Nuclear Magnetic Resonance Studies on Fluorides of Trivalent Phosphorus

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The P\(^{31}\), F\(^{19}\), and H\(^{1}\) nuclear magnetic resonance spectra of a new series of compounds of the types (RO)\(_n\)PF\(_3\)\(_n\) and (R\(_2\)N)\(_m\)PF\(_3\)\(_m\) (n = 1, 2) have been studied. A regular change in the chemical shifts and coupling constants has been observed with multiple substitution. The changes in the coupling constants have been explained on the basis of the electronegativity of the atoms attached to phosphorus. Some long-range coupling constants between hydrogen and fluorine separated by five bonds were observed.

P\(^{31}\) Nuclear magnetic resonance spectroscopy has become an important tool in the characterization of phosphorus compounds ever since the observation of Dickinson 1, according to which the P\(^{31}\) chemical shifts in compounds containing tri-or pentavalent phosphorus, respectively, are vastly different. Van Wazer and co-workers 2 attempted to formulate substituent rules and compared predicted and observed P\(^{31}\) chemical shifts in various types of compounds. Other workers 3, 4, however, have questioned the existence of “group shifts”, and concluded that there were no convenient correlations between the P\(^{31}\) chemical shift and the nature of the substituents on the phosphorus atom. Gutowsky and McCall 5 suggested that both the electronegativity of the substituent and its ability to engage in multiple bonding determine the magnitude of the phosphorus chemical shift.

As against the wealth of data available on numerous types of phosphorus compounds not containing phosphorus-halogen bonds, there is a notable absence of data especially on fluorides of trivalent phosphorus. We have synthesized the compound as described below.

The syntheses for all the compounds included in this study, except for [(CH\(_3\)\(_2\)N)\(_2\)]PF\(_2\), have been reported 8. Bis(dimethylamino)fluorophosphine has first been prepared by Fleming and Parr 9 by the dimethylamino-lysis of PF\(_3\). We have synthesized the compound as described below.

With exclusion of air and moisture, 46.4 g. (0.3 mole) of bis(dimethylamino)chlorophosphine 10 was added dropwise with stirring to a suspension of 25.2 g. (0.6 mole) of sodium fluoride in 120 ml. of tetramethylene sulfone over a period of 30 minutes, no change in temperature being observed. Then the temperature was increased to 80\(^\circ\) and the mixture was stirred for one hour. Finally, the mixture was heated to 120\(^\circ\) and was refluxed for another hour. Vacuum-distillation through a 10-inch glass-helix packed column gave 27.4 g. (66\%) of the fluoride, boiling point 52 to 65\(^\circ\).

1 W. C. Dickinson, Physic. Rev. 81, 717 [1951].
3 N. Muller, P. C. Lauterbach, and J. Goldenson, J. Amer. chem. Soc. 78, 5857 [1956].
55°/50 mm. The product was redistilled at atmospheric pressure b.p. 125° and was recovered unchanged. The boiling point in vacuo was 50 — 51°/50 mm; $n_2\text{D} = 1.4321$.

Anal. Calcd. for $C_4H_{12}FN_2P$ : C, 34.8; H, 8.8; F, 13.7; N, 20.3; P, 22.4. Found: C, 34.6; H, 8.8; F, 13.5; N, 20.0; P, 22.3.

All the $H^1$ spectra were obtained on a Varian A-60 analytical spectrometer, and the $F^{19}$ and $P^{31}$ spectra were obtained on a Varian HR-60 spectrometer equipped with a flux stabilizer. $F^{19}$ Spectra were recorded at 56.4 mc/sec. and $P^{31}$ spectra at 24.3 mc/sec. In the case of $F^{19}$, CFCI3 was used as internal reference, while a capillary tube containing 85% orthophosphoric acid was inserted to serve as external reference for $P^{31}$ spectra. For proton resonance, a tetramethylsilane internal reference was used as usual. Calibrations for fluorine and phosphorus were carried out by usual side-band technique whenever the spectra showed fine splittings; in other cases superposition technique was used. The chemical shifts are expressed in parts per million from the appropriate reference and the coupling constants are expressed directly in cycles per second. The estimated uncertainties in the coupling constants and chemical shifts are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimated Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_H$</td>
<td>± 0.03 p.p.m.</td>
</tr>
<tr>
<td>$\delta_F$</td>
<td>± 0.2 p.p.m.</td>
</tr>
<tr>
<td>$\delta_P$</td>
<td>± 0.5 p.p.m.</td>
</tr>
<tr>
<td>$J_{HP}$</td>
<td>± 0.5 c.p.s.</td>
</tr>
<tr>
<td>$J_{HF}$</td>
<td>± 0.5 c.p.s.</td>
</tr>
<tr>
<td>$J_{PF}$</td>
<td>± 5.0 c.p.s.</td>
</tr>
</tbody>
</table>

