Reprinted from "Curr. Sci.", January 5, 1980, Vol. 49, No. 1, 1–3

NMR SPECTRA OF 2-FLUOROPYRIDINE IN NEMATIC LIQUID CRYSTALS

N. SURYAPRAKASH,[+] A. C. KUNWAR[*] AND C. L. KHETRAPAL[+*]

[+]*Bangalore NMR Facility, Indian Institute of Science, Bangalore* 560 012, *India*

[*]*Raman Research Institute, Bangalore* 560 006, *India.*

ABSTRACT

The NMR spectra of 2-fluoropyridine in two nematic liquid crystal solvents have been investigated. The direct dipole-dipole coupling constants thus derived have been used to obtain the structural information. The values of the interproton distance ratios are found to be similar to those in pyridine. The results indicate negligible anisotropic contributions of ^{1}H–^{19}F indirect couplings.

INTRODUCTION

ALTHOUGH several papers have been published on the microwave spectroscopic studies on 2-fluoropyridine, the information on the molecular structure[1,2] has been obtained from the two in-plane rotational constants with the result that several assumptions on the molecular structure had to be made and only two geometrical parameters could be derived. The ^{1}H-NMR spectrum of 2-fluoropyridine oriented in a nematic solvent, on the other hand, provides more direct dipolar couplings[3] than required for the complete determination of the structure of the proton and fluorine skeleton and the molecular orientation. In addition, a study of the molecule in different liquid crystals may give an idea on the anisotropic contributions of the indirect H–F couplings. The results are discussed in the present communication.

EXPERIMENTAL

Commercially available 2-fluoropyridine was used without further purification. ^{1}H–NMR spectra were studied in N–(p-methoxybenzylidene -p-n-butylaniline (MBBA) and Merck Phase IV. 13·5 and 8·7 mole per cent solutions in the two phases respectively were studied on a WH-270 spectrometer at 21°C. 25 scans were accumulated and Fourier transformed with 20k memory computer. Typical spectrum in Merck Phase IV is shown in Fig. 1. The spectrum has lines with widths varying from 5 Hz to 30 Hz. Such differential broadening arises because of the quadrupolar relaxation of the ^{14}N nucleus in 2-fluoropyridine. Despite large widths of some of the lines, the NMR parameters could be derived fairly accurately.

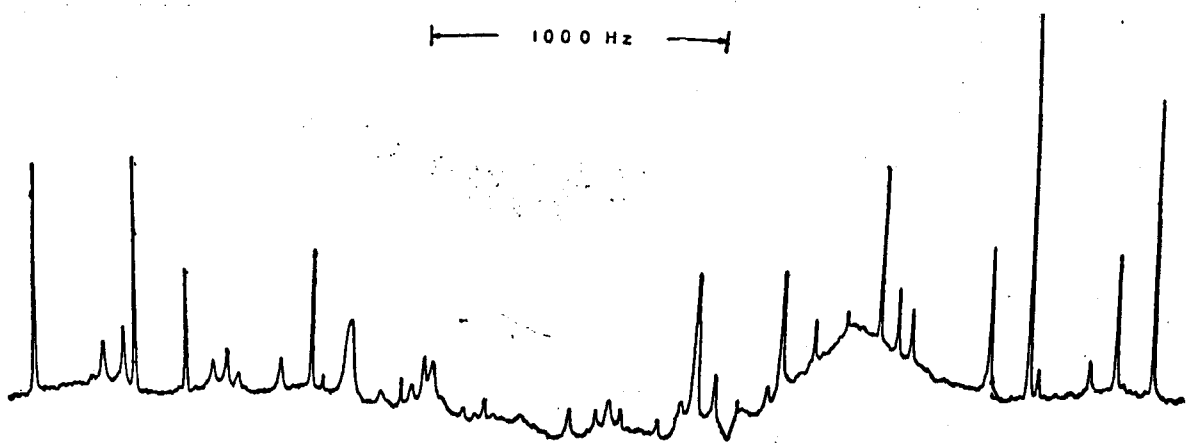


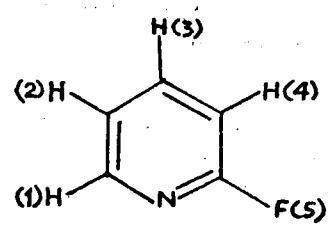
FIG. 1. The experimental NMR spectrum of 2-fluoropyridine in the nematic Merck Phase IV. Spectrometer frequency: 270 MHz; Concentration 8·7 mole per cent; Temperature : 21° C.

Spectral Analyses

The spectra were analysed on an IBM 360/44 computer using the LAOCOONOR program[4]. In the final analysis, only the direct dipolar couplings (D_{ij}'s) and the proton chemical shifts (ν_i's) were iterated upon. Indirect spin-spin coupling constants (J_{ij}'s) were given the same values as obtained from the spectrum in the isotropic phase[5]. For both the spectra, 50 lines were assigned and the derived spectral parameters are given in Table I. The errors of the parameters (Table I) are those given by the LAOCOONOR program.

