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The solution conformation and rotational dynamics of tetramesityldiphosphane studied by 2-D NMR spectroscopy

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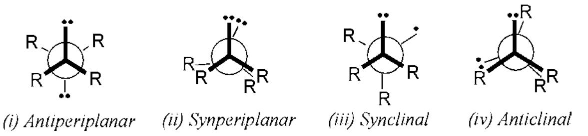
Detailed proton and ^{13}C dynamic NMR and 2-D EXSY studies of tetramesityldiphosphane at a field of 11.8 T over the temperature range 193–313 K showed that rotations about the P–P bond and two types of P–C$_{ipso}$ bond are associated with three different barriers. This supports a *gauche* conformation of this molecule in solution at low temperature rather than *trans* as found in the solid state, and is consistent with the pattern of coupling constants observed in the low temperature proton and ^{13}C spectra. It can be attributed to favoured electron lone pair/lone pair interactions allied to a propeller twist of the mesityl groups which minimises their effective steric requirements.

Introduction

The conformational preferences and barriers to rotation about the P–P bond of tetraorganodiphosphanes, RR′PPRR′, have been of interest for some time with most discussions centring on competition between electron lone-pair/lone-pair (l.p./l.p.) interactions which would be expected to favour a synclinal (iii) relationship and steric repulsions involving bulky substituents which would favour antiperiplanar (i) [see Scheme 1 for Newman projections down the P–P bond]. In the case of diphosphane, P$_2$H$_4$, itself the latter interactions are essentially absent, and from electron diffraction in the gas phase the structure is known[1] to be synclinal with a l.p./l.p. dihedral angle of 74°, implying that this gives the most favourable relationship. For tetramethyldiphosphane, Me$_2$PPMe$_2$, conflicting results were obtained from electron diffraction [(i)],[2] vibrational spectroscopy [(i) + (iii)],[3,4] photoelectron spectroscopy [(i) + (iii)],[5–7] and theoretical calculations [(i)].[8,9] In the solid this molecule adopts the antiperiplanar conformation,[10] but this may be a consequence of intermolecular contacts in the crystal lattice. Other available solid state structures show a further eight examples of antiperiplanar,[11–18] five of anticlinal[19–23] and none of synclinal or synperiplanar, although these can occur in diphosphanes with heteroatoms attached to phosphorus.[23]



(i) Antiperiplanar (ii) Synperiplanar (iii) Synclinal (iv) Anticlinal

Scheme 1

There have been a number of studies by solution state high resolution NMR of this problem, and these have always considered only two of these idealised models, namely (i) and (iii), although (ii) and (iv) were suggested[24] as possible excited states in rotation about the P–P bond of tetra-*tert*-butyldiphosphane, Bu$^t_2$PPBu$^t_2$. However, the low temperature proton and ^{13}C NMR spectra[24,25] of Bu$^t_2$PPBu$^t_2$ show the presence of two types of *tert*-butyl group, and are therefore inconsistent with either (i) or (ii) as the ground state in solution and (iii) has been assumed to be the conformation of this and of the only known[26] diastereomer of *P*,*P*′-di-*tert*-butyl-*P*,*P*′-dimethyldiphosphane, MeBu^{t}PPBu^{t}Me, even though the NMR data do not actually preclude (iv). Thus it is clear that the energetics of the different rotamers of ditertiaryphosphanes are finely balanced and that X-ray diffraction studies cannot be relied upon as a guide to solution conformations in this area.

In this connection the solution conformation of tetramesityldiphosphane, (2,4,6-Me$_3$C$_6$H$_2$)$_4$P$_2$, **1**, is of special interest, since the four mesityl substituents may be sufficiently bulky significantly to affect rotation around the P–P bond and also can themselves show effects due to restricted rotation about their P–C$_{ipso}$ bonds. In the solid[16] this molecule adopts a conformation that is essentially antiperiplanar with respect to the P–P bond, with a dihedral angle between the nominal lone-pair directions of 158° and a propeller twist of the mesityl groups such that the molecular symmetry approximates to C_2. In solution at low temperatures the 200 MHz proton NMR spectrum indicated frozen out rotation about the P–P and the P–C$_{ipso}$ bonds with a pattern of resonances that is consistent not only with the C_2 symmetry found in the solid, but also with C_s or C_i symmetry.[16] However, while C_{2h}, C_{2v} and C_1 symmetries can be excluded on the basis of this spectrum it should be borne in mind that certain synclinal and anticlinal rotamers will also have C_2 or C_i symmetry so that these too are consistent with the foregoing NMR data.

