Nitrogen Hyperfine Structure in the Rotational Spectra of Perfluoropyridine and Other Pyridine Derivatives

N. Heineking and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

Z. Naturforsch. **42 a**, 207–210 (1987); received October 30, 1986

We resolved and analysed the nitrogen nuclear quadrupole hyperfine structure (hfs) in the rotational spectrum of perfluoropyridine C_5F_5N. The results are discussed and compared with those of previously measured pyridine compounds.

The nitrogen nuclear quadrupole coupling in perfluoropyridine has been reinvestigated by means of microwave Fourier transform (MWFT) spectroscopy [1]. The accuracy of the results allows an interpretation of the coupling constants in terms of electronic parameters of the nitrogen nucleus molecular environment. These are compared with values obtained for pyridine itself, pyridine-[4-D] [2], 4-chloropyridine [3], 4-cyanopyridine [4], and 2,6-difluoropyridine [5].

Perfluoropyridine was first investigated by Doraiswamy and Sharma [6]. They used a conventional Stark modulated microwave spectrometer and reported the rotational and quadrupole coupling constants. The latter indicated an almost cylindrically symmetric electric field gradient tensor at the nitrogen nucleus.

The reinvestigation with the higher resolution of our MWFT spectrometer in the frequency range from 8.0 to 12.4 GHz [7] led to more reliable values for the rotational and quadrupole coupling constants and to a confirmation of the symmetry mentioned above.

The substance, a colorless, volatile liquid, was purchased from Aldrich Chemie, Steinheim. The spectra were recorded at temperatures of approximately $-40\,^{\circ}C$ and pressures below 1.5 mTorr (0.2 Pa). A sample of the measurements is given in Figure 1, showing the $J_{K_-K_+} = 13_{9,4} - 13_{8,5}$ and $20_{10,10} - 20_{9,11}$ rotational transitions, both triply split by the nitrogen nuclear quadrupole coupling. A listing of the recorded transitions is given in Table 1.

The hfs analysis was carried out as described in [2] for pyridine. The hypothetical unsplit transition frequencies were evaluated by adding the hfs corrections to the frequencies of the strongest multiplet components.

The lower J transition frequencies were then used to refine the rotational constants assuming rigidity of the molecule. We used our programs HT1NQ [8] and DH14KS [9] for the hfs- and DH9 [10] for the rigid rotor analysis. The results are given in Table 2.

The interpretation of the nitrogen nuclear coupling in substituted pyridines follows Gordy and Cook [11]. Because the two orbitals which form the N–C bonds are equivalent, there are only three electronic parameters unknown: the ionic character of the σ bonds i_σ, the hybridization parameter a_s^2, and the polarization i_π of the π-bond. From the CNC angle, which is known to be 117° [12] for pyridine and assumed to be the same for the substituted species, a_s^2 can be evaluated to $a_s^2 = 0.312$ [13].

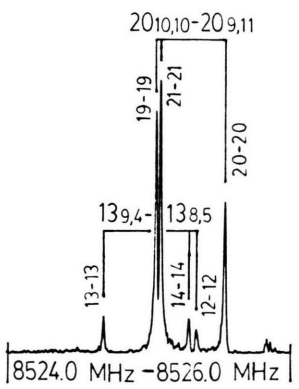

Fig. 1. Rotational transitions $J_{K_-K_+} = 13_{9,4} - 13_{8,5}$ and $20_{10,10} - 20_{9,11}$ of perfluoropyridine. Hyperfine components labelled with F quantum numbers. Range 2 MHz out of a 5 MHz recording. Cell temperature: $-33\,^{\circ}C$. Gas pressure: 0.3 mTorr = 0.04 Pa. Polarizing frequency: 8522.0 MHz. 10^7 averaging cycles. Spectral point distance: 5 kHz.

Reprint requests to Prof. Dr. H. Dreizler, Abteilung Chemische Physik im Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstr. 40, D-2300 Kiel 1, FRG.

0340-4811 / 87 / 0200-0207 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. Measured rotational transitions of perfluoropyridine. ν improved frequency of the hfs component, $\Delta\nu$ splitting referred to the strongest component, ν_0 hypothetical unsplit line frequency, $\Delta(\Delta\nu) = \Delta\nu - \Delta\nu_{calc}$, deviation of the splitting, $\Delta\nu_{calc}$ theoretical hyperfine splitting calculated with constants from Table 2, $\Delta\nu_0$ deviation from rigid rotor spectrum (derived from transition frequencies marked with asterisks).

