Sigma and Pi Electron Contributions to Long-range Spin-Spin Coupling Constants in the Methyl Derivatives of the Fluoropyridines

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Seven methyl derivatives of the 3- and 4-fluoropyridines are synthesized and their p.m.r. spectra are analyzed. The nuclear spin-spin coupling constants are compared with previous results for the four methyl derivatives of 2-fluoropyridine. A model in which the nitrogen atom polarizes primarily the σ electron system of the ring, leaving the π electron contribution to the coupling mechanism relatively unaffected, qualitatively accounts for the large majority of the coupling constants. For example, the coupling over six bonds between methyl protons and a fluorine nucleus, J_p^{F,CH_3} , is the same whether the fluorine atom or the methyl group is placed ortho to the nitrogen atom and is little different from its value in *p*-fluorotoluene. The model is consistent with significant σ electron contributions to long-range couplings over four and five bonds from methyl protons to fluorine nuclei or ring protons. Evidence is adduced for resonance structures in which fluorine conjugates with nitrogen or with ring carbon atoms. An earlier suggestion, that hyperconjugation of the methyl group with nitrogen is necessary to the interpretation of the observed couplings, is dropped. Instead, a substantial polarization of the σ electron core near C-2 and -6 is invoked but apparently does not extend appreciably beyond these atoms in the ring.

Sept dérivés méthylés des fluoro-3 et 4 pyridines sont synthétisés et leurs spectres r.m.n. analysés. Les constantes de couplage spin-spin sont comparées aux résultats antérieurs obtenus pour les quatre dérivés méthylés de la fluoro-2 pyridine. Un modèle dans lequel l'atome d'azote polarise principalement le système électronique σ du cycle laissant relativement inchangée la contribution électronique π au mécanisme du couplage, explique qualitativement la grande majorité des constantes de couplage. Par exemple, le couplage à travers six liaisons entre les protons du méthyle et le noyau de fluor, J_p^{F,CH_3} , est le même si le fluor ou le méthyle est placé en ortho par rapport à l'azote et diffère peu de la valeur obtenue dans le *p*-fluorotoluène. Le modèle est compatible avec les contributions importantes des électrons σ aux couplages à longue distance à travers quatre et cinq liaisons, à partir des protons du méthyle au noyau du fluor ou au protons du cycle. Une preuve de structures résonantes dans lesquelles le fluor se conjugué à l'azote ou aux atomes de carbone du cycle est apportée. La suggestion première selon laquelle l'hyperconjugaison du groupe méthyle avec l'azote est nécessaire à l'interprétation des couplages observés, n'est pas retenue. A la place, une polarisation substantielle des électrons σ proches du C-2 et du -6 est avancée mais ne s'étend pas apparemment au-delà de ces derniers de façon notable.

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Introduction

A model in which σ and π electron contributions to ring proton and to ring proton – fluorine spin-spin coupling constants are distinguished has been successfully applied to the methyl derivatives, 1–4, of 2-fluoropyridines (1, 2). In these compounds the signs and magnitudes of the long-range coupling constants between the methyl protons and the ring protons or the fluorine nucleus support the assumption (3) that the nitrogen atom primarily polarizes the proximate σ bonds, leaving the π electron contribution to the coupling constants mainly unaffected (2). Certain resonance structures of these molecules were invoked in the interpretation of the coupling data (2) apropos of which a referee pointed out the desirability of the examination of the methyl derivatives of the 3- and



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4-fluoropyridines. Accordingly the synthesis of a series of these derivatives is reported here, together with the analyses of their p.m.r. spectra. The ensuing spin-spin coupling data are discussed in terms of the earlier model.

Acquaintance with the earlier work (1, 2) is assumed in this final report.

Experimental

(1) Syntheses of Compounds

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These were prepared by Schiemann reactions (2) on the respective amines. To prepare 7, 8, 9, and 11 the amine was dissolved in excess 50% aqueous HBF_4 and then treated in the cold with solid NaNO₂ over several hours. After heating the solution at 50 °C for 1 h, it was diluted with water, neutralized, and extracted with ether. Distillation of the dried extracts gave poor yields of the methylfluoropyridines.