In this paper we report high field (11.8 T) dynamic proton (500 MHz) and ^{13}C (125 MHz) NMR studies of compound **1** which distinguish among some of these alternatives and favour synclinal as the preferred conformation in solution, with three different barriers to internal rotation about the P–P and two types of P–C$_{ipso}$ bonds. The measurements included band-shape analysis of ^{1}H and ^{13}C spectra over a range of temperatures and field strengths that cover timescales ranging from "frozen out" to essentially "free rotation" of all relevant bonds, together with 2-D ^{1}H EXSY, ^{1}H ROESY (rotating frame Overhauser enhancement spectroscopy),[27] and ^{1}H/^{13}C correlation, and ^{1}H-{^{31}P} and ^{13}C-{^{31}P} decoupling experiments.

Experimental

Tetramesityldiphosphane, **1**, was prepared[28] by the reaction of phosphorus trichloride with mesitylmagnesium bromide and an excess of metallic magnesium in thf and recrystallised from

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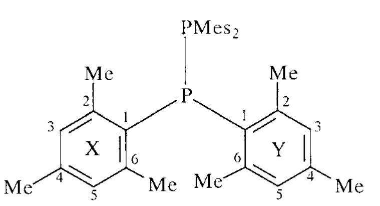


Fig. 1 Numbering scheme used for the two mesityl rings of tetramesityldiphosphane. No conformational assignment is to be inferred.

ethanol. Solutions in $CDCl_3$ and CD_2Cl_2 were examined in 5 mm o.d. spinning tubes on a JEOL Lambda 500 pulsed Fourier transform NMR spectrometer operating at frequencies of 500.2, 125.2 and 202.2 MHz with internal Me_4Si, internal Me_4Si, and external 85% H_3PO_4 as references for ^1H, ^{13}C, and ^{31}P respectively. Temperatures were calibrated down to 213 K using a standard anhydrous methanol sample. Two dimensional spectra were generally acquired using 1K data points in the t_2 dimension and 512 in t_1, with subsequent weighting with sine-bell functions and transformation into a 2K × 2K matrix, although for the stack plot of Fig. 3 the matrix was 8K (f_1) × 2K (f_2). Standard pulse sequences were used with phase cycling by the States method[29] for phase-sensitive 2-D spectra. The spin-locking field for the ROESY experiments had $\gamma B_2/2\pi = 4500$ Hz. DNMR spectra were simulated using the program *g*NMR.[30]

Results

At 11.8 T and at all temperatures in the range 198–333 K the proton-decoupled ^{31}P NMR spectrum of compound **1** in CD_2Cl_2 was a single resonance ($\delta(^{31}P)$ −31.3, $\nu_{\frac{1}{2}} < 3$ Hz) indicating chemical equivalence of the two $(Mes)_2P$ (Mes = 2,4,6-$Me_3C_6H_2$) moieties irrespective of the extent of any restricted rotation. At this field strength and at temperatures below 230 K the ^1H (as previously reported[16] at 200 MHz) and ^{13}C spectra showed four inequivalent *o*-methyl, two inequivalent *p*-methyl and four inequivalent *m*-CH sites. In addition the ^{13}C spectrum showed four inequivalent *o*-ring, two inequivalent *p*-ring and two inequivalent *ipso*-ring resonances. This is fully consistent with inequivalence of the two mesityl groups attached to a particular phosphorus and also with restricted rotation about the $P–C_{ipso}$ bonds which effectively lower the effective C_{2v} symmetry of each mesityl group. General NMR assignments used ^{13}C-{^{31}P} decoupling and 2-D HSQC (heteronuclear single quantum correlation) and HMBC (heteronuclear multiple bond correlation) experiments, and detailed intra-ring assignments for which it was necessary to establish the H^2/Me^3 and H^6/Me^5 spatial relationships are based additionally on 2-D proton ROESY spectra obtained at 198 K when exchange phenomena are essentially absent. The proton and ^{13}C NMR parameters in CD_2Cl_2 at 198 K are summarised in Table 1 for which the labelling scheme used is shown in Fig. 1. It should be noted that most of these parameters vary with temperature.

