

**Nuclear Magnetic Resonance of Phosphorus Compounds.
Phospholenes: Opposite Signs of Two ${}^2J_{\text{P-H}}$ Coupling Constants in the
Same P-CH₂ Fragment¹**

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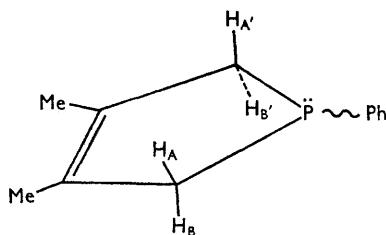
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ALL values reported in the literature on the ${}^2J_{\text{P-C-H}}$ coupling constants in three-co-ordinate phosphorus compounds are very small.² We report here an example where large values of opposite signs ($\pm 25 \mp 6$ c./sec.) are obtained in a cyclic three-co-ordinated phosphorus compound. This result may be interpreted as an influence of the lone-pair orientation of the phosphorus atom. Such an influence has been suggested in other

organophosphorus compounds for a ${}^4J_{\text{P-O-C-C-H}}$ ¹ for a ${}^3J_{\text{P-O-C-H}}$ ¹ and for other heterocyclic molecules.⁴

We have synthesized in the usual way the 3,4-dimethyl-1-phenylphosphacyclopentene,⁵ which was identified by its i.r. and n.m.r. spectra. The 100 Mc./sec. n.m.r. spectrum in deuteriochloroform consists of a complex multiplet (five phenyl protons) at τ 2.7, four broad unequal peaks

between τ 6.8 and 7.8 (four methylene protons) and the protons of the methyls at τ 8.3. An unambiguous analysis of the methylene part of the spectrum has been performed using the spin-decoupling technique and the recording of the spectrum at two different frequencies (100 and 66 Mc./sec.). The spectrum is an AA'BB'X spectrum;⁶ "A" refers to the low-field proton, and "B" to the high-field proton: $J_{AX} \pm 25$; $J_{BX} \mp 6$; $J_{AB} + J_{A'B'} 15.5$ c./sec.



$${}^2J_{PH_A} \pm 25 \text{ c./sec.}$$

$${}^2J_{PH_B} \mp 6 \text{ c./sec.}$$

This analysis gives some new and interesting results.

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The long-range coupling constants between the methylene protons being small, the geminal coupling constant is approximately $|J_{AB}|_{\text{gem}} 15.5$ c./sec. It is the first value reported of a J_{gem} where a methylene group proton is in the α -position of a three-co-ordinate phosphorus atom.

In the same P-CH₂ fragment, two different coupling constants ${}^2J_{PH}$ exist, and they are of opposite sign. Their large values are very different from the small values obtained in acyclic phosphines^{2a} or diphosphines.^{2b} The low coupling constants obtained in the latter compounds can be interpreted as average over positive and negative values caused by free rotation about the C-P bond.

With respect to the phosphorus, the two protons of the methylene differ mainly in the relative orientation of the lone pair, whose influence is clearly shown in the phospholene studied here.

Preliminary studies show that these results will be useful in the theoretical understanding of the geminal coupling constants⁷ and in the determination of preferred conformations in three-co-ordinate phosphorus compounds in free rotation about the P-C bond.