

The Negative Sign of the ^{31}P - ^{19}F Spin-Spin Coupling Constant in Di-isopropyl Fluorophosphate

By R. R. DEAN

(Division of Molecular Science, National Physical Laboratory, Teddington, Middlesex)

and W. McFARLANE*

(Chemistry Department, Sir John Cass College, Jewry Street, London, E.C.3)

MEASUREMENTS of the signs of nuclear spin-spin coupling constants between directly bonded atoms are important because they provide checks on the general validity of quantitative theories of chemical bonding. Finer and Harris¹ have suggested that Pople and Santry's² molecular-orbital treatment of spin-spin coupling constants between elements in the first row of the Periodic Table can be extended to later elements, and in particular they have suggested that the sign of the directly bonded ^{31}P - ^{19}F coupling constant is negative.

We have examined the readily available compound $[(\text{CH}_3)_2\text{CH}'\text{O}]_2\text{PFO}$, di-isopropyl fluorophosphate, to test this prediction. Heteronuclear "tickling" experiments were performed as described elsewhere^{3,4} by observing the proton spectrum at 100 Mc./sec. of a 50% v/v solution of the compound in benzene, and simultaneously irradiating at either the ^{31}P (ca. 40-48 Mc./sec.) or the ^{19}F (ca. 94.08 Mc./sec.) resonant frequency. Power at these frequencies was provided by a Rohde and Schwarz frequency synthesizer model XUA, and the signal given by the solvent was used to actuate the field-frequency locking circuits of the Varian HA 100 spectrometer. In this way the sign of the directly bonded ^{31}P - ^{19}F coupling was related to the vicinal $\text{H} \cdots \text{H}$ coupling which is known⁵ to be

positive, relative to a positive value for the direct ^{13}C - H coupling. The results of four sets of "tickling" experiments are given in the Table.

The resolution of the spectrometer was inadequate to measure $^4J(\text{H}' \cdots \text{F})$, but the absence of any line broadening of the H' resonance showed that this coupling was less than ca. 0.2 c./sec. This was demonstrated by ^{19}F irradiation which had no effect upon the appearance of the multiplet given by H' .

Directly bonded P-F coupling constants lie within the range 500-1500 c./sec.,⁶ and it seems likely therefore that they are all negative. Other relative sign determinations involving $^1J(\text{P}-\text{F})$ that have been reported include Heffernan and White's study⁷ of phosphonitrilics in which it was found that $^2J(\text{P} \cdots \text{P})$ and $^1J(\text{P}-\text{F})$ are of opposite sign, *i.e.*, $^2J(\text{P} \cdots \text{P})$ is positive; Harris and Woodman's work⁸ on fluoro-*NN'*-dimethyl-1,3,2,4-diazadiphosphetidine which shows $^3J(\text{P} \cdots \text{F})$ to be positive in this compound; and the work of Cunliffe *et al.*⁹ on $(\text{CF}_3)_2\text{PF}$ which shows that a negative value for $^1J(\text{P}-\text{F})$ leads to a positive $^2J(\text{P} \cdots \text{F})$ and a negative $^3J(\text{F} \cdots \text{F})$.

The magnetogyric ratios of both ^{31}P and ^{19}F are positive, so the reduced directly bonded coupling is also negative. Comparatively few large negative

TABLE. *Coupling constants in* $[(\text{CH}_3)_2\text{CH}'\text{O}]_2\text{PFO}$.

Coupling	J (c./sec.)	$K \times 10^{-20}$ (cm. ⁻³)	Ticked nucleus
$^3J(\text{H} \cdots \text{H}')$	$+6.3 \pm 0.05$	$+0.53$	^{31}P
$^3J(\text{H}' \cdots \text{P})$	$+6.3 \pm 0.05$	$+1.3$	H'
$^4J(\text{H} \cdots \text{P})$	$+0.8 \pm 0.1$	$+0.2$	^{19}F
$^1J(\text{P}-\text{F})$	-955 ± 5	-209	^{31}P
$^5J(\text{H} \cdots \text{F})$	$+0.8 \pm 0.1$	$+0.1$	—
$^4J(\text{H}' \cdots \text{F})$	0.0 ± 0.2	0	—

reduced coupling constants are known,^{10,11} other examples being $^1K(\text{C}-\text{F}) = -92 \times 10^{20}$ cm.⁻³ and $^1K(\text{C}-\text{Se}) = -108 \times 10^{20}$ cm.⁻³, $^1K(\text{C}-\text{Te}) = -170 \times 10^{20}$ cm.⁻³ in Me_2X . $^1K(\text{C}-\text{P}) = -12.3 \times 10^{20}$ cm.⁻³ in Me_2PhP .

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