TABLE I

The NMR spectral parameters obtained for 2-fluoropyridine in the nematic phase of MBBA (I) and Merck Phase IV (II) solutions*



Parameters	Value in (I) (Hz)	Value in (II) (Hz)
D_{12}	−212·81±0·08	−364·32±0·09
D_{13}	1·56±0·33	− 28·10±0·20
D_{14}	− 20·15±0·28	− 44·07±0·16
D_{15}	−100·19±0·16	−137·36±0·19
D_{23}	−144·97±0·22	−324·75±0·25
D_{24}	−100·69±0·22	−139·45±0·27
D_{25}	− 79·47±0·13	−101·21±0·15
D_{34}	−700·58±0·10	−893·20±0·09
D_{35}	− 89·95±0·31	−119·07±0·30
D_{45}	−175·03±0·35	−301·91±0·31
$\nu_2-\nu_1$	239·47±0·24	219·09±0·25
$\nu_3-\nu_1$	130·30±0·57	113·03±0·40
$\nu_4-\nu_1$	353·56±0·56	343·71±0·40

* Indirect spin-spin coupling constants have been taken from the literature[5]. $J_{12} = 4·88$, $J_{13} = 2·14$, $J_{14} = 0·81$, $J_{15} = 0·00$, $J_{23} = 7·16$, $J_{24} = 0·83$, $J_{25} = 2·49$, $J_{34} = 8·18$, $J_{35} = 8·19$ and $J_{45} = -2·63$ Hz.

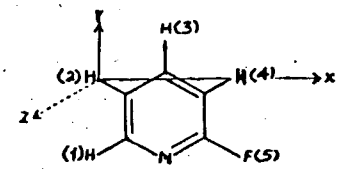
RESULTS AND DISCUSSIONS

The spectral analysis provides 10 different dipolar coupling constants. Since 2-fluoropyridine has one plane of symmetry, the molecular order is described by three independent S-parameters. Six internuclear distance ratios suffice for the complete specification of the geometry of the proton-fluorine skeleton. Thus, from the 10 dipolar couplings, six internuclear distance ratios and three order parameters should be determined. The system is overdetermined by one coupling constant as far as the determination of the structure of the proton and fluorine skeleton and molecular order is concerned. The computer program SHAPE[6] was used to derive the 'best fit' molecular geometry and the order parameters. The Root-mean-square error and the deviation between the observed and the calculated dipolar couplings were much less than the experimental error of the coupling constants in each case. The results are given in Table II. The agreement of the results in the two liquid crystals and the internal self-consistency of the direct dipolar couplings indicate negligible contributions of the anisotropy of the indirect couplings.

It is seen from Table II that the interproton distance ratios in 2-fluoropyridine do not deviate from those in pyridine included within parantheses in Table II. This justifies the assumption made in the microwave investigations[1,2].

TABLE II

Internuclear distance ratios in 2-fluoropyridine in MBBA (I) and Merck Phase IV (II) and in Pyridine[7]



Parameter	Value for 2-fluoropyridine in (I)	Value for 2-fluoropyridine in (II)
r_{12}/r_{24}	0·581	0·577
	(0·579)+	(0·579)+
r_{15}/r_{24}	0·986	0·990
r_{23}/r_{24}	0·586	0·581
	(0·583)+	(0·583)+
r_{25}/r_{24}	1·177	1·178
r_{34}/r_{24}	0·581	0·582
	(0·583)+	(0·583)+
r_{45}/r_{24}	0·593	0·595
S_{xx}*	0·0669	0·0926
S_{yy}	0·0233	0·0424
S_{zz}	−0·0902	−0·1350
S_{xy}	−0·0409	−0·0424

+ Average values for pyridine from the literature[7].

* $r_{24} = 4·3038$ Å (Assumed; Pyridine Value[8]). The right-handed Cartesian coordinate system used with X-axis joining protons 2 and 4 and Y-axis perpendicular to it in the plane of the ring.

By fixing the coordinates of the protons 2 and 4 and those of the ring atoms as those in pyridine[8] and using the distance ratios given in Table II, the C–F distance is estimated as 1·270 Å in Merck Phase IV and 1·265 Å in MBBA. These are small

compared to the normal value of 1·354 Å[9–10] for C(sp^2)–F distances. A similar tendency was observed in the microwave studies; when the ring was assumed undistorted (same geometry as that of pyridine), the C–F bond distance was obtained as 1·297 Å. The microwave results were interpreted in terms of the 'caving-in' of the ring. The NMR results are in agreement with the view.

The molecular orientation of 2-fluoropyridine is like that of most of the aromatics in the nematic phases[3]. The molecule orients preferentially with its plane along the magnetic field direction. The principal axis system for the order-parameter tensor is rotated by −31·0° in MBBA and −29·7° in Merck Phase IV solutions. The largest principal S value then almost points along the direction F–H(2) with values of 0·0915 and 0·1168 in MBBA and Merck Phase IV solutions respectively. The largest molecular dimensions are also along the F–H(2) direction.

1. Sharma, S. D. and Doraiswamy, S., *Curr. Sci.*, 1972, **41**, 475.
2. — and —, *Chem. Phys. Lett.*, 1976, **41**, 192.
3. Khetrapal, C. L. and Kunwar, A. C., *Adv. Magn. Resonance*, 1977, **9**, 301.
4. Diehl, P., Khetrapal, C. L. and Kellerhals, H. P., *Mol. Phys.*, 1968, **15**, 333.
5. Thomas, W. A., and Griffin, G. E., *Org. Magn. Resonance*, 1970, **2**, 503.
6. Diehl, P., Henrichs, P. M. and Niederberger, W., *Mol. Phys.*, 1971, **20**, 139.
7. Schumann, C. and Price, R., *Angew. Chem. (Int. Ed.)*, 1973, **12**, 930.
8. Sorensen, G. O., Mahler, L. and Andersen, N. R., *J. Mol. Struct.*, 1974, **20**, 119.
9. Nygaard, L., Bojesen, I., Pedersen, T. and Andersen, J. R., *Ibid.*, 1968, **2**, 209.
10. Yokozeki, A. and Bauer, S. H., *Topics Current Chem.*, 1975, **53**, 78.