$J'\ K'_-\ K'_+ - J''\ K''_-\ K''_+$	$F' - F''$	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ [kHz]	$\Delta\nu_0$ [kHz]
3 3 0 – 2 2 1	2 – 1	8 453.662	– 0.195		+ 3	
	4 – 3	8 453.857		8 453.888*		– 1
	3 – 2	8 454.049	+ 0.192		– 2	
3 3 1 – 2 2 0	3 – 2	8 151.093	– 0.688		– 2	
	4 – 3	8 151.781		8 151.610*		0
	2 – 1	8 152.023	+ 0.242		– 6	
4 3 1 – 3 2 2	3 – 2	10 832.038	– 0.186		+ 5	
	5 – 4	10 832.224		10 832.422*		– 1
	4 – 3	10 832.964	+ 0.740		– 3	
4 3 2 – 3 2 1	4 – 3	9 475.474	– 1.071		– 11	
	5 – 4	9 476.545		9 476.282*		+ 6
	3 – 2	9 476.917	+ 0.372		– 9	
5 2 4 – 4 1 3	5 – 4	8 335.626	– 0.621		+ 2	
	6 – 5	8 336.247		8 336.081*		0
	4 – 3	8 336.410	+ 0.163		+ 4	
5 3 3 – 4 2 2	5 – 4	10 496.948	– 1.079		– 7	
	6 – 5	10 498.027		10 497.745*		– 4
	4 – 3	10 498.321	+ 0.294		– 2	
6 3 3 – 5 4 2	5 – 4	8 618.099	– 0.251		+ 4	
	7 – 5	8 618.350		8 618.783*		0
	6 – 5	8 619.868	+ 1.518		+ 1	
8 4 4 – 7 5 3	7 – 6	11 960.647	– 0.149		+ 3	
	9 – 8	11 960.796		11 961.169		– 7
	8 – 7	11 962.046	+ 1.250		– 4	
8 8 0 – 8 7 1	8 – 8	8 740.452	– 0.674		+ 3	
	9 – 9	8 741.126		8 740.926		– 95
	7 – 7	8 741.218	+ 0.092		+ 7	
13 9 4 – 13 8 5	13 – 13	8 524.686	– 0.601		+ 5	
	14 – 14	8 525.287		8 525.100		–143
	12 – 12	8 525.337	+ 0.050		+ 3	
13 10 3 – 13 9 4	13 – 13	10 492.896	– 0.441		+ 5	
	14 – 14	10 493.337		10 493.199		–199
	12 – 12	10 493.373	+ 0.036		+ 2	
18 11 7 – 18 10 8	18 – 18	8 843.077	– 0.561		0	
	20 – 20	8 843.638		8 843.461		–228
	19 – 19	8 843.670	+ 0.032		+ 1	
20 10 10 – 20 9 11	19 – 19	8 525.060	– 0.024		– 1	
	21 – 21	8 525.084		8 525.228		–278
	20 – 20	8 525.538	+ 0.454		0	

The normalized valence orbitals of the nitrogen atom are

$$\psi_1 = (1 - 2a_s^2)^{1/2}\,\psi_s + (2a_s^2)^{1/2}\,\psi_{p_z} \quad \text{(lone pair)}$$

$$\psi_{2,3} = (a_s^2)^{1/2}\,\psi_s - (1/2 - a_s^2)^{1/2}\,\psi_{p_z} \pm (1/2)^{1/2}\,\psi_{p_x} \quad (1)$$
$$(\sigma \text{ bonds})$$

$$\psi_4 = \psi_{p_y} \quad (\pi \text{ bond})$$

with

a_s^2 = amount of s character in σ bond,
z = symmetry axis,
y = axis perpendicular to molecular plane,
x = in-plane-axis.

