Signs of Proximate ³¹P, ¹⁹F and ¹⁹F, ¹⁹F Spin–Spin Coupling Constants in 2-Trifluoromethylphenyldifluorophosphine

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In 2-trifluoromethylphenyldifluorophosphine the proximate couplings ${}^{4}J({}^{19}F^{31}P)$ and ${}^{5}J({}^{19}F^{19}F)$ are +68.3 and +8.3 Hz, respectively. ${}^{1}J({}^{13}C^{31}P)$ is -57.0 Hz, ${}^{2}J({}^{13}C-1, {}^{19}F)$ is +9.9 Hz and ${}^{2}J({}^{13}C-6, {}^{31}P)$ is +10.1 Hz. The trifluoromethyl substituent induces substantial changes in some coupling constants, particularly those between the ${}^{31}P$ and ring ${}^{13}C$ nuclei.

DISCUSSION

'Through-space' or proximate couplings are much larger in magnitude than anticipated on the basis of the formal number of bonds intervening between the coupled nuclei.¹ Attempts at their explanation or calculation have met with limited success.¹⁻¹⁸ In a number of instances the close approach, perhaps to within the sum of the van der Waals radii, of the atoms containing the coupled nuclei appears essential to the observation of large couplings. Some theoretical models also imply the importance of direct interactions involving rear lobes of the orbitals or lone-pairs on atoms adjacent to those carrying the nuclei of interest.⁸ The signs of the proximate couplings are important in any eventual satisfactory description of the coupling mechanisms.

For the side chain nuclei in 1, ${}^{5}J(FF)$ is +8.3 Hz



and ${}^{4}J(FP)$ is +68.3 Hz. By way of contrast, ${}^{3}J(CP)$ is ±2.5 Hz and ${}^{4}J(CF)$ is ±0.7 Hz. When PF₂ in **1** is replaced by PCl₂, ${}^{4}J(FP)$ becomes ±85.2 Hz.

In phenyldichlorophosphine, STO-3G MO calculations indicate a preference of 9.6 kJ mol⁻¹ for a conformation in which the lone-pair on phosphorus lies in the benzene plane.¹⁹ In phenyldifluorophosphine, similar calculations suggest that the lone-pair prefers a plane perpendicular to the ring, but only by 2.2 kJ mol⁻¹ and comparable to thermal energies near 300 K. In this compound, ${}^{5}J(F, C-4)$ is 1.8 Hz and is very likely dependent on the angle of rotation about the C--P bond.¹⁹ In **1**, ${}^{5}J(F, C-4)$ is also 1.8 Hz (Table 1), suggesting a similar conformational average for the PF_2 group in these two compounds. A tentative conclusion is that an important contribution to ${}^4J(FP)$ involves the proximity of the phosphorus lone-pair to the CF₃ group. It may be noted that the magnitude of ${}^4J(FP)$ is 53–55 Hz in triphenylphosphine derivatives in which one to three phenyl groups contain an *ortho* CF₃ substituent.¹⁰

 ${}^{5}J(FF)$ in **1** is somewhat smaller than the +13 Hz observed for ${}^{4}J(FF)$ in 2-fluorobenzotrifluoride or the 10.2 Hz for ${}^{5}J(FF)$ in *cis*-1,2-ditrifluoromethylethene; 14 this is understandable if these proximate interactions depend on significant overlap between orbitals centered on the coupled nuclei. ${}^{4.5}$ It is interesting that, where signs are known, all the plausibly proximate "J(FF) values are positive.

Our attempts at the calculation of ${}^{5}J(FF)$ and ${}^{4}J(FP)$ in **1** by INDO MO FPT methods²⁰ gave unsatisfactory results.