Results and Discussion

With the exception of $(CH_3CH_2O)_3P$ and $[(CH_3)_2N]_3P$, all the compounds reported in this study are new and were prepared in these Laboratories. Figures 1—4 show the $H^1$, $F^{19}$, and $P^{31}$ spectra of $CH_3CH_2CH_2OPF_2$,

$$\begin{array}{c}
\text{P} \\
\text{F} \\
\text{O} \\
\text{O} \\
\end{array}
$$

$(CH_3)_2NPF_2$, and $[(CH_3)_2N]_2PF$, respectively, as representative spectra for this series of compounds.

* Note added in proof: The value for the $H^1$ chemical shift of the b-hydrogen in $CH_3CH_2CH_2OPF_2$ (Fig. 1) should be $-102.0$ l.p.s., instead of $-120.0$ c.p.s.
All the compounds with oxygen attached to phosphorus gave sharp and well resolved spectra, while the compounds with nitrogen bonded to phosphorus gave rather broad peaks because of quadrupole broadening. All the compounds containing \( \text{PF}_2 \) groups show a basic triplet structure in the \( P^{31} \) resonance and a doublet in the \( F^{19} \) resonance, with further fine structure due to coupling with \( H^1 \). For the compounds containing \( >PF \) groups, both phosphorus and fluorine resonance showed doublet structures with fine splittings due to coupling with protons. In the proton region, the spectra are typical of the system, with additional coupling with fluorine and phosphorus atoms. The phosphorus and fluorine spectra are all first order type, and the coupling constants and chemical shifts were readily obtained by the spacings and centers, respectively. In the proton spectra there were some cases where the patterns were not first order and were fairly complicated; these would therefore require complete spectral analysis in order to obtain accurate chemical shifts and \( H - H \) coupling constants. However, since these values are not of utmost importance here, no attempt has been made to do so and the proton chemical shift values reported are only approximate.

All the chemical shifts and coupling constants in this series of compounds, including some from already published data, are given in Table I. The \( P^{31} \) chemical shifts in the group \( R\text{OPF}_2 \), where \( R \) is an alkyl group, are all constant within the experimental uncertainty of 0.5 p.p.m. This is not unexpected because, as long as the first carbon is saturated, the other part of the alkyl group will not influence the electronic structure of phosphorus and hence does not shift its resonance frequency. The \( F^{19} \) chemical shift in this group is also constant within 1 p.p.m., presumably for the same reason. \( P^{31} \) and \( F^{19} \) chemical shifts in

\[
\begin{align*}
\begin{array}{c}
\text{OPF}_2 \\
\text{PF}
\end{array}
\end{align*}
\]

are again the same, but \( \delta_P \) is about 2 p.p.m. higher and \( \delta_F \) about 4 p.p.m. lower than for the correspond-
NUCLEAR MAGNETIC RESONANCE STUDIES ON FLUORIDES

