Chemical Shift and Coupling Constant Nonequivalence of Isopropyl Methyl Protons in a Tertiary Phosphine

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THERE is currently much interest[1-3] in the magnetic nonequivalence of protons in methylene and isopropyl methyl groups in certain geometrical situations. This can arise when the group is attached to a centre which is asymmetric with respect to the group (although not necessarily with respect to the molecule as a whole) and is manifested as a chemical shift difference between protons which appear to be chemically equivalent. The effect has usually been observed when the asymmetric centre is a carbon atom, but has also been noticed when hetero-atoms are involved,[1] and we report here the first example in which tervalent phosphorus is the centre of asymmetry.

Figure Ia shows the ^{1}H n.m.r. spectrum (measured on a Varian A-60-A at 40°) of the methyl groups of di-isopropylphenylphosphine.[4] The splitting due to the α-proton is easily identified from the unequal intensities of the two components and shows $^3J(\mathrm{H}\cdots\mathrm{H}) = 6{\cdot}9$ c./sec. The remaining splittings may be assigned in two ways according to whether lines 1 and 3 or 1 and 4 (numbering from low- to high-field) are regarded as arising from the same proton. A spectrum measured at 56·4 Mc./sec. resolved this dilemma, and showed that $J(^{31}\mathrm{P}\cdots\mathrm{CH}_3^{\mathrm{A}}) = 14{\cdot}7$, $J(^{31}\mathrm{P}\cdots\mathrm{CH}_3^{\mathrm{B}}) = 11{\cdot}0$ c./sec., and δ (AB) = 0·17 p.p.m., with CH$_3^{\mathrm{A}}$ at lower field. The chemical shift difference is of the same order as those observed in isopropyl groups attached to asymmetric carbon atoms, but significant differences in coupling constants have previously been unknown in compounds of tervalent phosphorus.

Projection formulae (viewed along a C–P axis, with P at the rear) for the three staggered conformations of Pr$^i_2$PhP are shown in Figure 2. It is well established[5] that in such situations CH$_3$ and CH$_3'$ may be magnetically nonequivalent even if the energy barrier to rotation about the P–C bond is low. The failure of any of the lines in the spectrum of our compound to coalesce at temperatures up to 150° (Figure 1b) indicates that this is so in the present case. The observed nonequivalence thus arises from a combination of unequally populated conformations and inherent

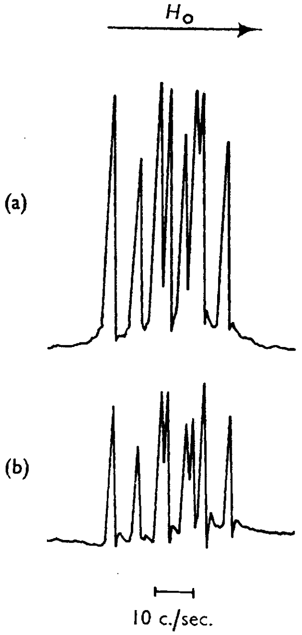

FIGURE 1. ^{1}H *n.m.r. spectrum of methyl groups in* Pr$^i_2$PhP *at* 60 *Mc./sec.*: (a) 40°; (b) 150°

asymmetry. The coupling constants and chemical shift difference change little between 40° and 150°, indicating that in fact the different conformations must be about equally populated, so the inherent asymmetry of the molecule must be the main cause of the observed nonequivalence.

It has been observed in conformationally rigid systems that coupling constants between protons and a phosphorus atom depend upon the orientation of the phosphorus lone-pair,[6] and it is now clear that the orientation of groups associated with the protons is also important, even in mobile systems.

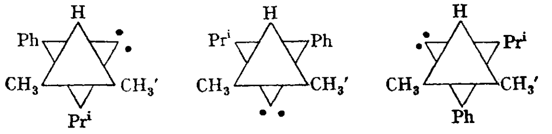

FIGURE 2. *Rotational conformations of* Pr^i_2PhP; P *is at the rear.*

It is not possible to say whether CH_3 or CH_3' of Figure 2 corresponds to CH_3^A, but it is clear that inversion of the phosphorus atom is slow on an n.m.r. time scale (*i.e.*, $\tau > 0{\cdot}1$ sec.), even at 150°. This is to be expected from the successful resolution of tertiary phosphines $R^1R^2R^3P$. This nonequivalence is not displayed by Pr^i_3P or Pr^iPh_2P, neither of which has the requisite lack of symmetry.

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