An improved method (4) was used to prepare 5, 6 and 10. The amine was dissolved in the minimum aqueous HBF_4 necessary to maintain fluidity and the cold mixture was treated with excess solid NaNO₂ over a period of 0.5 h. The mixture was quickly filtered and the diazonium fluoroborate was covered with pentane (hexane for 5). The salts decomposed smoothly on heating (6 and 10 were decomposing on the cool filter but 5 was stable in boiling pentane). A good yield of product was obtained by extraction with dilute HCl, neutralization, steam distillation of the extracts, extraction of the distillate with ether, and distillation under reduced pressure.

Only the amine precursor of 9 was commercially available. The 4-amino-2-picoline, 4-amino-3-picoline, and 4-amino-2,6-lutidine were obtained by nitration and catalytic reduction of the pyridine oxides (5). The 3-amino-2,6-lutidine was prepared via hydrogenation of the commercially available nitro compound in ethanol. 2-Chloro-5-nitro-3-picoline was obtained by nitration, hydrolysis, and treatment with phosphorous oxychloride from 2-amino-3-picoline (6, 7). Hydrogenation over Pd/C in ethanol at 1 atm gave 3-amino-5picoline. Similarly, 2-amino-4-picoline gave 3-amino-4picoline. No attempt was made to separate the intermediate isomeric mixtures.

All fluorine compounds had p.m.r. spectra consistent with

their structures and all had a mint-like odor. Compounds 5, 6, 7, and 10 have been previously reported (4, 6, 7) while the amine precursors for 8, 9, and 11 are known (5, 8).

(2) Proton Magnetic Resonance Measurements

Degassed samples were prepared as 17-30 mol % solutions in carbon disulfide, tetramethylsilane, or benzene- d_6 by the freeze-pump-thaw technique. The choice of solvents, all of low dielectric constant, was dictated by the desire to prevent, as far as possible, the overlap of peaks from different proton groupings.

The peaks belonging to H_2 or H_6 were fairly broad because of incompletely relaxed spin-spin coupling to ¹⁴N, but addition of small amounts of trifluoroacetic acid (1) did not sharpen these significantly.² In consequence the derived coupling constants between fluorine and H_2 or H_6 , and between H_2 and H_6 , have an uncertainty of about 0.1 Hz.

Proton magnetic resonance spectra were recorded on a Varian DA-60I spectrometer (10 was measured at 100 MHz on an HA100D spectrometer) in the frequency sweep mode, with internal tetramethylsilane serving as a locking material. The spectra were repeatedly calibrated at intervals of about 5 Hz by reading sweep and manual oscillator frequencies and were measured at a sweep width of 50 Hz at sweep speeds of 0.01 Hz/s. Decoupling as well as weak irradiation experiments (9) employed an HP-4204A audio oscillator and/or a Wavetek 114 sweep generator (10).

For the n.O.e. experiment (11, 12) on 6 in benzene- d_6 solution the spectrometer was locked on internal trifluoroacetic acid. Four scans were made of the H₂ and H₆ regions without strong irradiation of the methyl proton region, followed by four more during which the methyl protons were strongly irradiated. Peak areas were found by weighing and a 10% increase in the area from one set of peaks was taken as indicating that they originated in H₆.

(3) Spectral Analysis

Spectra were analyzed on an IBM 360/65 computer using the program LAME (13) in iterative or noniterative mode; followed by a plotting routine (devised by J.B.R.) which drove a CalComp incremental plotter. The plotting program gave each transition a Lorentzian shape of width 2a at halfheight, $\Delta v_{1/2} = 2a$, retaining this value until the highest point

²The splittings of H_6 in 1 were rather larger than those found in the present compounds.

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CANADIAN JOURNAL OF CHEMISTRY. VOL. 50, 1972 TABLE 1 Proton chemical shifts* and coupling constantst in some methylfluoronyridines