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_P^1$</th>
<th>$\delta_P^2$</th>
<th>$\delta_H^3$</th>
<th>$J_{PH}$</th>
<th>$J_{PF}^4$</th>
<th>$J_{HF}^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH$_3$CH$_2$CH$_2$OPF$_2$</td>
<td>-111.5</td>
<td>+49.1</td>
<td>-4.05 (a)</td>
<td>1288</td>
<td>6.8</td>
<td>0.5</td>
</tr>
<tr>
<td>2. CH$_3$CH$_2$CH$_2$OPF$_2$</td>
<td>-111.9</td>
<td>+49.2</td>
<td>-4.07 (a)</td>
<td>1288</td>
<td>6.8</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>3. CH$_3$CH$_2$CH$_2$OPF$_2$</td>
<td>-111.9</td>
<td>+48.7</td>
<td>-4.55 (a)</td>
<td>1290</td>
<td>6.4</td>
<td>0.5 ($J_{HF}$)</td>
</tr>
<tr>
<td>4. F$_2$POCH$_2$OPF$_2$</td>
<td>-112.0</td>
<td>+48.9</td>
<td>-4.30</td>
<td>1301</td>
<td>6.5</td>
<td>2.0</td>
</tr>
<tr>
<td>5. F$_2$POOPF$_2$</td>
<td>-110.1</td>
<td>+44.5</td>
<td>-7.126</td>
<td>1326</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>6. F$_2$PCH$_2$CH$_2$OPF$_2$</td>
<td>-109.8</td>
<td>+44.9</td>
<td>-7.00</td>
<td>1328</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>7.</td>
<td>-124.4</td>
<td>+40.9</td>
<td></td>
<td></td>
<td>1226</td>
<td>2.0</td>
</tr>
<tr>
<td>8.</td>
<td>-123.1</td>
<td>+37.0</td>
<td>-7.0 (a)</td>
<td>1307</td>
<td>-6.8 (b)</td>
<td>1.63 (c)</td>
</tr>
<tr>
<td>9. (CH$_3$CH$_2$O)$_2$P</td>
<td>-139.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. (CH$_3$)$_2$NPF$_2$</td>
<td>-143.0</td>
<td>+65.3</td>
<td>-2.71</td>
<td>1197</td>
<td>9.3</td>
<td>3.7</td>
</tr>
<tr>
<td>11. (CH$_3$)$_2$NPF$_2$</td>
<td>-144.0</td>
<td>+64.8</td>
<td>-3.17 (a)</td>
<td>1194</td>
<td>9.0</td>
<td>3.0</td>
</tr>
<tr>
<td>12. (CH$_3$)$_2$NPF$_2$</td>
<td>-139.1</td>
<td>+65.2</td>
<td>-3.15 (a)</td>
<td>1193</td>
<td>8.8</td>
<td>3.0</td>
</tr>
<tr>
<td>13. [(CH$_3$)$_2$N]PF$_2$</td>
<td>-151.0</td>
<td>+100.6</td>
<td>-2.5</td>
<td>1046</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>14. PF$_3$ (l. c. 5.17)</td>
<td>-97.0</td>
<td>+34.0</td>
<td></td>
<td>1400</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>15. [(CH$_3$)$_2$N]$_2$P (l. c. 2)</td>
<td>-122.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table I. Chemical shifts and coupling constants in the systems ROPF$_2$, (RO)$_2$PF, R$_2$NPF$_2$ and (R$_2$N)$_2$PF. - 1 In parts per million from 85% H$_3$PO$_4$ external reference. 2 In parts per million from CFC$_3$ internal reference. 3 In parts per million from Si(CH$_3$)$_4$ internal reference. 4 Coupling constant between the phosphorus and the hydrogens on the carbon attached to the phosphorus. 5 Coupling between fluorine and the nearest hydrogen. 6 The H$_1$ spectrum was a closely spaced multiplet. No analysis was carried out.

However, this constant effect due to the change of a substituent is not followed in the case of fluorine chemical shifts. For example, fluorine chemical shifts are $+34$ p.p.m. in PF$_3$, $+49$ p.p.m. in ROPF$_2$, and $+41$ p.p.m. in showing no regularity.

In the compounds where the substituent is - NR$_2$, the P$^{31}$ chemical shifts are considerably lower than in the corresponding - OR compounds, but reasonably constant for different R groups. The difference

\[ \text{[Resonance effect noticed as having appreciable influence on the P - F coupling constants also, and is discussed later.]} \]

12 J. Ito, J. Amer. chem. Soc. 80, 3502 [1958].
in the chemical shifts between mono- and disubstituted compounds is about 20 p.p.m., which is larger than in the case of — OR groups. However, the constancy of the substituent effects observed in phosphites does not hold in this series. This might be because multiple substitution by nitrogen atoms involves the d-orbitals of phosphorus to form partial double bonds. On the other hand, the fluorine chemical shifts change regularly on multiple substitution with — NR₂ groups. Thus, the change in fluorine chemical shift for each NR₂ is +31 p.p.m., Gutowsky and Hoffmann ¹⁴ have noticed that the shielding of the fluorine nucleus increases with decreasing electronegativity of the attached atom. In the series XPF₂ it is logical to expect that the electronegativity of phosphorus increases with increasing electronegativity of the X group. Thus, in the series FPF₂, ROPF₂ and R₂NPF₂, one would expect δF to increase from FPF₂ to R₂NPF₂ with ROPF₂ having an intermediate value. The same is expected to hold in the series FPF₂, R₂NPF₂ and (R₂N)₂PF. It is evident from Tables I and II that this is the case and in fact, δF is inversely proportional to the electronegativities of F, O, and N which are expected to determine the electronegativity of phosphorus. The proportionality constant is about 32 p.p.m. per unit change in the electronegativity. This did not hold in the case of FPF₂, ROPF₂ and

\[
\begin{align*}
\text{O} & \quad \text{PF} \\
\text{O} & \quad \text{PF}
\end{align*}
\]

in the latter case probably because the bond angles are different. The chemical shift of phosphorus is —112 p.p.m. in —CH₂OPF₂ and —143 p.p.m. in (CH₃)₂NPF₂. This difference of —32 p.p.m. in going from O to N is much larger than —10 p.p.m., suggested earlier by van Wazer and co-workers ² for other compounds of trivalent phosphorus.