Table 1 ^1H and ^{13}C NMR parameters of tetramesityldiphosphane in CD_2Cl_2 at 198 K

Site	$\delta(^1H)$[a]	$\delta(^{13}C)$[b]	$N(^{31}P–^{13}C)$[c]
X: 1	—	134.3	33.7
2	—	142.7	3.9
6	—	142.2	31.6
Me2	2.66 (2.71)	23.7	22.7
Me6	1.86 (1.89)	22.2	23.3
3[d]	6.75 (6.76)	130.3	0
5[d,e]	6.66 (6.73)	129.8	14.0
4	—	138.9	0
Me4	2.15 (2.17)	20.8	0
Y: 1	—	128.7	14.0
2	—	145.3	4.4
6	—	146.8	38.6
Me2	2.28 (2.29)	22.4	11.7
Me6	1.82 (1.81)	22.3	29.0
3[f]	6.61 (6.64)	130.1	0
5[f,g]	6.41 (6.42)	128.0	6.5
4	—	137.0	0
Me4	2.07 (2.10)	20.9	0

[a] In ppm ± 0.01 ppm; figures in parentheses refer to 223 K. [b] In ppm ± 0.1 ppm; variations of up to 1 ppm were found between 198 and 233 K. [c] In Hz ± 0.1 Hz, $N(^{31}P–^{13}C) = |^nJ(^{31}P–^{13}C) + ^{n+1}J(^{31}P–^{13}C)|$, variation < 0.6 Hz between 198 and 223 K. [d] $^4J(H^3–H^5) = 1.5$ Hz (see *h*). [e] $|^4J(^{31}P–H) + ^5J(^{31}P–H)| = 5.1$ Hz. [f] $^4J(H^3–H^5) = 1.8$ Hz (see *h*). [g] $|^4J(^{31}P–H) + ^5J(^{31}P–H)| = 5.1$ Hz. [h] Determined by selective homonuclear decoupling and band-shape analysis.

At higher temperatures the ^1H and ^{13}C NMR spectra displayed broadening phenomena characteristic of faster rotation about the bonds, although at a field strength of 11.8 T spectra showing full coalescence were not obtained up to 333 K. However, at lower field (2.1 T, corresponding to a contracted NMR timescale) the 22.5 MHz ^{13}C spectrum at this temperature shows all mesityl groups to be equivalent and there to be essentially free rotation about the $P–C_{ipso}$ bonds.

Fig. 2 shows the methyl region of the 2-D ^1H EXSY spectrum of compound **1** with a mixing time of 180 ms at 223 K and has off-diagonal peaks due to (a) Y2 $\longleftrightarrow$ Y6 exchange (*i.e.* rotation of ring Y), (b) X2 $\longleftrightarrow$ Y2, X6 $\longleftrightarrow$ Y6, and X4 $\longleftrightarrow$ Y4 exchange (*i.e.* interchange of ring environments), (c) X2 $\longleftrightarrow$ Y6 and X6 $\longleftrightarrow$ Y2 exchange (*i.e.* rotation of ring Y combined with ring interchange of ring environments), but none due X2 $\longleftrightarrow$ X6 exchange which requires rotation of ring X or alternatively two X $\longleftrightarrow$ Y interchanges with an intervening ring Y rotation. A view down the main diagonal of the aromatic part of the same spectrum is shown in Fig. 3 as a stacked plot to give a clearer picture of the intensities of the off-diagonal exchange peaks and also of the signal-to-noise ratio attained. This reveals the same pattern of exchange, *viz.* Y3 $\longleftrightarrow$ Y5 (strong), X3 $\longleftrightarrow$ Y3, X5 $\longleftrightarrow$ Y5, X3 $\longleftrightarrow$ Y5, X5 $\longleftrightarrow$ Y3 (all medium) and only a very weak signal for X3 $\longleftrightarrow$ X5. It is thus clear from the relative intensities of the off-diagonal peaks that the overall exchange process involves three separate rate constants which decrease in the order: ring Y rotation > interchange of ring environments with or without rotation of Y > ring X rotation.

