Nuclear Magnetic Resonance Spectra of Organophosphorus Compounds. II. The Relative Signs of the Coupling Constants between Phosphorus and Proton

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In a previous paper,[1] we have reported the long-range coupling between phosphorus and proton in some organophosphorus compounds and have found that the relative signs of the $^3J_{PH}$ and the $^4J_{PH}$ in $EtOPOCl_2$ are the same. Recently we have constructed a frequency-swept heteronuclear decoupling system on a Hitachi H-60 spectrometer. With it we can observe the proton resonance under irradiation with a phosphorus resonance around 24.29 Mcps. An example is shown in Fig. 1, which is the spectrum of $EtOPOCl_2$. In this compound, each line of the triplet of the methyl proton resonance shows a small splitting of about 1.2 cps which is due to the coupling

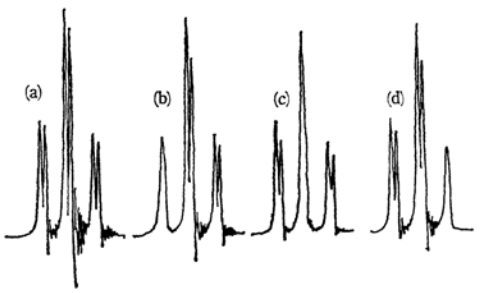

Fig. 1. The methyl proton resonance spectra of $EtOPOCl_2$ near at 60 Mcps: (a) normal pattern, (b) irradiated at 24.2901040 Mcps, (c) irradiated at 24.2900925 Mcps, (d) irradiated at 24.2900810 Mcps. The radio-frequency increases from right to left at a constant magnetic field.

$^4J_{PH}$. The higher- or lower-frequency splitting of the methyl triplet was decoupled by the irradiation of the frequency, respectively, higher or lower by 11.5 cps from the central frequency of the phosphorus resonance, as is shown in Fig. 1. This suggests that the relative signs of the $^4J_{PH}$ and the $^3J_{HH}$ in this compound are the same.

This technique was applied to several organophosphorus compounds; the results are shown in Table 1. The magnitude of the $^4J_{PH}$ in these compounds is so small that the sign of the $^4J_{PH}$ must be determined for each compound if we are to understand the mechanism of the nuclear spin-spin coupling. If one assumes that the $^3J_{HH}$ are positive in sign in the compounds studied, the signs of all the $^4J_{PH}$ listed in Table 1 are relatively positive. The $^3J_{PH}$ in Table 1 are rather large in magnitude, so they seem to be relatively positive in sign, similar to that of $EtOPOCl_2$, the relative signs of the $^4J_{PH}$ and the $^3J_{PH}$ of which have been reported on previously.[1]

Table 1. The coupling constants in some organophosphorus compounds in cps

Compound	$^4J_{PH}$	$^3J_{PH}$	$^3J_{HH}$
$EtOPCl_2$	± 0.4	8.5	± 7
$EtOPOCl_2$	± 1.2	± 11.5	± 7
$(EtO)_2POCl$	± 1.0	10	± 7
$(EtO)_3PO$	± 0.8	8.5	± 7
$EtOPSCl_2$	± 1.0	13	± 7
$(EtO)_2PSCl$	± 0.85	11	± 7
$(EtO)_3PS$	± 0.7	10	± 7
$(EtO)_3PSe$	± 0.6	10.5	± 7
$(EtO)_2PSSH$	± 0.65	10	± 7

The signs of the $^3J_{PH}$ and the $^4J_{PH}$ in similar compounds have been independently noted by Duval and Lucken.[2] They reported that the $^4J_{PH}$ of $(EtO)_3P$ is -0.55 cps. In this study the $^4J_{PH}$ of $EtOPCl_2$ is $+0.4$ cps. Therefore, the replacement of two ethoxy groups by two electronegative chlorines seems to cause the sign-reversing. This point is very interesting; further investigations will be described later.

1) K. Takahashi, T. Yamasaki and G. Miyazima, This Bulletin, **39**, 2787 (1966).

2) E. Duval and E. A. C. Lucken, *Mol. Phys.*, **10**, 499 (1966).