Determination of Spin-coupling Constants in Di-t-butylfluorophosphine by Heteronuclear INDOR-technique

By C. SCHUMANN and H. DREESKAMP*
(*Institut für Physikalische Chemie der Universität, 7 Stuttgart 1, Wiederholdstrasse 15, Germany*)
and O. STELZER
(*Institut für Anorganische Chemie der Technischen Universität, 33 Braunschweig, Pockelstrasse 4, Germany*)

Summary The spin-coupling constants in di-t-butylfluorophosphine and their signs relative to $^1J_{CH} > 0$ have been investigated by a heteronuclear INDOR-technique showing that $^1J_{PF} < 0$ and $^1J_{PC} < 0$.

FOR a satisfactory understanding of the mechanism of indirect spin coupling, a complete set of empirical coupling constants, including signs for different nuclei and bonding situations, appears desirable.[1,2] By heteronuclear double resonance a negative sign of $^1J_{PF}$ in 3- and 4-co-ordinate phosphorus compounds has been found, assuming a positive sign of $^1J_{PH}$ or $^3J_{HH}$,[3-5] while a positive sign of $^1J_{PC}$ in halogen-substituted phosphine has been postulated.[6] Since the validity of these assumptions may be disputed, a sign determination of the coupling constants, relative to $^1J_{CH}$ whose sign is generally accepted to be positive,[2] was made in Bu^t_2PF by heteronuclear double resonance with a modified Varian-60 MHz spectrometer, as previously described.[7] The compound[8] was used with 20 vol % C_6H_6 and 1 vol % Me_4Si as internal standards at ambient temperature (30°).

Coupling constants and chemical shifts (from Me_4Si) are given in the Table. The nuclei perturbed and the coupling constants relative to which a sign determination was made are listed in the second and third columns respectively. In the INDOR experiments a ^1H resonance was monitored while transitions of other nuclei were perturbed by a field derived from a General Radio frequency synthesizer.

Relative to $^1J_{CH} > 0$, the one-bond P–F coupling was found to be negative, confirming earlier assumptions.[3-5] $^1J_{PC}$ was found to be negative, in contradiction to the hypothesis advanced by Mavel and Green[6] but in analogy to the negative sign of $^1J_{PC}$ in PMe_3.[9] It thus appears doubtful whether the theory suggested by Harris and Finer[10] to explain the sign reversal of $^1J_{PP}$ can be extended to the case of $^1J_{PC}$. Magnitudes and signs of ^1H-, ^{13}C- and ^{31}P-long-range coupling constants were found to be similar to those found earlier in t-butylphosphines.[9]

Spin-coupling constants in Hz with signs relative to $^1J_{CH} > 0$ *and chemical shifts relative to* $\nu(Me_4Si) = 1$ *in* Bu^t_2PF

$^1J_{CH}$	$= +\ 126.45 \pm 0.1$		
$^1J_{PC}$	$= -\ 34.6 \pm 0.2$	; {C(PC)}	; $^3J_{PH}$
$^1J_{PF}$	$= -\ 873.6 \pm 0.2$	; {F}	; $^3J_{PH}$
$^2J_{CH}$	$= -\ 3.6 \pm 0.2^a$		
$^2J_{PC}$	$= +\ 16.4 \pm 0.2$	; {P}	; $^1J_{CH}$
$^2J_{FC}$	$= +\ 9.9 \pm 0.2$	; {C(PC)}	; $^4J_{FH}$
$^3J_{CH}$	$= +\ 5.2 \pm 0.2^a$		
$^3J_{PH}$	$= +\ 11.29 \pm 0.02$	; $\{C(CH_3)\}$	; $^2J_{PC}$
$^3J_{FC}$	$= +\ 3.6 \pm 0.2$	; $\{C(CH_3)\}$	; $^4J_{FH}$
$^4J_{HH}$	$= +\ 0.3 \pm 0.1$	; $\{C(CH_3)\}$	; $^3J_{CH}$
$^4J_{FH}$	$= +\ 1.74 \pm 0.02$	; {P}	; $^1J_{PF}$
$\nu(^1H)$	= 1·00 000 089		
$\nu(^{13}C)$	= 0·25 145 673	(CH_3)	
	= 0·25 145 891	(C–P)	
$\nu(^{19}F)$	= 0·94 073 891		
$\nu(^{31}P)$	= 0·40 489 320		

[a] Sign assumed by analogy with neopentane.[11]

We thank the Deutsche Forschungsgemeinschaft for the loan of the spectrometer.

(*Received, March 18th, 1970; Com.* 386.)

[1] H. Dreeskamp, Proc. XIII Coll. Ampere, Leuven, 1964, North Holland Publishing Co., 1965, p. 400.
[2] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1969, **51**, 2790.
[3] R. B. Johannesen, *J. Chem. Phys.*, 1967, **47**, 3088.
[4] R. R. Dean and W. McFarlane, *Chem. Comm.*, 1967, 840.
[5] S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Amer. Chem. Soc.*, 1967, **89**, 4544.
[6] G. Mavel and M. J. Green, *Chem. Comm.*, 1968, 742.
[7] K. Hildenbrand and H. Dreeskamp, *Z. phys. Chem.* (*Frankfurt*), 1970, in the press.
[8] M. Fild and R. Schmutzler, *J. Chem. Soc.* (*A*), 1970, in the press.
[9] H. Elser and H. Dreeskamp, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 619.
[10] R. K Harris and E. G. Finer, *Chem. Comm.*, 1968, 110.
[11] H. Dreeskamp, *Z. phys. Chem.* (*Frankfurt*), 1968, **59**, 321.