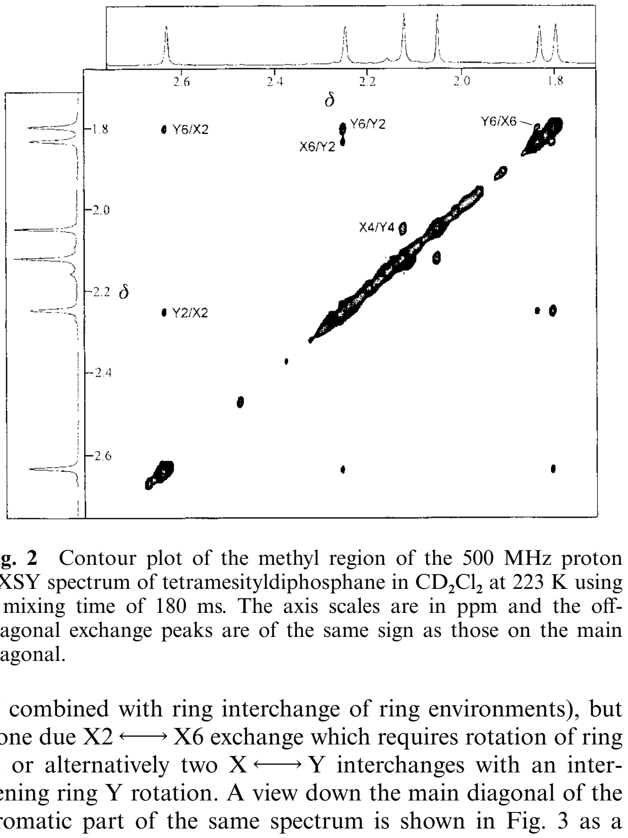


Fig. 2 Contour plot of the methyl region of the 500 MHz proton EXSY spectrum of tetramesityldiphosphane in CD_2Cl_2 at 223 K using a mixing time of 180 ms. The axis scales are in ppm and the off-diagonal exchange peaks are of the same sign as those on the main diagonal.

The rate of interchange of ring environments was readily derived by simulation of the ^1H *para*-methyl signals in DNMR

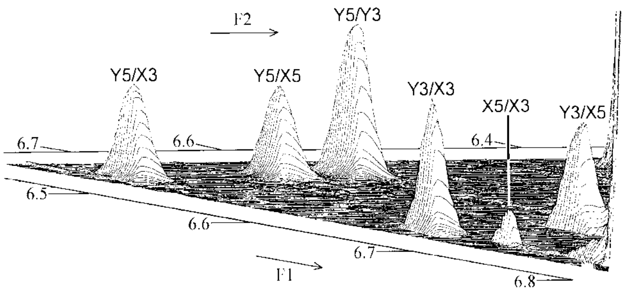


Fig. 3 Stack plot of part of the aromatic region of the 500 MHz proton EXSY spectrum of tetramesityldiphosphane in CD_2Cl_2 at 223 K using a mixing time of 180 ms. The axis scales are in ppm and the view is down the main diagonal.

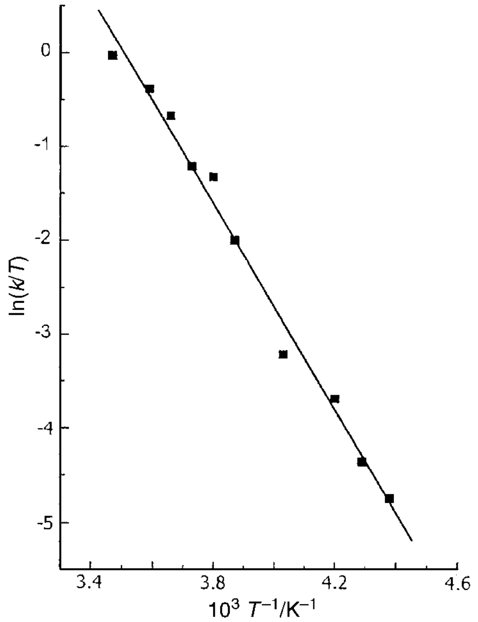


Fig. 4 Eyring plot of ln(k/T) against T^{-1} for the exchange of the *para*-methyl groups of tetramesityldiphosphane in CD_2Cl_2 over the temperature range 227–283 K.