Table 1. Spectral data for the ¹³C nuclei in 1

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	C-1: 139.1*	C-3: 126.8
	$^{1}J(CP) = -57.0(36.1)^{d}$	³ J(CP) = 2.4 (7.5)
	² J(CF) = +9.9 (10.6)	³ J(CF) = 5.3 (3.9)
	$^{3}J(CF) = ^{b}(3.9)$	⁴ J(CF) = ^{b,c}
	C-4: 133.2	C-5: 132.9
	$^{4}J(CP) = ^{b,c}$	band width $\Delta v_{1/2} = 4$ Hz
	⁴ J(CF) = ^{b,c}	⁵ J(CF) = (1.4)
	⁵ J(CF) = 1.8(1.8)	
	C-6: 129.4	C-7: 125.0
	² J(CP) = +10.1(28.2)	¹ J(CF) = (–)274.7
	³ J(CF) = 11.1(7.7)	³ J(CP) = 2.5
	$^{4}J(CF) = ^{b,c}$	⁴ J(CF) = 0.7

^a A 20 v/v% solution of 1 in CD₂Cl₂. The chemical shifts are given as δ values, taking $\delta_{CD_2Cl_2}$ as 53.8. The C-2 spectrum should consist of 24 peaks spread over *c*. 140 Hz, and was not reliably assigned.

^b Not resolved, less than 0.5 Hz in magnitude.

^c Not resolved in the parent compound, i.e. phenyldifluorophosphine¹⁹ or benzotrifluoride.^{24,25}

^d Numbers in parentheses refer to the magnitudes for the parent compound.

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The three other signs of J determined for 1 (Table 1) are the same as those previously assumed for phenyldifluorophosphine and phenyldichlorophosphine.¹⁹ The CF₃ substituent in 1 induces substantial changes in some J(CP) and J(CF) values (see Table 1). The most remarkable changes involve J(CP). For example, ¹J(CP) varies from (-) 8.1 Hz in phenylphosphine,¹⁹ and (-) 36.1 Hz in phenyldifluorophosphine,¹⁹ to -57.0 Hz in 1.

EXPERIMENTAL

The signs of the coupling constants are all relative to ${}^{1}J(\text{FP}) = -1198.6 \text{ Hz}$, and were determined by ${}^{19}\text{F}\{{}^{31}\text{P}\}$, ${}^{19}\text{F}\{{}^{19}\text{F}\}$, ${}^{13}\text{C}\{{}^{19}\text{F}\}$, and ${}^{13}\text{C}\{{}^{31}\text{P}\}$ experiments under conditions of ${}^{1}\text{H}$ noise decoupling on a WH-90 FFT spectrometer at a probe temperature of 298 K. ${}^{1}J(\text{FP})$ is known to be negative. 21,22 The assignment of the ${}^{13}\text{C}$ chemical shifts in Table 1 depended on the knowledge of the shifts in phenyldifluorophosphine} and benzotrifluoride, 23 as well as on characteristic spin-spin couplings (or their absence) to the ${}^{19}\text{F}$ and ${}^{31}\text{P}$ nuclei on the side chains.

The spectra were recorded at 84.700, 36.44 and 22.63 MHz for ¹⁹F, ³¹P and ¹³C nuclei, respectively. Double resonance frequencies were generated by a

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Shomandl ST0-100M synthesizer and a modified Bruker B-SV3 B decoupler (circuits available from the authors); all frequencies were phase-locked to the 10 MHz clock of the spectrometer. Simultaneous proton decoupling utilized the regular WH-90 decoupler and a matching network in the probe.

Molecular orbital calculations were performed on an Amdahl 470/V7 system.

2-Trifluoromethylphenyldifluorophosphine, 1, was prepared via the Grignard reagent derived from 2bromobenzotrifluoride. A stoichiometric amount of $(Et_2N)_2PCI$ was added to the Grignard reagent and the resultant solution of o-CF₃C₆H₄P(NEt₂)₂ was chlorinated by bubbling through HCl and cooling the reaction flask in a dry ice-acetone bath. The mixture was filtered, the ether was removed under vacuum, and the crude o-CF₃C₆H₄PCl₂ was used without further purification to prepare 1 by the method of Schmutzler.²⁶ The sulfolane solvent was distilled under vaccum from P₂O₅. It was necessary to heat the reaction mixture at 120–130 °C for at least 1 h under a nitrogen atmosphere so as to drive the reaction to completion.

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