be connected with the orientation effects of the lone pairs on *either* ^{31}P atom (such influences have been suggested[5] for $^1J_{PP}$ and $^nJ_{PC}$, $n = 1$—4), but if so one might expect a profound effect on $|{}^2J_{PCC} + {}^3J_{PPCC}|$ also, unless there is a fortuitous cancellation of contributions.

The spectra were recorded using a Varian XL-100 spectrometer operated in the Fourier transform mode for ^{13}C (25 MHz) and in the continuous wave mode for ^{31}P (40 MHz) and ^{1}H (100 MHz). A solution in CH_2Cl_2–CD_2Cl_2 was used for these studies, with the deuterium n.m.r. of CD_2Cl_2 providing a signal for field-frequency locking.

TABLE

N.m.r. data[a] for $Bu^t_2PP\,Bu^t_2$ at −55 °C

$\delta_H{}^b = 1{\cdot}23$ and $1{\cdot}13$; $|{}^3J_{PH} + {}^4J_{PH}| = 12{\cdot}8$ and $11{\cdot}9$ Hz, respectively
$\delta_P{}^b = 37{\cdot}40$ (at −52 °C)
δ_C (quaternary)^b = $36{\cdot}22$ and $33{\cdot}95$; $|{}^1J_{PC} + {}^2J_{PC}| = 45{\cdot}5$ and < 1 Hz, respectively.
δ_C (methyl)^b = $33{\cdot}84$ and $32{\cdot}48$; $|{}^2J_{PC} + {}^3J_{PC}| = 15{\cdot}6$ Hz and $21{\cdot}2$ Hz, respectively.

[a] We have shown by ^{13}C–{^{1}H} studies that the higher frequency ^{1}H, ^{13}C (methyl), and ^{13}C (quaternary) resonances all belong to the same tertiary butyl group.

[b] δ_H, δ_P, and δ_C are with respect to Me_4Si, 85% H_3PO_4, and Me_4Si, respectively, and are positive when the sample resonates at higher frequency than the reference.

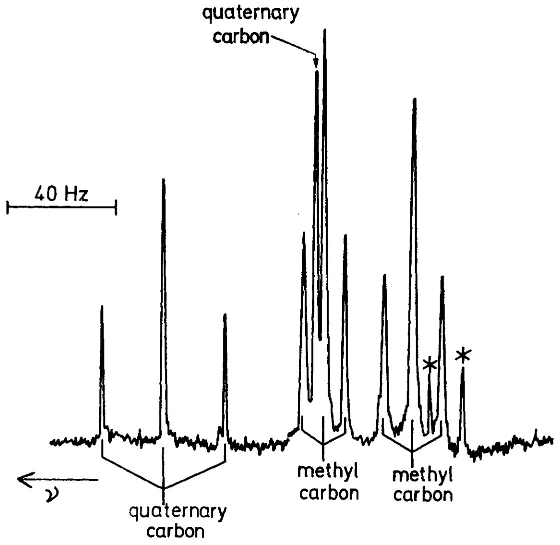


FIGURE. The observed ^{13}C–{^{1}H} noise-decoupled n.m.r. spectrum of $Bu^t_2PPBu^t_2$ at *ca.* −60 °C, with the assignments indicated. The peaks marked by asterisks are due to impurities.

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