1-D spectra over the temperature range 227–283 K, and the corresponding Eyring plot (Fig. 4) yields $\Delta H^\ddagger = 45.6 \pm 2$ kJ mol^{-1} and $\Delta S^\ddagger = -32 \pm 7$ J K^{-1} mol^{-1}, with $\Delta G^\ddagger = 51.9 \pm 3$ kJ mol^{-1} at 198 K. This was confirmed by simulation of the ^{13}C *p*-methyl and *para*- and *ipso*-ring signals although the precision was lower owing to the poorer signal-to-noise ratio. Attempts were made to simulate the DNMR spectra given at different temperatures by the *ortho*-methyl and *meta*-ring protons and the *ortho*-methyl and the *ortho*- and *ipso*-ring ^{13}C nuclei by using the now known rates of (b) and trial rates for (a) and (c). These were only partially successful owing to the significant chemical shift variations with temperature and the overall complexity of the exchange process, but it was clearly confirmed that rate (a) $\ll$ rate (c) as already demonstrated by the proton EXSY spectrum.

Discussion

The stereochemical rigidity of phosphorus(III) is maintained in diphosphanes, as is shown by the isolation of diastereomers of RR′PPRR′ that are stable at temperatures in excess of 373 K and thus the variable DNMR behaviour of compound **1** observed at temperatures up to 315 K cannot be attributed to inversion at phosphorus. Furthermore, it is clear that the low temperature proton and $H/^{13}C$ correlation spectra are too simple for hindered rotation of individual methyl groups to be the cause. It is convenient to consider the expected dynamic behaviour of the different types of rotamer on an individual basis.

(i) Antiperiplanar

It is important to appreciate that in this case the lowering of the symmetry from C_{2h} to the crystallographically determined C_2 is due to a propeller twist of the mesityl groups about their P–C_{ipso} bonds. Thus each phosphorus atom has one mesityl group (A) [no correspondence with X or Y in Table 1 is implied at this stage] with its plane approximately perpendicular to the P–P bond and one (B) parallel to it; in turn each mesityl group has one *exo* and one *endo ortho*-methyl group. Each phosphorus is therefore chiral, leading to the *RR* and *SS* enantiomers represented in Scheme 2 as idealised Newman projections down the P–P bond. [For convenience the mesityl group with its plane approximately parallel to the P–P bond is given lower priority than the other, although the argument does not depend upon this.] Interconversion of the enantiomers does not require complete rotation of the mesityl groups which would restore effective C_{2h} symmetry for the molecule. However, it can be achieved by *concerted* librational motions of all four mesityl groups. In this process the two types of ring interchange their environments, but individual methyl groups retain their identities as *exo* or *endo*.

It is to be expected from observations of "geared rotation"[31] that mesityl groups attached to the same phosphorus atom will be capable of concerted motion, but it is not immediately clear that there would also be a correlation with those on the other phosphorus in compound **1**. However, if this were not so, then the chemically distinct *SR* and *RS* diastereomers shown in Scheme 3 would also be present. These would have C_i symmetry and hence similar ^1H and ^{13}C spectral *patterns* to those of the *RR* and *SS* diastereomers, *but with different values of the parameters*. This would lead at low temperature to a doubling of the signals in the ^1H, ^{13}C, ^{31}P NMR spectra of **1** which is not in fact observed. It therefore appears that motions of mesityl groups on different phosphorus atoms would indeed need to be correlated. In the (static) crystal structure[16] there are non-bonded separations between *ortho*-methyl groups associated with different phosphorus atoms which are shorter than those between those associated with the same phosphorus.

