Determination of the Conformation and Stereoisomerism of Diphosphines using (P,C) Spin–Spin Coupling Constants

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Summary Values of $|N_{PC}| = |{}^1J_{PC} + {}^2J_{PPC}|$ are presented for a number of tetra-alkyldiphosphines, and it is shown that this parameter is characteristic of the orientation of the alkyl group concerned relative to the phosphorus lone pairs; this fact leads to assignments of conformation and stereoisomeric configuration.

RECENTLY interest has been expressed in the conformation of diphosphines[1,2] in relation to stereoisomerism and to isomeric forms produced by hindered internal rotation about the P–P bond. For $Bu^t_2PPBu^t_2$ internal rotation becomes[1] slow on the ^{13}C n.m.r. timescale below *ca.* −25 °C, and the stable form has *gauche* lone pairs. The results of ^1H-$\{^{31}P\}$ double resonance experiments have been used[2] to discuss the conformation of $[MeBu^tP]_2$. We have now studied a number of tetra-alkyldiphosphines of general formula $[R^1R^2P]_2$ using ^{13}C-$\{^1H\}$ n.m.r. spectroscopy, and are able to make unequivocal assignments of conformations. If it is assumed that the predominant forms of these compounds have *gauche* lone pairs,[1,2] then the diastereoisomers, racemic (I) and meso (II), may exist as the rotamers (Ia), (Ib), (IIa) and (IIb) (together with equivalent forms). It has been shown[3] that for $R^1 = R^2 = Me$ the ^1H n.m.r. spectrum is invariant with temperature down to −65 °C. McFarlane and McFarlane[2] state this is also true for $R^1 = Me$, $R^2 = Bu^t$ and $Me_2PPBu_2{}^t$. We have also proved this to be true for the ^{13}C spectra of $Pr^i_2PPPr^i_2$ and $[MeBu^tP]_2$ (there is a small variation in N_{PC} in the latter case). Consequently we must expect the processes (Ia) ⇌ (Ib) and (IIa) ⇌ (IIb) to be rapid on the n.m.r. timescale at room

Table. Values of $|N_{PC}|$ /Hz for the α-carbon atoms of tetra-alkyldiphosphines

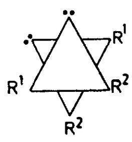
Group observed	Me				Et(α-C)		Pr^i(α-C)		Bu^t(α-C)	
R^1R^2	Me_2	MeEt	$MePr^i$	$MeBu^t$	Et_2	MeEt	Pr^i_2	$MePr^i$	Bu^t_2	$MeBu^t$
trans[a] to lone pair	—	15·6 (I)	25·5 (I)	33·7 (I)	—	—	—	—	45·5[b]	—
gauche[a] to lone pair	—	—	—	—	—	<2 (I)	—	<1·0 (I)	<1[b]	0·8 (I)
Average	8·6	9·3 (II)	9·7 (II)	—	8·5	6·5 (II)	12·0	9·3 (II)	24	—

[a] The assignment depends on the assumption that (Ib) is more stable than (Ia). [b] Data from low-temperature studies.[1]

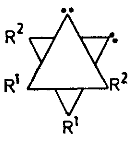
temperature. There is an important difference between the isomers (I) and (II), *i.e.* forms (IIa) and (IIb) are equivalent whereas forms (Ia) and (Ib) are not (unless $R^1 = R^2$). Therefore any property characteristic of *e.g.* R^1, which differs markedly depending on whether the group is *gauche* or *trans* to a lone pair, may be used to differentiate between stereoisomers (I) and (II) since in the latter case an average value will be observed, but in the former case an extreme value will be seen [unless (Ia) and (Ib) are accidentally very close in energy]. In principle (P,C) coupling constants are suitable parameters[4] and the low temperature data for $Bu_2^tPPBu_2^t$ show[1] that this is borne out in practice. The values of $|N_{PC}| = |{}^1J_{PC} + {}^2J_{PC}|$ for the quaternary carbons of the Bu^t groups *gauche* and *trans* to the lone pair are < 1 Hz and 45·5 Hz (no assignment was made in the earlier report[1]). The data for $[MePr^iP]_2$ and $[MeEtP]_2$ in the Table show that in each case one stereoisomer has $|N_{PC}|$ (for the α-carbon of the Pr^i and Et groups) < 2 Hz whereas the other has $|N_{PC}|$ 8—12 Hz. The latter value is in the same region as the data for $[Et_2P]_2$ and $[Pr^i_2P]_2$ and quite clearly corresponds to an *average* for alkyl groups *gauche* and *trans* to the lone pair. It follows that the low values of $|N_{PC}|$ are for stereoisomers (I) and the higher values for stereoisomers (II). There is a complementary variation of $|N_{PC}|$ for the methyl groups of $[MeR^2P]_2$, as expected.

It also follows that the only diastereoisomer known for $[MeBu^tP]_2$ is (I), as postulated by McFarlane and McFarlane.[2] These authors also reasonably suggested that the stable rotamer for this stereoisomer is (Ib) with $R^1 = Me$, $R^2 = Bu^t$. If that is true the data show that the low values for $|N_{PC}|$ are for groups *gauche* to the lone pair, and therefore that the large value (45·5 Hz) found for one pair of t-butyl groups in $[Bu_2^tP]_2$ at low temperature is for t-butyl *trans* to the lone pair. The spectral assignments and the relation of $|N_{PC}|$ to both stereoisomerism and internal rotation are therefore now fully known.

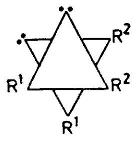
The data presented in the Table show the consistency of the pattern of (P,C) coupling constants. It is clear that the value of $|N_{PC}|$ for *trans* groups increases markedly with substituent bulk, as, of course, does the average value. Presumably this is due to bond-angle changes or, possibly, to some conformational variations.



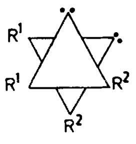
(Ia)



(Ib)



(IIa)



(IIb)

Intensity measurements show that in the solutions of $[MeEtP]_2$ we studied, the isomers (I) and (II) were present in the ratio *ca.* 7:6, for $[MePr^iP]_2$ the concentration ratio was *ca.* 2:1, and for $[MeBu^tP]_2$ we could not detect any of isomer (II). These facts emphasize the importance of *gauche* steric interactions between the larger alkyl groups, and strongly support the suggestion that (Ib) is preferred to (Ia). Our detailed conclusions regarding the assignment of the *gauche* and *trans* values of N_{PC} rely on this suggestion. Small amounts of conformations with *trans* lone pairs would not affect our discussion greatly. It is clear that measurements of $|N_{PC}|$ are of great value in establishing the conformations and isomerism of diphosphines. The values of $|N_{PC}|$ were measured directly from the spacing between the outer lines of deceptively simple triplets.

One of us (E.M.McV.) thanks the Northern Ireland Department of Education for the award of a research studentship. We thank N.A.T.O. for financial support which makes the co-operation between the Universities of East Anglia and Braunschweig possible.

(*Received*, 11*th August* 1975; *Com.* 926.)

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