Nuclear Quadrupole Coupling Effects in the Rotational Spectrum of 4-Cyanopyridine

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The quadrupole coupling of the two nitrogen nuclei was investigated by microwave Fourier transform spectroscopy. The results contribute to a comparison of substituent effects in different pyridine derivatives.

We investigated the nitrogen hyperfine structure (hfs) in the rotational spectrum of 4-cyanopyridine or isonicotinonitrile, $C_6H_4N_2$, by use of microwave Fourier transform (MWFT) spectroscopy [1]. This paper is the third in a series, in which the effects of different substituents on the electronic environment of the pyridine ring nitrogen nucleus are compared.

The pure rotational spectrum of 4-cyanopyridine has been analysed by Ford [2], who reported the rotational constants and the dipole moment. He could not resolve the complex hyperfine structure.

Using our MWFT-spectrometers in the range from 5.3 to 26 GHz [3–6] we recorded some thirty rotational transitions at pressures of 0.4–1.5 mTorr (0.05–0.2 Pa) and temperatures between +25 °C and −20 °C. The hyperfine structure could not always be completely resolved, but the information gained proved sufficient to distinguish the two nitrogen nuclei and allowed an interpretation of the quadrupole coupling.

The white, crystalline substance (mp.: 78 °C) was purchased from FLUKA, Neu-Ulm, and sublimated for purification.

A selection of the measurements is given in Table 1. The complete list is available under TNA 6 at the Universitätsbibliothek Kiel*. The multiplets were simulated by line shape analysis [7] to account for interference of neighbouring components. A sample of the recordings is given in Fig. 1, showing the K-doublet transitions $J_{K_-K_+} = 8_{71} - 7_{70}$ and $8_{72} - 7_{71}$ split into nine hyperfine components by the coupling effects of the two nitrogen nuclei.

The nuclear quadrupole coupling energies being small compared with the rotational energy, a first order hfs analysis [8] is sufficient. Because the coupling energies of the ring and cyano nitrogen nuclei are of equal magnitude we predetermined the hfs by use of the three possible coupling schemes ($I_1 = I$ (ring N), $I_2 = I$ (cyano N))

$$F_1 = J + I_1; \quad F_1 + I_2 = F;$$
$$F_1 = J + I_2; \quad F_1 + I_1 = F;$$
$$I = I_1 + I_2; \quad J + I = F.$$

We used the coupling constants of pyridine ($\chi_{aa} = -4.908(3)$ MHz, $\chi_{bb} = 1.434(3)$ MHz, $\chi_{cc} = 3.474(3)$ MHz, $\eta = |(\chi_{bb} - \chi_{cc})/\chi_{aa}| = 0.416(2)$ [9]) for the

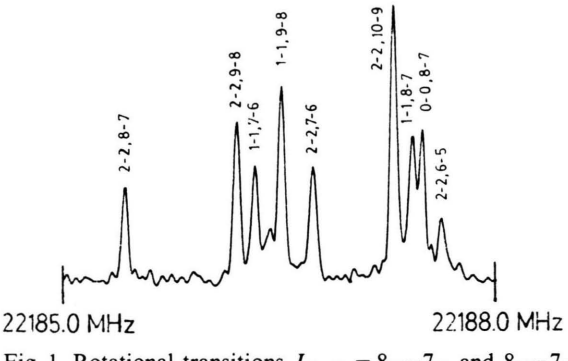

Fig. 1. Rotational transitions $J_{K_-K_+} = 8_{71} - 7_{70}$ and $8_{72} - 7_{71}$ of 4-cyanopyridine, showing nuclear quadrupole hyperfine structure (I and F quantum numbers given). A range of 3 MHz out of a 25 MHz recording, polarizing frequency 22187 MHz, cell temperature 8 °C, gas pressure 0.4 mTorr = 0.05 Pa, $8 \cdot 10^6$ averaging cycles, sampling interval 20 ns. 1024 data points were supplemented by 3072 zeros prior to Fourier transformation.

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Table 1. Selection of measured rotational transitions of 4-cyanopyridine. ν observed frequencies, $\Delta\nu$ hyperfine splittings referred to strongest multiplet components. ν_0 unsplit transition frequencies, $\Delta(\Delta\nu)$ deviations of the splittings from calculated values, $\Delta\nu_0$ deviations from rigid rotor spectrum. The latter two were calculated with the quadrupole and rotational constants from Table 2.

