Relative Signs of the $^{31}\text{P}-^{1}\text{H}$ and $^{31}\text{P}-^{13}\text{C}-^{1}\text{H}$
Nuclear Magnetic Resonance Coupling Constants

By George M. Whitesides, Jesse L. Beauchamp, and John D. Roberts
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Sir:

The possibility that terms other than Fermi contact interaction make significant contributions to nuclear spin-spin coupling with heavy nuclei has stimulated considerable interest in the n.m.r. spectra of compounds containing heteroatoms. In particular, relative signs and magnitudes of $J_{XCH}$ and $J_{XCCCH}$ have been reported for ethyl derivatives of several heavy isotopes of spin $^1/2$. In order to understand better the factors responsible for spin coupling with a representative heavy nucleus, we have analyzed the spectra of $(\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_2\text{PH}$, and $(\text{CH}_3)_2\text{PH}$ and have obtained relative signs and magnitudes of $J_{\text{PH}}$ and $J_{\text{PCH}}$.

The proton spectrum of methylphosphine (Fig. 1) may be treated as the superposition of an $\alpha\beta\gamma$ and an $\alpha\alpha\alpha$ spectrum, using the method of effective chemical shifts. Inspection of the spectrum suggests that the methyl region can be separated into a triplet at lower field and a more complicated group of lines at higher field. Association of the triplet with the simpler half of the $\text{P}$-$\text{H}$ spectrum, also occurring as the lower field part, immediately suggests that $J_{\text{PH}}$ and $J_{\text{PCH}}$ have the same sign. The spectrum observed for $\text{CH}_3\text{PH}_2$ and the spectrum calculated using the parameters in the table are shown in Fig. 1. In both methyl- and dimethylphosphine $J_{\text{PH}}$ and $J_{\text{PCH}}$ have the same sign; double-resonance experiments performed by Drs. G. Juvinall and S. L. Manatt of the Jet Propulsion Laboratory confirm this conclusion.

TABLE I

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J_{\text{PH}}$</th>
<th>$J_{\text{PCH}}$</th>
<th>$J_{XCH}$</th>
<th>$J_{XCCCH}$</th>
<th>$\delta_{\text{PH}}$</th>
<th>$\delta_{\text{PCH}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PH}_3$</td>
<td>182.2</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{PH}_2$</td>
<td>$\pm 180.6$</td>
<td>$\pm 4.1$</td>
<td>8.2</td>
<td>157.7</td>
<td>58.5</td>
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<tr>
<td>$(\text{CH}_3)_2\text{PH}$</td>
<td>$\pm 191.6$</td>
<td>$\pm 3.6$</td>
<td>6.7</td>
<td>187.7</td>
<td>63.8</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{P}$</td>
<td>2.7</td>
<td></td>
<td></td>
<td></td>
<td>50.3</td>
<td></td>
</tr>
</tbody>
</table>

* Chemical shifts and coupling constants were moderately temperature dependent; the values reported are for $33^\circ$. Chemical shifts are given in c.p.s. at 60 Mc.p.s. from tetramethylsilane as internal standard.

Anet has recently demonstrated by double-resonance experiments that $J_{\text{CH}}$ and $J_{\text{HCH}}$ have opposite sign in $\text{H}_{2}^1\text{H}^3\text{COH}$; Lynden-Bell and Sheppard have reached the same conclusion for $J_{\text{CCCH}}$ and $J_{\text{HCCCH}}$ in $\text{H}_{3}^1\text{C}^3\text{CH}_2$ by analysis of the high-resolution spectrum. In contrast, $J_{\text{CH}}$ and $J_{\text{PCH}}$ have the same sign. Theoretical treatments have indicated that contact interaction will dominate the coupling of directly bonded atoms; more approximate treatments of $\text{HCH}$ and $\text{HCCCH}$ lead to the same conclusion.

The observed difference in relative sign of $J_{\text{XCH}}$ and $J_{\text{XCCCH}}$ for $X = ^1\text{H}$, $^1\text{C}$ and for $X = ^{31}\text{P}$ suggests that some mechanism other than the usual $\sigma$-bond interactions contribute to spin-spin coupling with phosphorus. Spin-orbital and electron-dipole interaction would be expected to be relatively more important in

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coupling to $^{31}\text{P}$ than to $^1\text{H}$ or $^{13}\text{C}$ due both to the greater anisotropy of the screening around phosphorus and to the relatively small degree of s-character of its bonding orbitals. However, Klose has been able to justify the spectrum of $(\text{CH}_2\text{CH}_2)_3\text{P}$ semiquantitatively by a valence-bond treatment using only contact interactions. Alternately, the d orbitals and nonbonding electrons of phosphorus may be involved in coupling through structures of the "ylene" type (I). Spin-orbital or magnetic-dipole interactions might give $J_{\text{PH}}$ the observed sign; important contributions from I certainly would. It is not possible to decide which factor is most important on the basis of available experimental evidence.

It is unfortunately not possible to assign an absolute sign to $J_{\text{PH}}$, although such an assignment would be of considerable interest. Recent calculations for several paramagnetic transition metal ions indicate that the contributions of a spin-polarized 3s orbital to the contact term may be opposite in sign to that of a 1s or 2s orbital; this result suggests that $J_{\text{PH}}$ may be either positive or negative, depending upon the relative contributions of the 1s, 2s, and 3s electrons to the coupling.

Acknowledgment.—We are deeply indebted to Dr. F. C. Caserio, Jr., for the phosphine samples used in this research.

(9) The bond angles in methylphosphine suggest that the phosphorus bonding orbitals in this compound have predominantly p-character: $Z\text{CPH} = 97^\circ30'$, $Z\text{PH} = 93^\circ23'$; see E. L. Breig and C. C. Liu, J. Chem. Phys., 35, 2139 (1961).
(10) This structure is analogous to the hyperconjugative structures used to explain long range coupling in hydrocarbons. Although unimportant in determining the total energy of the molecule, such structures may be very important in spin-spin coupling. See R. A. Hoffman and S. Gronowitz, Arkiv. Kemi., 16, 471 (1960).