NMR SPECTRA OF 2-FLUOROPYRIDINE IN NEMATIC LIQUID CRYSTALS

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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 $^1H-^{19}F$ 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 ^1H-NMR spectrum of 2-fluoropyridine oriented in a nematic solvent, on the other hand,

(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.
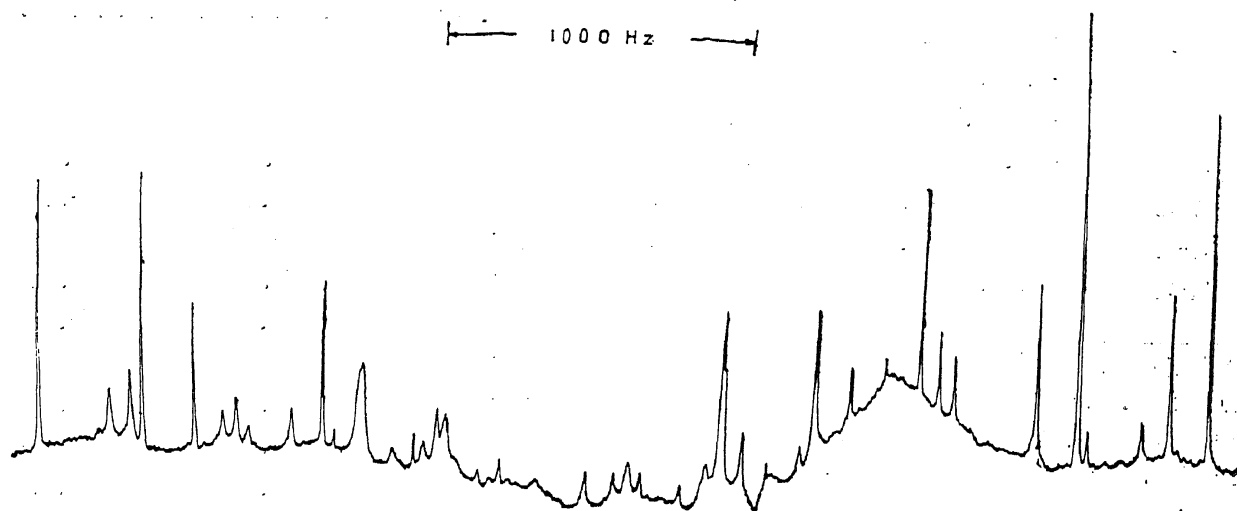

|— 1000 Hz —|

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.

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. ^1H-NMR spectra were studied in N-(p-methoxybenzylidene-p-n-butylaniline

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-fluoro-pyridine in the nematic phase of MBBA (I) and Merck Phase IV (II) solutions
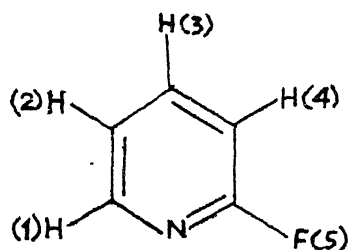
Parameters	Value in (I) (Hz)	Value in (II) (Hz)
D_{12}	$-212 \cdot 81 \pm 0 \cdot 08$	$-364 \cdot 32 \pm 0 \cdot 09$
D_{13}	$1 \cdot 56 \pm 0 \cdot 33$	$- 28 \cdot 10 \pm 0 \cdot 20$
D_{14}	$- 20 \cdot 15 \pm 0 \cdot 28$	$- 44 \cdot 07 \pm 0 \cdot 16$
D_{15}	$-100 \cdot 19 \pm 0 \cdot 16$	$-137 \cdot 36 \pm 0 \cdot 19$
D_{23}	$-144 \cdot 97 \pm 0 \cdot 22$	$-324 \cdot 75 \pm 0 \cdot 25$
D_{24}	$-100 \cdot 69 \pm 0 \cdot 22$	$-139 \cdot 45 \pm 0 \cdot 27$
D_{25}	$- 79 \cdot 47 \pm 0 \cdot 13$	$-101 \cdot 21 \pm 0 \cdot 15$
D_{34}	$-700 \cdot 58 \pm 0 \cdot 10$	$-893 \cdot 20 \pm 0 \cdot 09$
D_{35}	$- 89 \cdot 95 \pm 0 \cdot 31$	$-119 \cdot 07 \pm 0 \cdot 30$
D_{45}	$-175 \cdot 03 \pm 0 \cdot 35$	$-301 \cdot 91 \pm 0 \cdot 31$
$v_2 - v_1$	$239 \cdot 47 \pm 0 \cdot 24$	$219 \cdot 09 \pm 0 \cdot 25$
$v_3 - v_1$	$130 \cdot 30 \pm 0 \cdot 57$	$113 \cdot 03 \pm 0 \cdot 40$
$v_4 - v_1$	$353 \cdot 56 \pm 0 \cdot 56$	$343 \cdot 71 \pm 0 \cdot 40$