It has been shown by Packer ¹⁵ that in the series (CF₃)₂PX the phosphorus chemical shift decreases with increasing electronegativity of X. In contrast to Packer’s observations, in the present series it is found that the phosphorus chemical shift increases with increasing electronegativity (see Table II).

The P–F coupling constants in the ROPF₂ series where R is aliphatic are constant within 2 c.p.s. as expected. The P–F coupling constant in C₆H₅OPF₂ is about 40 c.p.s. larger than in the corresponding aliphatic compounds. It has been shown ¹⁵ that in the XP(CF₃)₂ series, the more electron withdrawing the group X is, the stronger is the P–F coupling. Also, in the series PF₃, PF₂Cl and PFCl₂, Jₚ–F decreases in the same order ¹⁶. Hence, it is obvious, from the fact that Jₚ–F is larger in C₆H₅OPF₂ than in ROPF₂, that the oxygen atom attached to an aromatic ring is more electronegative than one attached to an aliphatic group since the oxygen releases the lone pair of electrons into the aromatic ring, thereby becoming more electronegative. Jₚ–F in

\[
\begin{align*}
\text{O} & \quad \text{PF} \\
\text{O}' & \quad \text{PF}
\end{align*}
\]

is appreciably smaller than in ROPF₂, suggesting that replacing fluorine by a less electronegative oxygen atom will reduce the coupling constant, in agreement with earlier observations ¹⁶. The same trend is noticed in C₆H₅OPF₂ and

\[
\begin{align*}
\text{O} & \quad \text{PF} \\
\text{O} & \quad \text{PF}
\end{align*}
\]

except that the magnitude of the change is smaller. In the case of R₂NPF₂, Jₚ–F is smaller than in ROPF₂, which again agrees with the above concept because nitrogen is less electronegative than oxygen.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δP (p.p.m from H₃PO₄)</th>
<th>δF (p.p.m from CFCl₃)</th>
<th>Jₚ–F (c.p.s.)</th>
<th>Electronegativity of the atom attached to phosphorus²</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₃P–F</td>
<td>— 97</td>
<td>+34</td>
<td>1400</td>
<td>4.0</td>
</tr>
<tr>
<td>F₃P–OCH₂CH₂CH₂</td>
<td>— 112</td>
<td>+49</td>
<td>1288</td>
<td>3.5</td>
</tr>
<tr>
<td>F₂P–N(CH₃)₂</td>
<td>— 143</td>
<td>+65</td>
<td>1197</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table II. Chemical shifts, coupling constants and the electronegativities of the substituent atoms in some trivalent phosphorus compounds. ² From l.c.¹⁸.

In the series FPF\(_2\), RO – PF\(_2\) and
\[
\begin{array}{c}
O \\
PF, \\
O \\
\end{array}
\]
\(J_{P-F}\) drops from 1400 to 1290 to 1225 c.p.s., respectively. Similarly, in going from FPF\(_2\) to (R\(_2\)N)\(_2\)PF, \(J_{P-F}\) drops from 1400 c.p.s. to 1045 c.p.s. However, the decrease in \(J_{P-F}\) with multiple substitution is not regular. It seems that the second substituent reduces the coupling constant by only about 70\% as much as the first substituent.

The \(\delta_P\), \(\delta_F\), and \(J_{P-F}\) in the series FPF\(_2\), ROPF\(_2\), and R\(_2\)NPF\(_2\), along with the electronegativities of F, O, and N, are shown in Table II. It seems that in this series there is a definite relationship between the chemical shifts and coupling constants and the electronegativity of the atom attached to phosphorus. It can be seen that \(\delta_P\) shifts to higher field with increasing electronegativity of the substituent atom, but the relationship is not linear. On the other hand, \(\delta_F\) decreases linearly with increasing electronegativity and \(J_{P-F}\) is directly proportional to the electronegativity of the substituent atom, in agreement with the observations of Holmes and Gallagher\(^1\) in the series PF\(_3\), PF\(_2\)Cl and PFCl\(_2\), except for the magnitude. The larger changes in the present series can be attributed to involvement of d-orbitals.

The authors wish to thank Mr. M. J. Dippier for his assistance in obtaining and calibrating the spectra.

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