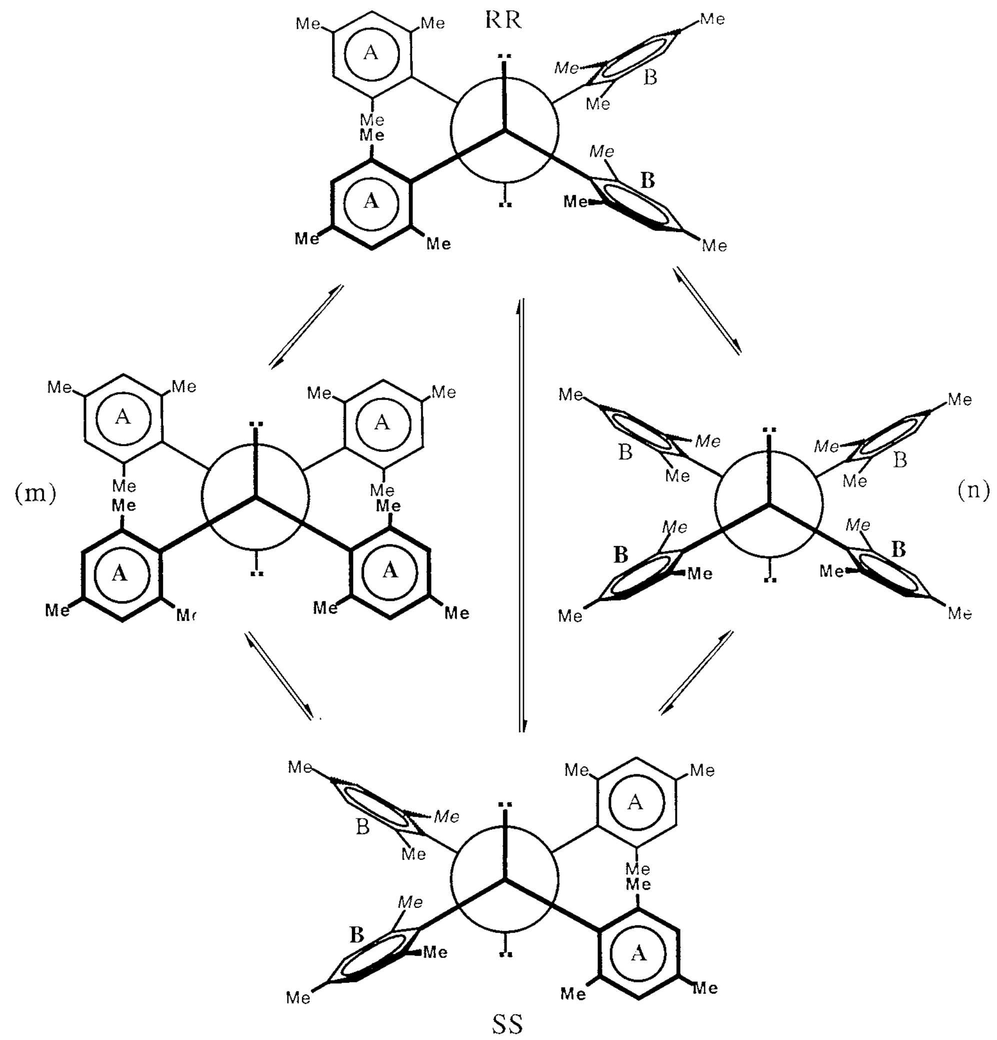
Experimentally, the process with the lowest barrier is rotation of *one type* of mesityl group, whereas rotation of the other has the highest barrier. The first of these will involve a transition state such as (m) or (n) in Scheme 2, but not both. Since each transition state has essentially C_{2h} symmetry relaxation to a new ground state can occur either by continued rotation of the same ring (leading to A2 ⟷ A6 and A3 ⟷ A5, or to B2 ⟷ B6 and B3 ⟷ B5 exchange) or by rotation of the other ring through *ca.* 90°. This latter will not interchange 2/6 and 3/5 positions but will interchange the environments of A and B rings. Thus interchange of the environments of the A and B rings would be associated with same energy barrier as the readiest ring rotation. Hence only two rate constants, rather than the experimentally observed three, should be found, implying that in solution the low temperature conformation cannot be antiperiplanar.