* Indirect spin-spin coupling constants have been taken from the literature[5]. $J_{12} = 4 \cdot 88$, $J_{13} = 2 \cdot 14$, $J_{14} = 0 \cdot 81$, $J_{15} = 0 \cdot 00$, $J_{23} = 7 \cdot 16$, $J_{24} = 0 \cdot 83$, $J_{25} = 2 \cdot 49$, $J_{34} = 8 \cdot 18$, $J_{35} = 8 \cdot 19$ and $J_{45} = -2 \cdot 63$ 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]
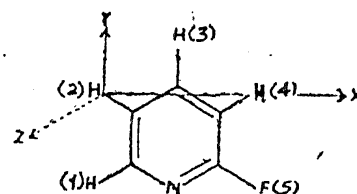
Parameter	Value for 2-fluoropyridine	
	in (I)	in (II)
r_{12}/r_{24}	$0 \cdot 581$	$0 \cdot 577$
	$(0 \cdot 579)^+$	$(0 \cdot 579)^+$
r_{15}/r_{24}	$0 \cdot 986$	$0 \cdot 990$
r_{23}/r_{24}	$0 \cdot 586$	$0 \cdot 581$
	$(0 \cdot 583)^+$	$(0 \cdot 583)^+$
r_{25}/r_{24}	$1 \cdot 177$	$1 \cdot 178$
r_{34}/r_{24}	$0 \cdot 581$	$0 \cdot 582$
	$(0 \cdot 583)^+$	$(0 \cdot 583)^+$
r_{45}/r_{24}	$0 \cdot 593$	$0 \cdot 595$
S_{xx}*	$0 \cdot 0669$	$0 \cdot 0926$
S_{yy}	$0 \cdot 0233$	$0 \cdot 0424$
S_{zz}	$-0 \cdot 0902$	$-0 \cdot 1350$
S_{xy}	$-0 \cdot 0409$	$-0 \cdot 0424$

+ Average values for pyridine from the literature[7].
* $r_{24} = 4 \cdot 3038$ 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 $1 \cdot 270$ Å in Merck Phase IV and $1 \cdot 265$ Å in MBBA. These are small

compared to the normal value of 1·354 Å[9-10] for C(sp²)–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 ¹1·297 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.

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A STANDARD SYSTEM OF KEYS FOR PROGRAMMABLE CALCULATORS

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ABSTRACT

A standard system of keys involving 36 keys that are used for programming has been proposed for a calculator.

INTRODUCTION

PROGRAMMABLE calculators (PCs) will become widespread in the near future. These are suitable machines for processing small scale data. Programming in a calculator is a much more challenging task than programming in a higher level language such as FORTRAN. Here all the manipulations have to be made within the very limited capacity of the machine. At present the use of a programme is confined to that particular model alone. One way to get over this difficulty is to choose the most popular brand as standard and then to identify and redesignate the keys of other machines by those of the standard. Sometimes two or more keys have to be identified with a single key of the standard or *vice versa*. If the keys are designated by a single symbol, the programme will look elegant. Unfortunately in the existing PCs many of the keys are characterised by more than one symbol and so are not suitable for treating as standard. Further, not all keys given are necessary. The author discusses a few keys of PCs (each designated by a single symbol) which are capable of solving problems that require versatility of the order of

FORTRAN. Once the keys of a PC are identified with those given here, programmes can be written using these symbols. In this manner, calculator programmes, like computer programmes, can be made machine independent. A programme written in this system or a particular calculator will have to be slightly modified in the same way as a computer programme, to run in other machines. In short, this system will serve the purpose of a language for PCs.

MATERIALS AND METHODS

The PC discussed in this paper has the following features.

Programme steps

Each pressing of a key is reckoned as a programme step or simply step for brevity. A step can be stored in what is called a programme memory. There are 1000 programme memories serially numbered in three digits from 000 to 999. A step is always associated with a programme memory where it is stored. We call the serial number of this programme memory as step number. There is a place in the machine,