| Parameter | 5(C ₆ D ₆ , 21)‡ | 6(C ₆ D ₆ , 24) | 7(CS ₂ , 20) | 8(TMS, 30) | 9 (CS ₂ , 17) | 10 (C ₆ D ₆ , 24) | 11(CS ₂ , 17) |
|----------------------------------|--|---------------------------------------|-------------------------|--------------|---------------------------------|--|--------------------------|
| v ₂ v ₃ | 8.26 | 8.20 | (2.461) 6.786 | 8.36 (2.162) | 6.371 | (2.381) | (2.408) |
| V ₄ | (1.899) | 6.743 | _ | / | (2.274) | 6.815 | _ |
| v ₅ | 6.626 | (1.882) | 6.756 | 6.934 | 6.725 | 6.515 | 6.549 |
| v ₆ | 8.10 | 8.08 | 8.35 | 8.34 | (2.329) | (2.315) | (2.408) |
| $J_o^{\rm H, H}$ | +4.80 | | +5.69 | +5.55 | — | 8.34 | _ |
| $J_m^{\rm H, H}$ | <0.3 | +2.79[2,4] | +2.47 | < 0.3 | 1.20 | | |
| | — | +1.78[4,6] | — | | — | — | — |
| | — | <0.5[2,6] | _ | — | — | — | _ |
| $J_p^{\mathrm{H,H}}$ | ÷0.51 | | +0.50 | +0.43 | — | — | _ |
| $J_o^{\rm H,F}$ | +1.5 | +0.7[2] | 9.85[3] | +9.50 | -2.24 | 9.34 | 9.51 |
| | | +9.46[4] | +8.57[5] | — | | — | |
| $J_m^{\rm H,F}$ | +6.54 | _ | +8.9 | +10.2[2] | | 3.61 | _ |
| | | _ | _ | +7.8[6] | | | |
| $J_p^{\mathrm{H,F}}$ | +1.2 | +2.2 | | | +2.20 | | - |
| $J_o^{\rm H,CH_3}$ | (-)0.79 | -0.75[4] | -0.51 | -0.81 | (-)0.77[3,4] | (-)0.52 | ş |
| - | | -0.70[6] | | _ | (-)0.60[4,5] | | <u> </u> |
| | — | — | | | (-)0.60[5,6] | — | _ |
| J_m^{H,CH_3} | +0.34[2] | | 0.27 | +0.41 | _ | 0.35[2] | _ |
| | +0.34[6] | — | | | | 0.33[6] | |
| $J_p^{\rm H, CH_3}$ | | -0.63 | -0.55 | -0.62 | (-)0.60 | (-)0.59 | § |
| $J_o^{\rm F,CH_3}$ | +1.71 | _ | _ | +1.63 | _ | 3.03 | _ |
| $J_m^{\mathrm{F,CH_3}}$ | | (-)0.10 | -0.27 | | (-)0.17[4] | _ | (-)0.25 |
| | | _ | _ | <u> </u> | (-)0.59[6] | | _ |
| $J_p^{\rm F,CH_3}$ | _ | _ | <u> </u> | | _ | 1.21 | _ |
| $J_m^{\rm CH_3, CH_3}$ | _ | _ | | <u> </u> | (-)0.17 | (-)0.21 | |

*In p.p.m. to low field of internal TMS; parentheses indicate methyl protons.
†In Hz; when the sign is omitted or is given in parentheses it was not determined. Square brackets indicate ring positions.
‡Solvent and concentration (mol %).
§In 11 one can find only |J^{H,CH₃} + J^{P,CH₃} = 1.08 Hz because of the symmetrical nature of the spectrum.

on the peak was reached, then changing to a Lorentzian shape with $\Delta v_{1/2} = 2b$ for the remainder of the peak. Thus the composite computed peak was determined by two parameters: the width, a + b, and the asymmetry, a/(a + b). The asymmetry parameter was generally set at 0.6-0.65 to best simulate the experimental effects of finite sweep times. A total width of about 0.15 Hz generally reproduced the experimental linewidth best but a width of up to 0.8 Hz was used to simulate the broad peaks from H_2 or H_6 .

Analysis of the spectra was generally straightforward, particularly when decoupling of specific methyl protons was employed in extracting preliminary spectral parameters for ring protons and fluorine. For 9, 10, and 11 all transitions were assigned and all parameters (except, of course, the fluorine shift) were allowed to vary in the final iterations. The transitions associated with H_2 and/or H_6 in the other compounds were not assigned and therefore their chemical shifts as well as their couplings to fluorine and to each other could not be allowed to vary. These were determined by trial and error methods employing the noniterative mode of LAME. The r.m.s. deviations between calculated and observed transitions were always less than 0.023 Hz, standard deviations of the spectral parameters were less than 0.01 Hz and correlation coefficients were less than 0.3 except between the chemical shift of H_5 and ${}^{3}J_{\theta}^{45,H^{6}}$ in 7, which was 0.8; this is a consequence of the incomplete assignment of transitions to observed peak positions in the H_6 region.