J'	K'_-	K'_+	$-J''$	K''_-	K''_+	$I'-I''$,	$F'-F''$	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ [kHz]	$\Delta\nu_0$ [kHz]
2	0	2	−1	0	1	1−1,	3−2	5518.130	−0.294		0	
						1−1,	2−1	5518.259	−0.165		+34	
						2−2,	4−3	5518.424		5518.222*		−11
						2−2,	3−2	5518.518	+0.094		+12	
2	1	1	−1	1	0	1−1,	3−2	5849.378	−0.706		+11	
						2−2,	4−3	5850.084		5849.538*		+12
2	1	2	−1	1	1	1−1,	3−2	5218.999	−0.774		−22	
						2−2,	4−3	5219.773		5219.190*		+10
3	0	3	−2	0	2	2−2,	2−1	8236.660	−0.793		+17	
						2−2,	3−2	8237.141	−0.312		− 4	
						0−0,	3−2					
						1−1,	4−3	8237.271	−0.182		−30	
						1−1,	3−2					
						2−2,	5−4	8237.453		8237.327*		− 2
						2−2,	4−3					
						1−1,	2−1	8237.552	+0.099		+15	
3	1	2	−2	1	1	2−2,	3−2	8763.349	−0.832		+ 5	
						2−2,	2−1	8763.735	−0.446		−12	
						2−2,	4−3					
						1−1,	2−1	8763.820	−0.361		+ 8	
						1−1,	4−3					
						0−0,	3−2	8764.181		8763.946*		+ 3
						2−2,	5−4					
						1−1,	3−2	8764.262	+0.081		+ 2	
3	1	3	−2	1	2	2−2,	3−2	7818.306	−0.888		+16	
						2−2,	2−1	7818.700	−0.494		+14	
						2−2,	4−3					
						1−1,	2−1	7818.833	−0.361		+27	
						1−1,	4−3					
						2−2,	1−0	7819.083	−0.111		−28	
						0−0,	3−2					
						2−2,	5−4	7819.194		7818.917*		+ 5
						1−1,	3−2					
3	2	1	−2	2	0	2−2,	3−2	8363.716	−2.669		− 7	
						1−2,	4−3	8364.321	−2.064		−29	
						2−2,	4−3	8364.403	−1.982		−19	
						1−1,	2−1	8364.595	−1.790		− 1	
						1−1,	4−3	8365.374	−1.011		− 8	
						2−1,	4−3	8365.435	−0.950		−19	
						2−2,	5−4	8366.385		8365.724*		− 3
						1−1,	3−2	8366.853	+0.468		−16	
						2−2,	2−1					
						0−1,	3−2					
						2−2,	1−1					
						1−0,	3−2	8367.242	+0.857		−14	
						0−0,	3−2					
3	2	2	−2	2	1	2−2,	3−2	8299.480	−2.704		−14	
						2−2,	4−3	8300.169	−2.015		−10	
						1−1,	2−1	8300.311	−1.873		−36	
						1−1,	4−3	8301.189	−0.995		−11	
						2−2,	5−4	8302.184		8301.520*		−10
						1−1,	3−2	8302.671	+0.487		− 9	
						2−2,	2−1					
						0−0,	3−2	8303.054	+0.870		− 5	

ring nitrogen and those of benzonitrile ($\chi_{aa} = -4.187(70)$ MHz, $\chi_{bb} = 2.301(53)$ MHz, $\chi_{cc} = 1.886(53)$ MHz, $\eta = 0.099(30)$ [10]) for the cyano nitrogen. All calculations gave the same result. In Table 1 we give the quantum numbers of the third coupling scheme.

For each multiplet, the hypothetical unsplit transition frequency was calculated by adding the hfs correction to the frequency of the strongest component. The low-J-transitions (up to J = 3) were used for a rigid rotor analysis to refine the rotational constants. This refinement did not influence the hfs analysis. We used our programs Q2SIM [11], Q2FIT [12], and QUAD2 [13] for the hfs- and DH9 [14] for the rotational analysis. The rotational and nuclear quadrupole coupling constants are given in Table 2. The assignment to the two nitrogen nuclei was based on a comparison with the coupling constants of pyridine and benzonitrile.

