# Spin–Spin Coupling in the $^{31}P$ Resonance of Phenylphosphines

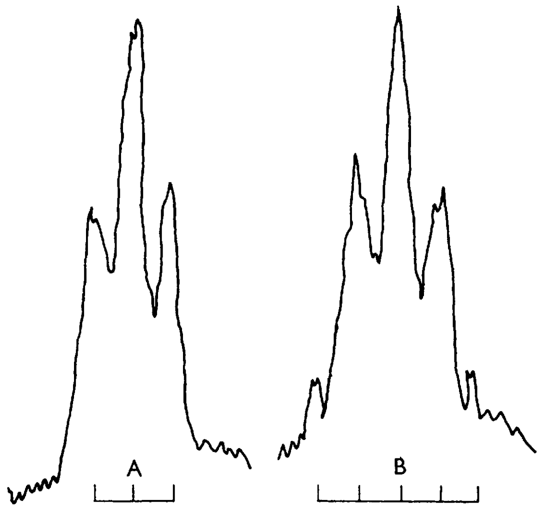
By J. W. AKITT, R. H. CRAGG, and N. N. GREENWOOD
(*Department of Inorganic Chemistry, University of Newcastle upon Tyne*)

COUPLING between phosphorus and the $\alpha$-hydrogen atoms of phenyl groups has been observed in the proton magnetic resonance of selected compounds,[1] but has not previously been observed in the $^{31}P$ spectrum.[2] We have examined the $^{31}P$ spectra of pure liquid phenyl- and diphenyl-phosphine in 9 mm. spinning tubes at 20 Mc./sec. and find that, in addition to the expected triplet and doublet due to direct P–$H_2$ and P–H coupling respectively, there is a second, smaller splitting in each of the multiplet peaks. Typical forms of each of the individual peaks are shown in the diagram: each component of the phenylphosphine triplet itself approximates at 1 : 2 : 1 triplet while each component of the diphenylphosphine double approximates at 1 : 4 : 6 : 4 : 1 quintet. These small splittings are therefore assigned to the coupling of phosphorus with the $\alpha$-protons of the phenyl group. The peaks are presumably broadened by small couplings with the other phenyl protons[1] since, qualitatively, the liquids seem sufficiently mobile to rule out viscosity broadening. The coupling constants are given in the Table. The directly bonded P–H coupling constants were measured using sidebands of a separate standard of 85% $H_3PO_4$ and the P–C–H coupling constants were then estimated by interpolation of several spectra. The chemical shifts, $\delta$, are upfield from 85% $H_3PO_4$.

TABLE

| Compound | $\delta$ (p.p.m.) | $J_{P\text{-}H}$ (c./sec.) | $J_{P\text{-}C\text{-}H}$ (c./sec.) | $J_{P\text{-}H}/J_{P\text{-}C\text{-}H}$ |
|---|---|---|---|---|
| $Ph_2PH$ .. .. .. | 43·8 ± 0·2 | 239 ± 4 | 7·9 ± 0·2 | 30·2 |
| $PhPH_2$ .. .. .. | 123·5 ± 0·4 | 201 ± 4 | 6·6 ± 0·1 | 30·4 |

It is of interest to note that for both molecules the ratio between the two coupling constants is




A One component of the $^{31}P$ triplet of $PhPH_2$
B One component of the $^{31}P$ doublet of $Ph_2PH$

the same. A full interpretation of this involves a more detailed analysis of the wave functions.[3] Such an analysis emphasizes the importance of distinguishing between hybridization and bond occupancy on the one hand and *s*-electron density at a nucleus on the other, since even when the hybridization remains unaltered, the *s*-electron density at the nucleus can vary if the radial functions alter.

The $^{31}P$ spectrum of liquid dichlorophenylphosphine was also obtained; it was a single triplet and the coupling between the phosphorus and the $\alpha$-hydrogen atoms in this case was $J = 9$ c./sec. The $^{31}P$ spectrum of a benzene solution of triphenylphosphine was also measured but no coupling was observed, presumably because the expected 1 : 6 : 15 : 20 : 15 : 6 : 1 septet was lost among the noise.

(*Received, December* 30*th*, 1965; *Com.* 809.)

[1] C. E. Griffin, *Tetrahedron*, 1964, **20**, 2399.
[2] K. Moedritzer, L. Maier, and L. C. D. Groenwegh, *J. Chem. Eng. Data*, 1962, **7**, 307.
[3] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.