In one or two cases the derived spectral parameters were not immediately assignable to specific protons. For instance, in 10 the protons of the two methyl groups differ only in their chemical shifts and in their coupling to fluorine. They were assigned on the basis that ${}^{6}J_{p}^{F,CH_{3}}$ is smaller than ${}^{4}J_{c}^{F,CH_{3}}$, and is almost independent of substituent effects, even of the presence of a heteroatom (2, 14, 15). Again, the ring protons in 9 were assigned on the basis of their relative chemical shifts by analogy with 2 and 4, measured in the same solvent (2) while the methyl protons were assigned so that the couplings to fluorine agreed with those in 2 and 4(2).

Results and Discussion

The spectral parameters of 5-11 are given in Table 1. Tickling experiments provided the relative signs of the couplings in many cases. When the sign is shown in parentheses it was not determined directly but was assigned on the basis of well-documented previous work (1, 2, 15-18). Attempts at confirming the signs of certain couplings failed, usually because the relevant splittings in the spectrum were not sufficiently well resolved. Thus the sign of ${}^{4}J_{m}^{\mathrm{H}_{2},\mathrm{H}_{6}}$ is not known from this study but is known to be negative in pyridine itself (17); the sign of ${}^{5}J_{m}^{\text{F,CH}_{3}}$ in 6 is also unknown from the present measurements.

For reasons of space the observed and computed spectra are not displayed here, but show excellent agreement with each other and are certainly not inferior to those portrayed in detail for 1(1).

(1) The Methyl Proton – Ring Proton Coupling Constants

(a) Over Six Bonds, ${}^{6}J_{p}^{\text{H.CH}_{3}}$ In toluene (19) $J_{p}^{\text{H.CH}_{3}}$ is -0.62 ± 0.02 Hz, the same as in 6, 8, 9, and 10; confirming the data on 1 and 4(1, 2) and bearing out the earlier conclusion (2) that, as this coupling constant arises from a π electron mechanism (16, 20, 21), the nitrogen and fluorine atoms are ineffectual in altering the π electron contribution to $J_n^{\mathrm{H,CH_3}}$. The smaller value of -0.55 Hz in 7 is considered as insufficiently different from that in the other compounds to weaken this conclusion.

(b) Over Four Bonds, ${}^{4}J^{H,CH_{3}}_{o}$

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In ref. 2 it was argued that, as the negative π electron contribution to J_o^{H,CH_3} is expected to increase as the mobile bond order of the intervening C = C bond increases, the data for 1, 2, and 3 were consistent with a contribution from the resonance structure 12. Extension of the argument to 5, 6, and 8 involves 13, 14, and 15, where on a priori grounds 12 and 15 may well be favored over 13 or 14 because the strong nitrogen acceptor is placed ortho or para to the fluorine donor in 12 and 15. In 2 one has $J_a^{H_3,CH_3}$ equal to 0.81 Hz (2), the same as in 8 and indicating 12 and 15 as equally important structures; in accord with quadrupole resonance data (22) and relevant to a referee's comment on ref. 2 concerning the importance of structures of this type. The somewhat smaller magnitudes of this coupling in 5 and 6 suggest that contributions from 13 and 14 are less important than those of 12 and 15.

The even smaller magnitudes of -0.5 to -0.6Hz occurring for $J_a^{\rm H, CH_3}$ when a methyl group is situated ortho to the nitrogen atom, as in 4(2), 7, 9, and 10, were originally (2) attributed either to a structure of the type 16 which decreases the



mobile bond order between C-5 and -6; or to a decrease in the negative σ electron contribution to J_o^{H,CH_3} , caused by a polarization of the σ core by the nitrogen atom and operating to decrease the σ density near C-6. The former proposal now appears untenable for the following reasons. The methyl group is undoubtedly a weaker π electron donor than a fluorine atom (23). Now because 12 and 15 have here and previously (2) been shown to be fairly important structures in the interpretation of the coupling data, it follows that in 7, where 15 applies and acts to increase the mobile bond order between C-2 and -3, $J_{a}^{\mathrm{H,CH_{3}}}$ should have roughly the same magnitude as in 8. Yet it is 0.3 Hz smaller in magnitude. We think it unlikely that a structure of the type 16 would outweigh one of the type 15. Again the two different magnitudes of $J_a^{\text{H,CH}_3}$ in 2 (2) are in accord with a substantial contribution from 12 but not from 17.

