Nuclear Magnetic Resonance of Phosphorus Compounds: Dihedral Dependence of the $^2J_{P-C-H}$ Spin Coupling in Phosphines

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RECENT investigations on the ^2J-coupling constants in n.m.r. have revealed the influence of bond-orientation around one of the coupled atoms.[1] We have reported evidence concerning the influence of bond orientation around phosphorus on the J_{PH} coupling constants in three-co-ordinated phosphorus compounds.[2] An example of this is the 3,4-dimethyl-1-phenylphosphacyclopentene (I), where the two $^2J_{P-C-H}$ differ by 31 c./sec. and are of opposite signs.[3]

In order to investigate this influence in tervalent phosphorus compounds, we have analysed the n.m.r. spectra of some cyclic phosphines and one hindered rotation phosphine. To eliminate any influence of the nature of the substituents, the phosphorus atom is attached to one phenyl group throughout.

We have studied spin-coupling of one phosphorus atom with:

the *syn-* and *anti*-protons of the 3,4-dimethyl-1-phenyl-3-phosphacyclopentene (I) (*syn* and *anti* with respect to the phenyl group),

the axial and equatorial protons of the 3,3,5,5-tetradeuterio-1-phenyl-4-phosphorinanone (II), and

the two methylene protons of benzylphenylphosphine (III), which are nonequivalent, the phosphorus atom being an asymmetric centre, as previously observed in other compounds.[4]

Proton assignments and sign attributions are complete. Previous results have been used; in particular the proton assignment for (I) used the isomers attribution of T. J. Katz and his co-workers for 9-phenyl-9-phosphabicyclo[4,2,1]-nonatriene.[5] The signs were determined from the results of H. Goldwhite and his co-workers on the phosphiran.[6] The n.m.r. spectrum of (III) was recorded at low temperature to obtain only the more probable staggered conformation and the assignment of the protons was done with reference to the mean $^{2}J_{P-C-H}$ value (3·6 c./sec.) observed for the free-rotating methyl of methylphenylphosphine.[7] Hence, the signs of the two $^{2}J_{P-C-H}$ are related to the known, positive, $^{1}J_{P-H}$.

A complete discussion will be presented in a full paper.[8]

If α denotes the dihedral angle of the two planes defined by the P, C, and H atoms and by the C–P bond, together with the three-fold axis of the bonds around phosphorus (assuming a regular pyramidal arrangement, with a bond-angle value of 100° for all compounds), $^{2}J_{P-C-H}$ can be plotted against α (Figure 1). The range of α was reduced to 180° from 360° not by symmetry considerations but by examination of $^{2}J_{P-C-H}$ in variously substituted phosphines.

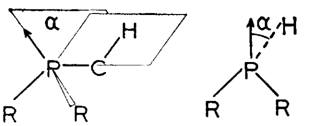

FIGURE 1. *Representation of the dihedral angle* α *in space and in Newman projection.*

The function $^{2}J_{P-C-H} = f(\alpha)$ has two maxima, at $\alpha = 0°$ ($^{2}J_{P-C-H} = +26$ c./sec.) and 180° ($^{2}J_{P-C-H} \simeq 0$ c./sec.) and a minimum at $\alpha = 110°$ ($^{2}J_{P-C-H} = -6$ c./sec.) (Figure 2).

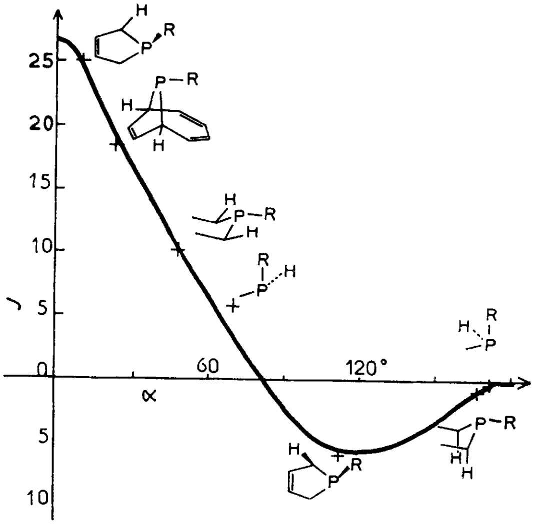

FIGURE 2. *Curve* $^{2}J_{P-C-H} = f(\alpha)$

This curve may be of use in the field of stereochemistry, for proton assignments and isomer attributions in three-co-ordinated phosphorus compounds.

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