^{15}N–^{19}F Spin Coupling Mechanism in 2-Fluoropyridine Studied by Selective Population Transfer in ^{15}N Nuclear Magnetic Resonance

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Summary The magnitude and sign of $^2J(^{15}N–^{19}F)$ ($-52{\cdot}64$ Hz) in 2-fluoropyridine is determined from natural abundance proton-coupled ^{15}N Fourier transform n.m.r. spectra using selective population transfer; a lone-pair effect or 'through-space' coupling dominates the $^2J(^{15}N–^{19}F)$ spin coupling mechanism.

LONE-PAIR effects[1] and spin coupling mechanisms involving nonbonding electrons (*e.g.* 'through-space' coupling)[2] are known to influence both the sign and magnitude of several types of spin coupling constants. These effects are very useful in obtaining molecular structure information. Despite the small magnetic moment for ^{15}N some unusually large ^{15}N–^{19}F coupling constants were reported a decade ago for 2-fluoropyridine (**1**) and chlorinated 2,6-difluoropyridines [$|^2J(^{15}N–^{19}F)|$ *ca.* 53 Hz] from spin-echo measurements (inaccurate data)[3] and ^{15}N satellites in ^{19}F spectra,[4] respectively. For comparison ^2J(C–F) is $+21{\cdot}0$ Hz in fluorobenzene.[5] As preliminary results in our studies of ^{15}N–^{19}F coupling constants we report the determination of the sign and magnitude of $^2J(^{15}N–^{19}F)$, as well as those of ^{15}N-^{1}H couplings, in (**1**) from selective population transfer (SPT) in natural abundance ^{15}N Fourier transform (FT) n.m.r. spectroscopy. The results are consistent with a coupling mechanism which is influenced by the proximity of the nitrogen and fluorine lone-pair orbitals.

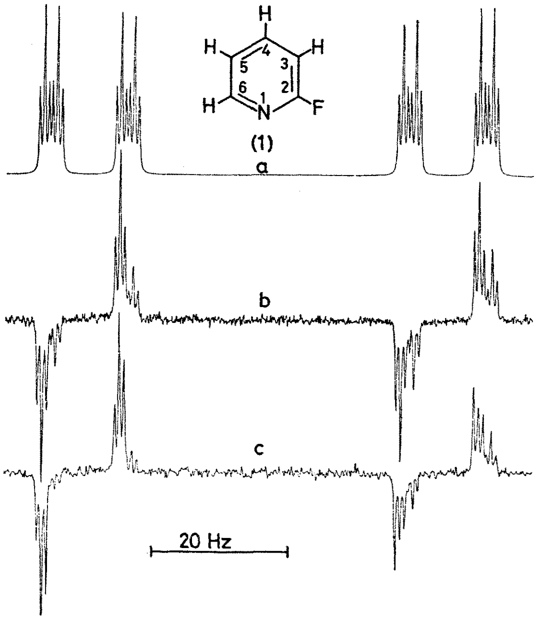

FIGURE. Coupled natural abundance ^{15}N (10·15 MHz) Fourier transform n.m.r. spectra of 2-fluoropyridine (**1**) [85% v/v in $(CD_3)_2CO$]. (a) Simulated spectrum (coupling constants from Table, linewidth 0·25 Hz). (b and c) ^{15}N-{H-6} SPT spectra each obtained after 2000 transients (5 h) and using 0·30 Hz *lower* frequency for the ^{1}H π-pulse in (b) than in (c); acquisition time 8 s, no line broadening, $\gamma H_2/2\pi = 0{\cdot}50$ Hz and $\pi = 1{\cdot}0$ s. Spectra were recorded on a Varian XL-100-15 spectrometer equipped with Nicolet's MONA multinuclear accessory and 18 mm probe.