This conclusion leaves the alternative proposal of σ electron polarization of C-2 or -6 by the nitrogen atom as an explanation of the small magnitude of $J_o^{\rm H,CH_3}$ in those compounds where the methyl group is attached to these carbon atoms. An apparent objection cites the fact that $J_{a}^{\rm H,CH_3}$ is -0.81 Hz in 8, involving the ring



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proton at C-2, and asks why the decrease in a σ electron contribution to $J_{a}^{H, CH_{3}}$ occurs only when the methyl group is attached at C-2. A probable answer cites the possible coupling pathways recently discussed in detail (24, 25). In brief, the exchange integrals involved in the coupling mechanism in a valence bond formulation may be quite different in the two situations (25). Quantitative calculations by a molecular orbital method (26) on propene derivatives predict a marked positive shift in the *cisoid* allylic coupling when substitution occurs at C-2, in agreement with experiment; while the observed change in this coupling on substitution (by fluorine) at C-1 is zero (27). The situation is analogous to our observations, with nitrogen playing the role of the substituent and $J_a^{\rm H, CH_3}$ the role of the *cisoid* allylic coupling, ${}^{4}J_{L}^{H,CH_{3}}$, in the propene derivatives.

In terms of our model the positive shift in $J_{a}^{\mathrm{H,CH}_{3}}$, occurring when the methyl group is bonded to C-2 or -6, is a σ electron effect. Further evidence that it is not a π electron effect can be adduced from two sources. First, a π electron coupling of this kind is proportional to $Q_{\rm CCH}$, the hyperfine interaction constant of a methyl proton with the π electron system (28– 30). In a series of radical anions of the methylpyridine derivatives no marked dependence of this parameter on the position of the methyl group is found (31). Second, a decrease in the $Q_{\rm CCH}$ value at C-2 and -6, which would account for the small magnitudes of the corresponding $J_o^{\rm H,CH_3}$ values, should then also be reflected in a decrease of $J_o^{\rm F,CH_3}$ in 10 relative to its values in 1, 5, and 8. The opposite occurs.

(c) Over Five Bonds, ${}^{5}J_{m}^{H,CH_{3}}$

In ref. 2 it was reasoned that, as $J_m^{\rm H,CH_3}$ contains a substantial positive σ electron contribution (16, 21), the values of 0.28 Hz in 2 and 4 (0.1 Hz smaller than the 0.4 Hz observed in 1 and 3) are in agreement with a σ electron polarization at C-2 or -6 by the nitrogen atom. In 2 and 4 these carbon atoms are involved in the coupling path. The couplings of 0.41 Hz in 8 and of 0.27 Hz in 7 are consistent with this assumption.

However, in 5 and 10 the J_m^{H,CH_3} values lie midway between the above extremes of 0.27 and 0.41 Hz but they are expected to lie near 0.27 Hz on the basis of the σ electron picture. There is the possibility that, because in 5 and 10 the fluorine atom is placed para to C-6 and ortho

to C-2, resonance structures of the type 13 will enhance the π electron contribution to $J_m^{\rm H, CH_3}$ and thereby partially compensate for the reduction in the σ electron contribution. This is a reasonable proposal insofar as the fluorine is located meta to the nitrogen in 5 and 10, disallowing its preferred conjugation with the latter; and a structure of type 13 certainly increases the π electron density at C-6, enlarging the relevant Cp, orbital and thereby enhancing somewhat the hyperconjugative interaction with the methyl group orbitals. A similar argument would follow for position C-4 in 5.³

In any event the contention that the π electron mechanism is relatively unaffected by the presence of the nitrogen atom is nicely supported by the values of (-) 0.17 and (-) 0.21 Hz for ${}^{6}J_{m}^{CH_{3},CH_{3}}$ in 9 and 10. They compare with a corresponding value of -0.19 Hz in a *m*-xylene derivative (16). As one or both of the methyl groups in 9 and 10 are bonded to C-2 and/or C-6 and as ${}^{6}J_{m}^{CH_{3},CH_{3}}$ is probably accounted for by a π electron mechanism (21), one may strongly infer that the nitrogen atom acts to polarize the σ electron system without affecting the π electron contribution to $J_m^{\rm H,CH_3}$ and also that structures of type 16 are unnecessary in the explanation of the coupling data. Note that ${}^{4}J_{m}^{\hat{H}_{2},H_{6}}$ in pyridine is -0.13 Hz (17), in benzene it is 1.37 Hz (33) yet $J_m^{CH_3,CH_3}$ in 10 is the same as in a *m*-xylene derivative, a good example of the application of the present model.

