Assignment of *Meso* and (±) Diastereoisomers of Diphosphines Using ^{31}P Nuclear Magnetic Resonance Spectroscopy in a Chiral Solvent

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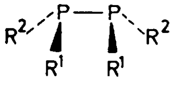
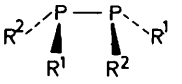
Summary The assignment of the n.m.r. peaks due to the (±) and *meso* forms of 1,2-diphenyldiphosphine has been made possible by recording their ^{31}P n.m.r. spectra in an optically active solvent at 40 and 111 MHz.

Diphosphines of the type $R^1R^2P-PR^1R^2$ may exist in two diastereoisomeric forms, *meso* (I) and (±) (II), which produce separate and distinct resonances in their ^{31}P and ^{1}H n.m.r. spectra.[1] Previous attempts to generate only one diastereoisomer have failed. Assignment of the n.m.r. signals due to each diastereoisomer was based[2] on the assumption that the predominant conformation of alkyl-substituted diphosphines corresponded to *gauche* lone pairs[3].



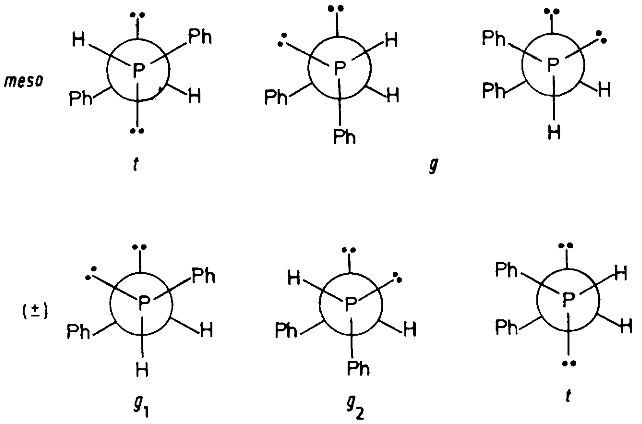
(I)



(II)

We report here the first unambiguous assignment of the signals due to the (±) and *meso* forms of 1,2-diphenyldiphosphine based on the $^{31}P\{^1H\}$ n.m.r. spectra recorded in an optically active solvent at 111 and 40 MHz.

In the *meso* form of the diphosphine $(R^1PR^2)_2$ the two phosphorus atoms have opposite absolute configurations and become diastereotopic in a chiral solvent. Thus the proton-decoupled ^{31}P spectra ($^{31}P\{^1H\}$) will show a four-line AB pattern. In a given [(+) or (−)] molecule, the two phosphorus atoms have the same absolute configuration and remain isochronous in a chiral medium. However, the (+) and (−) molecules which are otherwise enantiomeric have a diastereoisomeric relationship in this medium. Thus, the (±) mixture will exhibit two one-line A_2 patterns in their n.m.r. spectra.[†]



The $^{31}P\{^1H\}$ n.m.r. spectrum of 1,2-diphenyldiphosphine recorded in an achiral solvent (pyridine) or in a racemic mixture of (+) and (−) 1-phenylethylamine shows two peaks at 67·6 (a) and 71·2 p.p.m. (b), respectively. Recorded at 40·5 MHz in the chiral solvent (+)- or (−)-1-phenylethylamine, the high-field peak is split into a doublet ($\Delta\delta$ 0·8 Hz) while the low-field peak remains a singlet. Owing to the large value of ^1J(PP) in both isomers of 1,2-diphenyldiphosphine (191·5 and 190·8 Hz)[4] it is not possible to assign the observed splitting of the high-field line to an AB system or to two A_2 systems. However, by recording the spectra at two different frequencies, ν_1 and ν_2, the ratio $\Delta_1 : \Delta_2$ of the splittings must be equal to $\nu_1 : \nu_2$ in the

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[†] Use of a chiral solvent to distinguish *meso* from (±) diastereoisomers was first performed by Pirkle *et al.* (M. Kainosho, K. Ajisaka, W. H. Pirkle, and S. D. Beate, *J. Amer. Chem. Soc.*, 1972, **94**, 5924).

case of A_2 systems and to $(\nu_1:\nu_2)^2$ in the case of an AB system ($J >> \delta_{AB}$). The splitting of 0·8 Hz observed at 40·5 MHz becomes 2·2 Hz when observed at 111 MHz. Thus the splitting observed is proportional to the recording field strength and peak (b) (71·2 p.p.m.) corresponds to the (±) isomer while peak (a) (67·6 p.p.m.) corresponds to the *meso* isomer. The n.m.r. spectral parameters, J and δ, for the diastereoisomers of 1,2-diphenyldiphosphine are given in the Table.[4]

TABLE. N.m.r. coupling constants and phosphorus chemical shifts in the diastereoisomers of 1,2-diphenyldiphosphine.[a]

	$\delta(^{31}P)$	$^1J(PH)$	$^2J(PH)$	$^1J(PP)$	$^3J(HH)$
(a) *meso*	67·6	+206·0	+12·6	191·5	4·8
(b) (±)	71·2	+208·2	+10·0	190·8	11·7

[a] Coupling constants are given in Hz. The signs are given assuming that $^1J(PH)$ is positive.

The small difference observed for $^1J(PP)$ indicates that the two diastereoisomers probably have the same conformation[5] in which the phosphorus lone pairs adopt a *gauche* disposition[3]. The most striking difference between the n.m.r. parameters of the *meso* and (±) isomers is the $^3J(HH)$ coupling which has a higher value in the (±) isomers. This is interpreted as due to the presence of the conformation g_2 in the (±) form in which the H–P–P, P–P–H dihedral angle is close to 180°. Thus a ***trans*** disposition of the P–H bond gives rise to a higher value of the $^3J(HH)$ coupling than the ***gauche*** disposition, as observed for a $^3J(HH)$ coupling through an H–C–C–H fragment. This result, which previously only had been assumed, based on the fact that adjacent phosphorus lone pairs prefer a ***gauche*** orientation, is now sufficiently certain to be of use in further conformational studies.

In a recent report[6] the *meso* and (±) isomers of 1,2-bistrifluoromethyldiphosphine, $CF_3P(H)P(H)CF_3$, have been tentatively assigned on the basis of the observed $^1J(P\text{–}P)$ couplings. Assuming this assignment is correct, the $^3J(H,H)$ couplings in this diphosphine show the same trend as those obtained in our results.

The high-field experiments (111 MHz) were performed on the Fourier transform n.m.r. spectrometer of the Groupe de Biophysique, Ecole Polytechnique. We thank Professor M. Gueron for help with the measurements.

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