Nitrogen Hyperfine Structure in the Rotational Spectra of 4-Pyridinecarbaldehyde and 3-Pyridinecarbaldehyde

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We have resolved and analysed the nuclear quadrupole hyperfine structure in the rotational spectra of 4-pyridinecarbaldehyde and 3-pyridinecarbaldehyde, C_5H_4NCHO. The results are discussed and compared to those of previously measured pyridine compounds. The electron withdrawing effect of the aldehyde-function, in the 3- and 4-position at the ring system, has been calculated, and the differences in the results are discussed.

Introduction

The nitrogen nuclear quadrupole coupling has been investigated for 3-pyridinecarbaldehyde and reinvestigated for 4-pyridinecarbaldehyde, by means of microwave Fourier transform (MWFT) spectroscopy [1]. The results allow, because of their accuracy, an interpretation of the coupling constants in terms of electronic parameters of the molecular environment of the nitrogen nucleus. These data are compared to those of pyridine [2], cyanopyridine [3] and to those which appear in the earlier literature [4, 5].

4-pyridinecarbaldehyde was first investigated by Georgiou and Roussy [4]. They used a Stark modulated microwave spectrometer and reported the rotational and quadrupole coupling constants. The latter were indicated to be similar to those of pyridine. 3-pyridinecarbaldehyde was first investigated by Haeck and Roussy [5] with the same technique. The authors reported the ground state rotational constants for the O–N s-trans form but no quadrupole coupling constants. Our studies with the higher resolution of MWFT spectrometers in the frequency range 8–26 GHz [6–8] have led to more reliable values of the quadrupole coupling constants of 4-pyridinecarbaldehyde and to first determinations of these constants of 3-pyridinecarbaldehyde. The improvement of the rotational constants was not our aim.

Experimental details and analysis

The substances, amber colored liquids, were purchased from Aldrich Chemie, Steinheim, and purified by a vacuum distillation. The spectra were recorded in both cases at a temperature of approximately $-15\,^\circ$C and a pressure of about 2.7 Pa (20 mTorr). Although the pressure seems to be high, detection of the molecular signals was in general difficult and at lower pressures as the above mentioned, no signals were obtained. On the contrary, these conditions allowed a good resolution for the demands of a hfs analysis. Our measurements are given in Tables 1 and 2. All frequencies used in the hfs analysis were determined by a least squares fit of the time domain signals of the multiples to minimize overlap effects [9].

The first order hfs analyses were carried out as in [2] for pyridine. The hypothetical unsplit transition frequencies were evaluated by adding the hfs corrections to the frequencies of the strongest multiplet component. For the hfs analyses, we used our programmes HT1NQ [10] and DH14KS [11]. The rotational constants were obtained by fitting these constants to the measured frequencies. For this calculation we used our programme DH9. The results are given in Table 3. The coupling constants have turned out to be influenced by the substitution-pattern of the ring system.

Discussion

To calculate the withdrawing effect of the aldehyde-function, the experimental data have been used for a

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Table 1. Measured rotational transitions of 4-pyridinecarbaldehyde. ν frequency of the hfs component, $\Delta\nu$ observed hyperfine splitting, referred to the strongest component. ν_0 hypothetical unsplit line frequency calculated from the measurements, $\Delta(\Delta\nu) = \Delta\nu - \Delta\nu^{\mathrm{calc}}$ deviation of the observed splitting from the calculated value, $\Delta\nu^{\mathrm{calc}}$ theoretical hyperfine splitting calculated with the constants from Table 3. ν_0^{calc} calculated unsplit line frequency, $\delta_0 = \nu_0 - \nu_0^{\mathrm{calc}}$.

J	K_-	K_+	J′	K'_-	K'_+	F–F′	ν[MHz]	$\Delta\nu$[MHz]	ν_0[MHz]	$\Delta(\Delta\nu)$ [kHz]	ν_0^{calc} [MHz]	δ_0 [kHz]
2	1	2	1	0	1	3–2	9167.544		9167.523		9167.500	+23
						2–1	9167.811	+0.267		−6		
						1–0	9165.999	−1.544		−4		
						2–2	9166.350	−1.194		+2		
						1–1	9169.689	+2.145		+10		
3	2	1	3	1	2	4–4	11484.819		11485.039		11485.042	−3
						3–3	11485.719	+0.901		+13		
						2–2	11484.497	−0.322		−11		
3	1	2	3	0	3	4–4	5252.844		5253.069		5253.051	+18
						3–3	5253.732	+0.888		−11		
						2–2	5252.534	−0.310		+4		
3	2	2	2	1	1	4–3	20205.650		20205.733		20205.728	+5
						3–2	20206.020	+0.370		−9		
						2–1	20205.440	−0.210		0		
3	2	1	2	1	2	4–3	21340.840		21341.125		21341.110	+15
						3–2	21342.110	+1.270		−3		
						2–1	21340.150	−0.69		+1		
4	3	2	3	3	1	5–4	11141.951		11141.602		11141.628	−26
						4–3	11140.518	−1.433		+10		
						3–2	11142.508	+0.557		−4		
4	3	1	4	2	2	5–5	20417.850		20418.155		20418.178	−23
						4–4	20418.990	+1.140		−9		
						3–3	20417.560	−0.290		+5		
4	2	2	4	1	3	5–5	11035.993		11036.119		11036.111	+8
						4–4	11036.471	+0.477		+2		
						3–3	11035.869	−0.124		−2		
6	1	5	6	0	6	7–7	8766.377		8766.597		8766.581	+16
						6–6	8767.151	+0.774		+3		
						5–5	8766.245	−0.131		−1		
7	1	6	7	0	7	8–8	10627.744		10627.972		10627.977	−5
						7–7	10628.528	+0.784		+5		
						6–6	10627.630	−0.114		−2		