One may also conclude that σ electrons play a substantial part in the transmission of spin information in J_o^{H,CH_3} and J_m^{H,CH_3} , this part being proportionately larger in the latter; in agreement with recent molecular orbital calculations on toluene (21) which imply a preponderant σ electron contribution to $J_m^{\rm H, CH_3}$. If this implication is indeed valid it helps to account for the present observation of a greater sensitivity of $J_m^{\rm H,CH_3}$ than of $J_o^{\rm H,CH_3}$ to the proposed σ core polarization at the carbon atoms proximate to the nitrogen atom.

(2) The Methyl Proton – Fluorine Couplings In p-fluorotoluene J_p^{F,CH_3} is 1.15 Hz (15) while in **3** it is 1.25 Hz (2), the fluorine atom lying ortho to the nitrogen atom. In 10, where the positions of the fluorine atom and of the methyl

³This argument is perhaps an over-refinement of our model and we recognize that it smacks of "enthusiastic yodelling in the blue distance of ... conjecture''(32).

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group have been interchanged, $J_p^{\rm F,CH_3}$ is 1.21 Hz. As it is unlikely that other than a π mechanism is important for this coupling (14, 21) the heteroatom has very little influence on the π contribution to $J_p^{\rm F,CH_3}$ in 3 and 10, as predicted by the model. The variation in $J_p^{\rm H,F}$ between 1.2 and 2.5 Hz in 1–11 can therefore be attributed mainly to a σ electron effect.

Considering now $J_o^{\text{F,CH}_3}$ one has 1.45 Hz in 1 (1), 1.71 Hz in 5, 1.63 Hz in 8, and 2.1 Hz in a derivative of *o*-fluorotoluene (14), in line (1) with a dominant π electron contribution to $J_o^{\text{F,CH}_3}$; the variation in magnitude being attributable to a variable σ electron contribution to this coupling over four bonds. When the methyl group is bonded to C-2 as in 10, $J_o^{\text{F,CH}_3}$ is 3.03 Hz, representing a substantial positive shift from the magnitudes in the other compounds, and is at least qualitatively in line with the positive shift of the analogous $J_o^{\text{H,CH}_3}$ values. Nevertheless the variations are small compared to the corresponding $J_o^{\text{H,F}}$ values which range from -3.12Hz in 4 (2) to +9.85 Hz in 7.

Finally, although $J_m^{\text{H,F}}$ varies between -1.02 Hz in 1 (1) and +10.2 Hz in 8, the range of $J_m^{\text{F,CH}_3}$ is only from (-) 0.10 Hz in 6 to -0.60 Hz in 4 (2) and does not deviate greatly from its value of -0.4_3 Hz in a derivative of *m*-fluorotoluene (14). On the basis of the model the large changes in $J_m^{\text{H,F}}$ arise mainly via the distortion of the σ core by the nitrogen atom.

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(3) Ring Proton and Ring Proton – Fluorine Couplings

The data in Table 1 are in accord with the previous detailed discussion (1, 2) of such parameters in 1–4 and will not be fully described here. In brief they are consistent with an alternating (3, 34) electronegativity effect of the substituents, acting primarily through the σ electron system. Unfortunately we were unable to determine the sign of ${}^{4}J_{H_{2}}^{H_{2},H_{6}}$ in 5, 6, and 8. This coupling is negative in pyridine (17) but for 8 the additivity scheme (2) predicts + 0.1 Hz.

for 8 the additivity scheme (2) predicts + 0.1 Hz. The value of 10.2 Hz for $J_m^{H_2,F}$ in 8 is the largest known meta proton-fluorine coupling and is larger than all known $J_o^{H,F}$ values in derivatives of fluorobenzene, except that of 10.4 Hz in *o*-difluorobenzene (35).

Conclusions

The majority of the proton-proton and proton-fluorine spin-spin coupling constants in

11 methyl derivatives of the 2-, 3-, and 4fluoropyridines can be rationalized in terms of a model in which the nitrogen atom polarizes the σ electron core predominantly at C-2 and -6 but does not strongly alter the π electron contribution to the coupling mechanisms. Thus, in these compounds J_p^{H,CH_3} and J_p^{F,CH_3} are little different from their values in toluene and *p*-fluorotoluene. The results also indicate an appreciable σ electron contribution to long-range couplings over four and five bonds from methyl protons to ring protons or fluorine nuclei.

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