

The Fluorine-19 NMR Spectrum of Methylthiotetrafluorophosphorane

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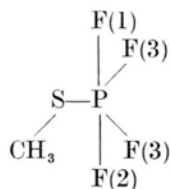
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¹⁹F NMR, Magnetic nonequivalence, Computer-simulation, Accidental overlap

The low-temperature ¹⁹F NMR spectrum of the stereochemically non-rigid compound, CH₃SPF₄, shows three fluorine environments, one for the equatorial and two for the nonequivalent axial fluorine atoms. Each of the twelve lines of the upfield ¹⁹F-(axial) resonance shows further fine structure, due to coupling between ¹⁹F and the protons of the CH₃S group. The center peaks of the two multiplet components reveal apparent quintet structure which, based on a computer simulation of the ¹⁹F spectrum of CH₃SPF₄, is rationalized in terms of accidental overlap of two quartets.

The ¹⁹F NMR spectrum of methylthiotetrafluorophosphorane, CH₃SPF₄, at low temperature shows signals from fluorine in three distinct environments^{1,2}.



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The equatorial fluorines remain equivalent, while the two axial fluorines show chemical shifts and coupling constants which are distinct from one another. The signal from each of the axial fluorines is a doublet (J_{PF}) of triplets ($J_{F(1)F(3)}$; $J_{F(2)F(3)}$) of doublets ($J_{F(1)F(2)}$). The upfield signal, F(2), is additionally split into multiplets by coupling to the methyl protons, while the analogous coupling to the downfield fluorine, F(1), shows itself as an unresolved broadening of all the lines. The multiplet splitting of the F(2) signal by protons is a quartet for the outer lines of the triplets, but apparently a quintet for the center lines of the triplets. This additional splitting of the center lines of the F(2) fluorines was initially puzzling, since a quartet was expected.

We report here the resolution of this apparent conflict by a computer simulation of the NMR spectrum of CH₃SPF₄. When this is done it becomes apparent that the wave functions of the F(3) fluorines, and hence of the entire molecule, occur in two non-interacting sets which are symmetric and *anti*-symmetric with respect to the plane of the molecule. Each of these wave functions leads to a quartet in the F(2) region; it is accidental that the two quartets are so displaced as to give the appearance of a quintet. The computer simulation of the spectrum was done using the program UEAITR³ with the values of chemical shifts and coupling constants given in the accompanying table. No iteration on measured line positions was done, since

Table. Constants used for computer simulation of CH₃SPF₄ NMR spectrum.

Chemical shifts ^a	Coupling constants ^b
$\delta_{F(1)}$ 14.1	$J_{PF(1)}$ — 930.0 Hz
$\delta_{F(2)}$ 19.8	$J_{PF(2)}$ — 1088.0
$\delta_{F(3)}$ 66.1	$J_{PF(3)}$ — 1075.0
δ_P 34.2	$J_{F(1)F(2)}$ \pm 19.1
δ_H — 2.26 ^c	$J_{F(1)F(3)}$ \pm 91.0 ^d
	$J_{F(2)F(3)}$ \pm 105.3 ^d
	$J_{HF(1)}$ 1.3
	$J_{HF(2)}$ 3.0
	$J_{HF(3)}$ 0.0
	J_{HP} 24.8 ^c

^a Fluorine shifts in ppm upfield from internal CFCl₃; phosphorus shift in ppm upfield from external 85% phosphoric acid; proton shift downfield in ppm from internal TMS.

^b Lacking double resonance information, we assume^{5,6} all of the J_{PF} are < 0 . The relative intensities then agree only if all J_{FF} are of the same sign.

^c Reference 7. Measured at room temperature. A value of 12 Hz was used in the computer calculations since the correct value was not then available. The fluorine spectrum is unaffected by the value of J_{HP} .

^d Reference 4.

the spectrum is very nearly first order. The computer calculated spectrum was in satisfactory agreement with the observed spectrum, including the additional lines in the centers of the F(2) triplets.

Experimental

Methylthiotetrafluorophosphorane was prepared under the conditions described by PEAKE and SCHMUTZLER². No attempt was made to purify the thermally unstable compound. The ¹⁹F NMR spectrum was recorded at -90 °C, on a Perkin Elmer R 10 spectrometer at 56.4 MHz without signal locking. Fluorotrichloromethane and toluene were used as an internal reference and solvent, respectively. The ³¹P NMR spectrum was recorded at -90 °C on a Perkin Elmer R 10 spectrometer at 24.3 MHz without signal locking. External 85% phosphoric acid was used as a chemical shift reference.

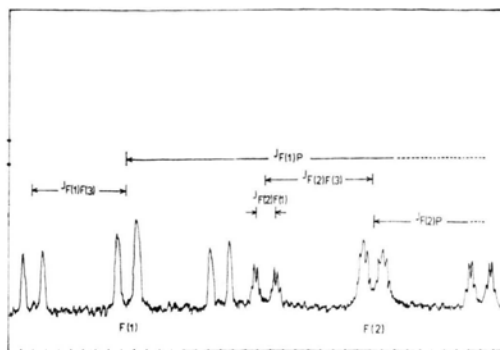


Fig. 1. ¹⁹F NMR spectrum of CH₃SPF₄ at -90 °C (scale expansion of the lower axial fluorine atom region). F(1), F(2) refer to the two axial fluorine atoms; F(3) refers to the two equatorial fluorine atoms.

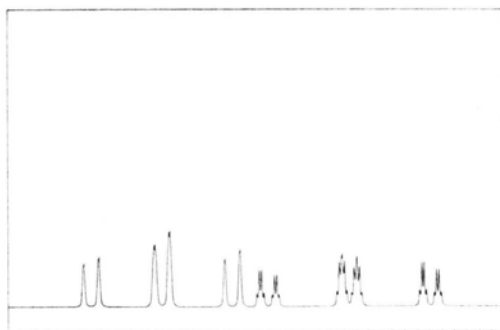


Fig. 2. Computer-simulated ¹⁹F NMR spectrum of CH₃SPF₄ (lower axial fluorine atom region).

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⁴ Note the values of J_{FF} for the pair F(1)F(3) and F(2)F(3) were accidentally interchanged in Ref. 1 and 2.

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