(ii) Synperiplanar

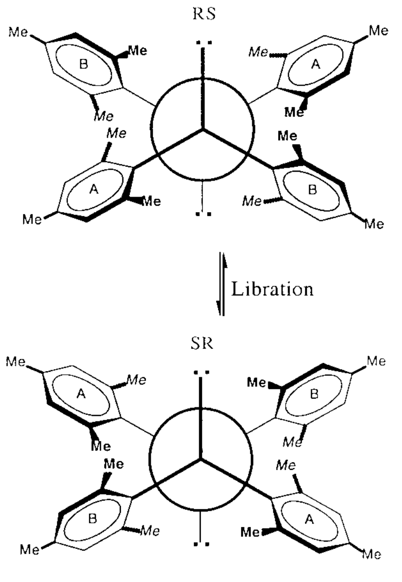
This conformation would also require a propeller twist of the mesityl groups to account for the observed low temperature spectra, and its dynamic behaviour should also be described by only two rate constants, so that it too can be rejected.

(iii) Synclinal

In this case two types of mesityl group occur irrespective of their degree of twist, although restricted rotation about the



Scheme 2 Newman projections down the P–P bond of *SS* and *RR* C_2-symmetric antiperiplanar rotamers of tetramesityldiphosphane with possible transition states, (m) and (n), for their interconversion.



Scheme 3 Newman projections down the P–P bond of antiperiplanar rotamers of tetramesityldiphosphane with C_i symmetry.

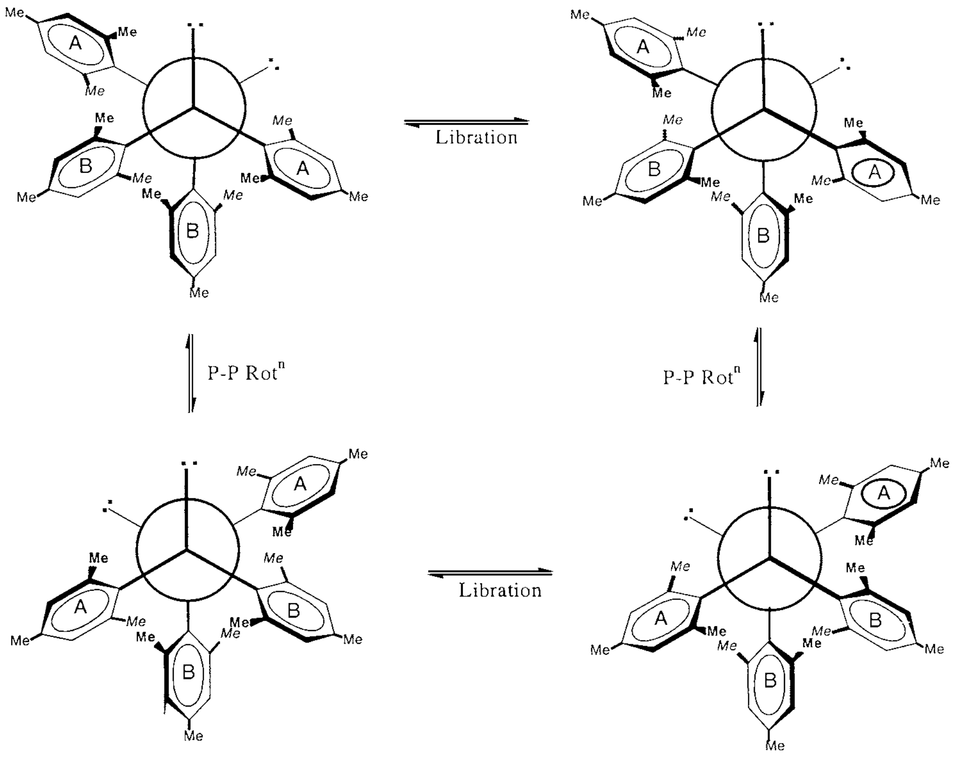
P–C_{ipso} bonds is necessary for the 2 and 6 and the 3 and 5 positions to be different, as illustrated in Scheme 4.

A propeller twist would again lead to *RR* and *SS* enantiomers which will be interchanged by a librational motion of the mesityl groups although this will lead to neither 2/6 and 3/5 exchange nor A/B mesityl group exchange. The static (low temperature) proton and ^{13}C NMR spectra are thus consistent with this conformation, and the absence of line doubling in these and the ^{31}P spectrum implies that diastereomers are not present, *i.e.* the librational motion is rapid, as seems reasonable. The dynamic behaviour of this conformation will involve three separate rate constants, associated with rotation of ring A, interchange of the environments of rings A and B, and rotation of ring B. This is in accord with observation, and it is reasonable to assume that A will be less hindered than B so that A can be equated with Y and B with X in Table 1.