Recently the ^{1}H SPT π-pulse technique[6] was shown to afford a large increase in ^{15}N FT n.m.r. sensitivity (time saving factors of 10^2—10^4).[7] This enhancement results from the favourable ratio $\gamma(^1H)/\gamma(^{15}N) = 10$ and from the possibility of sampling the ^{15}N spectrum with a repetition rate determined by the relaxation rate of the protons rather than by the often very slow spin–lattice relaxation of the observed ^{15}N nucleus (*e.g.* for ^{15}N-pyridine $T_{1N} =$ *ca.* 50 s[8]). The sensitivity gain offered by this technique is markedly illustrated by the ^{15}N FT n.m.r. study of (**1**). Thus, for a given number of transients, the proton noise-decoupled ^{15}N spectrum (a doublet, $|^2J(^{15}N–F)|$ 52·7 Hz) gave a much poorer S/N ratio than obtained from a SPT π-pulse proton-coupled spectrum (Figure). Signs and magnitudes for the ^{15}N–^{19}F and ^{15}N–^{1}H coupling constants (Table) were obtained from proton-coupled SPT ^{15}N FT n.m.r. spectra for which the selective ^{1}H π-pulse was applied in the region of the H_6 transitions. The coupled apparently first-order spectrum was analysed (LAOCN3) as the X part of an ABCDMX spin system; all ^{15}N–^{1}H coupling assignments were confirmed from the SPT results.

TABLE. ^{15}N–^{19}F and ^{15}N–^{1}H coupling constants in 2-fluoropyridine (**1**) and pyridine[a]

	2-Fluoropyridine[b]	Pyridine[c]
$^2J(^{15}N–^{19}F)$	$-52{\cdot}64$	—
$^3J(^{15}N\text{-H-}3)$	$-0{\cdot}69$	$-1{\cdot}48$
$^4J(^{15}N\text{-H-}4)$	$+0{\cdot}69$	$+0{\cdot}27$
$^3J(^{15}N\text{-H-}5)$	$-1{\cdot}94$	$-1{\cdot}48$
$^2J(^{15}N\text{-H-}6)$	$-11{\cdot}35$	$-10{\cdot}93$
R.m.s. error	0·014	0·007

[a] In Hz with errors within $\pm 0{\cdot}03$ Hz. [b] From ^{15}N n.m.r. spectra, this work, 24 assigned lines. [c] From ^{1}H n.m.r. spectra, ref. 1, 107 assigned lines.

The negative sign for $^2J(^{15}N–^{19}F)$, *i.e.* a positive reduced coupling constant $^2K(^{15}N–^{19}F)$ [$=4\pi^2\ ^2J(^{15}N–^{19}F)/h\gamma(^{15}N)\gamma(^{19}F)$], follows from the experiments in the Figure, which show that $^2K(^{15}N–F) \times {}^4K(H\text{-}6–F) < 0$, and from a recent ^{13}C n.m.r. study on (**1**) [$^4J(H\text{-}6–F) < 0$].[9] The resulting positive sign and unusually large magnitude for $^2K(^{15}N–F)$ ($= +\,4{\cdot}60 \times 10^{20}$ N A^2 m^{-3}) is consistent with a spin coupling pathway involving lone-pair electrons on the coupled nuclei. Recent studies have demonstrated that proximity of lone-pair electrons makes a positive contribution to reduced two-bond couplings, $^2K_{ij}$, for a number of nuclei i and j.[1] The present report appears to be the first example of such an effect on a ^{15}N–^{19}F coupling, a coupling scarcely reported so far in the literature.[10] Spin coupling constants, referred to as 'through-space' coupling, are also

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characterized by a large positive contribution to K_{ij}, as judged from the few cases (^{19}F–^{19}F and ^{19}F–^{31}P)[11,12] where the sign has been determined for such couplings. It is tempting to propose that the lone-pair effect,[1] which influences the sign and magnitude of *e.g.* ^{15}N–^{1}H and ^{15}N–^{13}C coupling constants, occurs in a way closely related to the coupling between nuclei mediated by electrons not in bonds, so-called 'through-space' coupling.

The ^{15}N–^{1}H couplings in (**1**) are in general similar in both magnitude and sign to those observed in pyridine[1,13] (Table). As expected the largest fluorine substituent effect is observed for the coupling $^{3}J(^{15}N\text{-H-3})$, across the substituted carbon C-2. Interestingly, the decrease observed in the values for $^{3}K(^{15}N\text{-H-3})$ and $^{4}K(^{15}N\text{-H-4})$ parallels the decrease for $^{3}J(\text{C-2–H-6})$ and $^{4}J(\text{C-2–H-5})$ in fluorobenzene[14] relative to benzene.[15]

Finally, the present study shows that using SPT even rather complex coupled ^{15}N spectra may be obtained at the natural abundance level in a time comparable to that used for obtaining coupled ^{13}C spectra.

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