An interpretation of the ring nitrogen coupling will be given in a forthcoming paper. The discussion of the cyano nitrogen coupling is comparable to that of the chlorine coupling in aryl chlorides [15]. Unfortunately one has to make more assumptions:

The cyano nitrogen is σ bonded by a partially s-hybridized p_z orbital, and π bonded by two p_x and p_y orbitals, respectively. The counterhybridized orbital contains the lone pair electrons. Because the polarisations i_σ, i_{π_z}, and i_{π_y} of the σ, π_x, and π_y bonds and the hybridization parameter a_s^2 are unknowns there are four parameters and only two experimental data. We assume that the π_x bond in the molecular plane is entirely homeopolar, i.e. $i_{\pi_z} = 0$, and that the ionicity of the σ bond is 25%. This follows from the electronegativities of nitrogen and carbon with an empirical relation [16]. The occupation numbers of the nitrogen p orbitals are then given by

$$n_x = 1\,,\quad n_y = 1 + i_{\pi_y}\,,\quad n_z = (1 + i_\sigma)\,(1 - a_s^2) + 2a_s^2. \quad (1)$$

With the charge correction [17] applied, the following expressions result [18]:

$$\chi_{zz} = \chi_{aa} = \frac{a_s^2(1 - i_\sigma) + i_\sigma - \frac{1}{2} i_{\pi_y}}{1 + \varepsilon \cdot i_\sigma + \varepsilon \cdot i_{\pi_y}} eQq_{210}\,, \quad (2)$$

$$\chi_{xx} = \chi_{bb} = \frac{-\frac{1}{2} a_s^2(1 - i_\sigma) - \frac{1}{2} i_\sigma - \frac{1}{2} i_{\pi_y}}{1 + \varepsilon \cdot i_\sigma + \varepsilon \cdot i_{\pi_y}} eQq_{210}\,,$$

where χ_{gg} are the nuclear quadrupole coupling constants, $g = x, z, a, b$; eQq_{210} is the quadrupole coupling of an electron in n l m = 210 state; ε = the shielding constant.

Equations (2) yield

$$i_{\pi_y} = \frac{1 + \varepsilon \cdot i_\sigma}{\frac{-\frac{3}{2} eQq_{210}}{\chi_{aa} + 2\chi_{bb}} - \varepsilon} \quad (3a)$$

and with $\varepsilon \cdot i_{\pi_y} \ll 1 + \varepsilon \cdot i_\sigma$

$$a_s^2 = \frac{(\chi_{aa} - \chi_{bb}) \cdot (1 + \varepsilon \cdot i_\sigma)}{\frac{3}{2} eQq_{210} \cdot (1 - i_\sigma)} - \frac{i_\sigma}{(1 - i_\sigma)}\,. \quad (3b)$$

With the experimental results for the coupling constants (see Table 2) and the values $\varepsilon = 0.3$ [17] and $eQq_{210} = -9.38$ MHz [19], we get

$$i_{\pi_y} = 3.5\% \quad \text{and} \quad a_s^2 = 34\%\,.$$

Because these values are rather sensitive to the assumptions no standard errors are given.

It should be noted that the hybridization parameter a_s^2 cannot (according to (3)) reach 50% ("sp"-hybridization) unless the σ bond polarity is nearly zero, what would leave unexplained the high dipole moment of approximately 4 D of the cyano group.

Table 2. Rotational and quadrupole coupling constants of 4-cyanopyridine. σ standard deviation of the fit. $|(B, C)|$ maximum correlation coefficient; derived parameters below the line, $\eta = |(\chi_{bb} - \chi_{cc})/\chi_{aa}|$. Quoted errors are single standard errors.

A	= 6001.2(5)	MHz
B	= 1541.175(2)	MHz
C	= 1226.002(2)	MHz
σ	= 10	kHz
$\lvert(B, C)\rvert$	= 0.792	
χ_{aa} (ring N)	= −5.02(4)	MHz
χ_{bb} (ring N)	= 1.41(11)	MHz
χ_{aa} (cyano N)	= −4.28(4)	MHz
χ_{bb} (cyano N)	= 2.37(10)	MHz
σ	= 21	kHz
$\lvert(\chi_{aa}$ (ring N), χ_{aa} (cyano N))$\rvert$	= 0.891	
χ_{cc} (ring N)	= 3.61(12)	MHz
η (ring N)	= 0.438(45)	
χ_{cc} (cyano N)	= 1.91(11)	MHz
η (cyano N)	= 0.107(48)	

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