The population numbers of these orbitals are

$$n(\psi_1) = 2;\ n(\psi_2) = n(\psi_3) = 1 + i_\sigma;\ n(\psi_4) = 1 + i_\pi \quad (2)$$

and from (1) with orthonormality for the occupation numbers

$$\begin{aligned} n(p_x) &= 1 + i_\sigma, \quad n(p_y) = 1 + i_\pi, \\ n(p_z) &= (1 + i_\sigma)(1 - 2a_s^2) + 4a_s^2, \\ n(\sigma) &= 2 - 2a_s^2(1 - i_\sigma). \end{aligned} \quad (3)$$

Table 2. Rotational and quadrupole coupling constants [MHz] of perfluoropyridine. σ standard deviation of the fit [kHz]. $|(A, B)|$ maximum correlation coefficient. Derived parameters below the line (single standard errors in units of last digit).

		[6]
A	= 1481.5813(3)	1481.539(3)
B	= 1075.3725(2)	1075.384(4)
C	= 623.1115(4)	623.101(1)
σ	= 4	
$\|(A, B)\|$	= 0.57	
χ^+	= − 1.97(1)	
χ^-	= − 5.90(2)	
σ	= 5	
$\|(\chi^+, \chi^-)\|$	= 0.71	
χ_{aa}	= 1.97(1)	1.94(25)
χ_{bb}	= − 3.94(1)	− 4.08(6)
χ_{cc}	= 1.97(1)	2.14(25)

Table 3. Ring nitrogen nuclear quadrupole coupling constants and derived electronic parameters of pyridine compounds. i_π, i_σ polarization of π and σ bond respectively.

Compound	Coupling constants (MHz)	Derived parameters
Perfluoropyridine [this work]	$\chi_{xx} = \chi_{aa} = +1.97(1)$ $\chi_{zz} = \chi_{bb} = -3.94(1)$	$i_\pi = 20.4\%$ $i_\sigma = 20.3\%$
2,6-Difluoro-pyridine [5]	$\chi_{xx} = \chi_{aa} = +1.82(5)$ $\chi_{zz} = \chi_{bb} = -4.16(2)$	$i_\pi = 16.0\%$ $i_\sigma = 20.3\%$
4-Chloro-pyridine-[^{35}Cl] [3]	$\chi_{xx} = \chi_{bb} = +1.64(4)$ $\chi_{zz} = \chi_{aa} = -4.81(1)$	$i_\pi = 5.4\%$ $i_\sigma = 17.6\%$
4-Chloro-pyridine-[^{37}Cl] [3]	$\chi_{xx} = \chi_{bb} = +1.5(1)$ $\chi_{zz} = \chi_{aa} = -4.7(1)$	$i_\pi = 6\%$ $i_\sigma = 20\%$
Pyridine [2]	$\chi_{xx} = \chi_{bb} = +1.434(3)$ $\chi_{zz} = \chi_{aa} = -4.908(3)$	$i_\pi = 2.70\%$ $i_\sigma = 18.96\%$
Pyridine-[4-D] [2]	$\chi_{xx} = \chi_{bb} = +1.442(5)$ $\chi_{zz} = \chi_{aa} = -4.907(3)$	$i_\pi = 2.76\%$ $i_\sigma = 18.89\%$
4-Cyanopyridine [4]	$\chi_{xx} = \chi_{bb} = +1.41(11)$ $\chi_{zz} = \chi_{aa} = -5.02(4)$	$i_\pi = 1.0\%$ $i_\sigma = 18.4\%$

The quadrupole coupling constants may then be expressed by

$$\frac{\chi_{zz}}{eQq_{210}} = \frac{2a_s^2 + (1/2 - 2a_s^2)\, i_\sigma - 1/2\, i_\pi}{1 + 2\varepsilon\, i_\sigma + \varepsilon\, i_\pi},$$
$$\frac{\chi_{xx}}{eQq_{210}} = \frac{-a_s^2 + (1/2 + a_s^2)\, i_\sigma - 1/2\, i_\pi}{1 + 2\varepsilon\, i_\sigma + \varepsilon\, i_\pi}, \tag{4}$$

where the charge correction [14] is applied ($\varepsilon = 0.3$, $eQq_{210} = -9.38$ MHz [15]).