(iv) Anticlinal

The foregoing considerations also apply to this conformer, although it might be expected to be more sterically hindered than the synclinal, and our observations do not permit us to distinguish between (iii) and (iv).

Our conclusion is that although the static proton, ^{13}C and ^{31}P solution NMR spectra of tetramesityldiphosphane are consistent with any of four limiting idealised conformations with respect to rotation about the P–P bond, this is not so when the dynamic spectra are considered. The antiperiplanar (*trans*) and synperiplanar (eclipsed) conformations can then be rejected, even though the first of these is found in the solid. It is not possible to distinguish between anticlinal (*gauche*) and synclinal (eclipsed *gauche*), and indeed it is likely that the average conformation is intermediate between these. Whereas the NMR spectra would require effective cessation of librational motion of the mesityl groups in the first two (excluded) conformers this is not so for the proposed one, and it may be noted that this



Scheme 4 Newman projections down the P–P bond of synclinal rotamers of tetramesityldiphosphane with C_2 symmetry.

phenomenon has not been reported in other systems. It further follows that the thermodynamic parameters for the interchange of rings X and Y given above actually do relate to the barrier to rotation about the P–P bond, although the situation would be more complicated if the solution conformer were *trans* or eclipsed.

The various ^{31}P–H and ^{31}P–^{13}C coupling constants are also consistent with this conclusion, in that nuclei on one side of a mesityl ring have generally much larger couplings to phosphorus than those on the other. However, since most will depend upon the interplay of several angular relationships it is difficult to draw firm conclusions. Nonetheless, we tentatively suggest from known relationships with lone-pair orientations[32] that positions 2 and 3 (with small couplings to ^{31}P) are *endo*, and that 5 and 6 (large couplings) are *exo*. Such reasoning could also apply to the antiperiplanar rotamer, but the large difference between the values of $N(^{31}\mathrm{P}–^{13}\mathrm{C}^1)$ for rings X (33.7 Hz) and Y (14.0 Hz) argues strongly against this. This parameter has contributions from $^1J(^{31}\mathrm{P}–^{13}\mathrm{C}^1)$ and $^2J(^{31}\mathrm{P}–^{13}\mathrm{C}^1)$ neither of which should be seriously affected by the extent of rotation about the P–C_{ipso} bonds, which is the origin of the difference between rings A and B in the antiperiplanar and synperiplanar rotamers. However, in the other two rotamers the dihedral angles C^1PP(lone pair) are *ca.* 60 and 180° for rings A and B respectively, and this should lead to large differences[32] in the corresponding values of $^2J(^{31}\mathrm{P}–^{13}\mathrm{C}^1)$ and hence of $N(^{31}\mathrm{P}–^{13}\mathrm{C}^1)$, even though $^1J(^{31}\mathrm{P}–^{13}\mathrm{C}^1)$ alone may be little affected.

That tetramesityldiphosphane is able to adopt an essentially *gauche* conformation in solution is not surprising in view of the same behaviour of tetra-*tert*-butyldiphosphane.[25] It is true that a freely rotating mesityl group has more effective bulk than a *tert*-butyl, *e.g.* the cone angles of $\mathrm{Bu}^t{}_3$P and (Mes)$_3$P are 195 and 220° respectively. However, as we have previously shown[32] in the case of (Mes)Bu^{t}PH and its derivatives, the steric requirements of a mesityl group may be greatly reduced if it can rotate to a favourable position, and models indicate that this is entirely feasible in the case of the *gauche* rotamer of compound **1**. This view is also supported by values of $\Delta G^‡$ for rotation about the P–P bond of diphosphanes. In $\mathrm{Bu}^t{}_2\mathrm{PPBu}^t{}_2$ this is estimated[24] to be 53 kJ mol^{-1} at 228 K which is the same as that for **1** at the same temperature, while for the presumably less hindered $\mathrm{Pr}^i{}_2\mathrm{PPPr}^i{}_2$ the corresponding figure[33] is 29.3 kJ mol^{-1} at 165 K which may be compared with a calculated 50.1 kJ mol^{-1} for **1** at this temperature.

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