Rearrangement of these equations leads to

$$\{4\varepsilon\chi_{zz} - (1 - 4a_s^2)\, eQq_{210}\}\, i_\sigma + \{2\varepsilon\chi_{zz} + eQq_{210}\}\, i_\pi = -2\chi_{zz} + 4a_s^2\, eQq_{210},$$
$$\{4\varepsilon\chi_{xx} - (1 + 2a_s^2)\, eQq_{210}\}\, i_\sigma + \{2\varepsilon\chi_{xx} + eQq_{210}\}\, i_\pi = -2\chi_{xx} - 2a_s^2\, eQq_{210}. \tag{5}$$

Introducing the abbreviations

$$a = 4\varepsilon\chi_{zz} - (1 - 4a_s^2)\, eQq_{210},$$
$$b = 2\varepsilon\chi_{zz} + eQq_{210},$$
$$c = -2\chi_{zz} + 4a_s^2\, eQq_{210},$$
$$d = 4\varepsilon\chi_{xx} - (1 + 2a_s^2)\, eQq_{210},$$
$$e = 2\varepsilon\chi_{xx} + eQq_{210},$$
$$f = -2\chi_{xx} - 2a_s^2\, eQq_{210}. \tag{6}$$

(5) simplifies to

$$a \cdot i_\sigma + b \cdot i_\pi = c,$$
$$d \cdot i_\sigma + e \cdot i_\pi = f, \tag{7}$$

and therefore

$$i_\sigma = \frac{ce - bf}{ae - bd} \quad \text{and} \quad i_\pi = \frac{af - cd}{ae - bd}. \tag{8}$$

Insertion of the experimental data χ_{gg}, $g = x, z$ in (6) followed by application of (8) yields the results given in Table 3.

Contrary to the i_σ values, the results for i_π show a significant variation from perfluoropyridine (highest) to 4-cyanopyridine (lowest value). Although the derived data might not be very exact due to the simplifying assumptions of the model, the relationship between the electron excess i_π and the π donor (or acceptor) quality of the substituent is obvious. While the halogens tend to form double bonds to the adjacent ring carbon atom, thus raising the electron density in the ring π orbital (mesomeric or $+M$-effect), the cyano group lowers the π electron density ($-M$-effect) by drawing electrons out of the ring. In organic chemistry, these effects are known from reactivity phenomena, but cannot be measured directly. However, some predictions can be made concerning other pyridine derivatives. Nitro groups e.g. are supposed to be comparable to the cyano group considering their influences on the ring π system. Therefore, the ring nitrogen coupling tensor of 4-nitropyridine should resemble that of 4-cyanopyridine, while in case of 4-aminopyridine the coupling constants should be similar to those of 4-chloropyridine. Both substances mentioned have not yet been investigated with respect to their quadrupole coupling.

Acknowledgements

We thank the members of our group for help and discussions, the Deutsche Forschungsgemeinschaft and Fonds der Chemie for funds. The calculations were made at the computer centre of the Kiel University.

[1] H. Dreizler, J. Mol. Phys. **59,** 1 (1986).
[2] N. Heineking, H. Dreizler, and R. Schwarz, Z. Naturforsch. **41 a,** 1210 (1986).
[3] N. Heineking and H. Dreizler, Z. Naturforsch. (1986), **41 a,** 1297 (1986).
[4] N. Heineking and H. Dreizler, Z. Naturforsch. (1986), to be published.
[5] O. L. Stiefvater, S. Lui, and J. A. Ladd, Z. Naturforsch. **31 a,** 53 (1976).
[6] S. Doraiswamy and S. D. Sharma, Chem. Phys. **6,** 76 (1974).
[7] G. Bestmann and H. Dreizler, Z. Naturforsch. **37 a,** 58 (1982).
[8] Author: G. Herberich, Aachen.
[9] Author: H. Mäder, Kiel.
[10] Author: G. Herberich, Aachen.
[11] W. Gordy and R. L. Cook, Microwave Molecular Spectra, John Wiley & Sons, New York 1984, 3rd edition; chapter 14.13.
[12] G. O. Sørensen, L. Mahler, and N. Rastrup-Andersen, J. Mol. Struct. **30,** 119 (1974).
[13] P. W. Atkins, Molecular Quantum Mechanics, Oxford University Press, 1983, 2nd Edition; p. 270 (10.83).
[14] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, Dover Publications Inc., New York 1955, chapter 9.4.
[15] W. Kasten, H. Dreizler, and R. L. Kuczkowski, Z. Naturforsch. **40 a,** 1262 (1985).