Table 2. Measured rotational transitions of 3-pyridinecarbaldehyde. Symbols as in Table 1.

J	K_-	K_+	J′	K'_-	K'_+	F–F′	ν[MHz]	$\Delta\nu$[MHz]	ν_0[MHz]	$\Delta(\Delta\nu)$ [kHz]	ν_0^{calc} [MHz]	δ_0 [kHz]
2	1	1	1	1	0	3–2	5975.332		5975.323		5975.313	+10
						2–1	5975.043	−0.289		+8		
						1–0	5976.471	+1.139		−7		
						2–2	5976.079	+0.747		+6		
3	1	2	2	1	1	4–3	8947.518		8947.477		8947.483	−6
						3–2	8947.429	−0.088		+8		
3	2	2	2	2	1	4–3	8426.185		8426.102		8426.081	+21
						3–2	8425.812	−0.373		−2		
						2–1	8426.402	+0.217		+10		
4	3	1	3	3	0	5–4	11285.861		11285.790		11285.758	+32
						4–3	11285.566	−0.295		+2		
						3–2	11285.985	+0.123		−1		
4	3	2	3	3	1	5–4	11279.869		11279.795		11279.762	+33
						4–3	11279.547	−0.322		−15		
						3–2	11279.996	+0.127		+1		
5	4	2	4	4	1	6–5	14096.687		14096.615		14096.617	−2
						5–4	14096.400	−0.287		−8		
						4–3	14096.781	+0.094		+6		
6	5	2	5	5	1	7–6	16912.114		16912.045		16912.098	−53
						6–5	16911.871	−0.243		+12		
						5–4	16912.182	+0.069		+4		

semiempirical "Townes-Dailey calculation". The point of a comparison between 4- and 3-pyridinecarbaldehyde was, that we expected the electronic environment of the ring system in the 3-aldehyde to be nearly unaffected by the aldehyde-function, in contrast to the ring system of the 4-aldehyde. Due to these circumstances, the polarisation of the π and σ bonds of the 3-substituted system ought to be similar to those of unsubstituted pyridine, whereas the polarisation of π and σ bonds in the 4-substituted system ought to show a noticable effect.

Table 3. Rotational and quadrupole coupling constants [MHz] of 4- and 3- pyridinecarbaldehyde, σ standard deviation of the fit, $\overline{\Delta v}$ mean experimental splitting [MHz].

Values from [4]	This work	Correlation	
4-pyridinecarbaldehyde			
$A = 5519.040\ (84)$	$A = 5519.114\ (3)$		
$B = 1559.174\ (32)$	$B = 1559.205\ (2)$		
$C = 1216.114\ (22)$	$C = 1216.129\ (2)$		
$\chi^+ = 4.67\ (9)$	$\chi^+ = 4.900\ (8)$	1	
$\chi^- = -2.29\ (17)$	$\chi^- = -2.543\ (11)$	−0.053	1
$\chi_{aa} = -4.67\ (9)$	$\chi_{aa} = -4.900\ (8)$		
$\chi_{bb} = 1.19\ (26)$	$\chi_{bb} = 1.179\ (9)$		
$\chi_{cc} = 3.48\ (26)$	$\chi_{cc} = 3.721\ (9)$		
	$\sigma = 0.007$		
	$\overline{\Delta v} = 0.724$		

Values from [5]	This work	Correlation	
3-pyridinecarbaldehyde			
$A = 5417.8\ (4)$	$A = 5414.2\ (37)$		
$B = 1583.289\ (9)$	$B = 1583.310\ (14)$		
$C = 1225.389\ (9)$	$C = 1225.384\ (23)$		
	$\chi^+ = 1.156\ (10)$	1	
	$\chi^- = -5.768\ (40)$	0.033	1
	$\chi_{aa} = -1.156\ (10)$		
	$\chi_{bb} = -2.306\ (25)$		
	$\chi_{cc} = 3.462\ (25)$		
	$\sigma = 0.008$		
	$\overline{\Delta v} = 0.315$		

For the interpretation of the nitrogen nuclear coupling in substituted pyridines we followed Gordy and Cook [12].

Because of the equivalence of the two orbitals which form the C−N−C bonds, three electronic parameters can be considered as unknown: i_σ, the ionic character of the σ-bonds, i_π, the polarisation of the π-bond, and a_s^2, the hybridisation parameter.

We assume that the CNC angle is unaffected by the substituents; it is known to be 117° [13] from pyridine. With this assumption, a_s^2 can be evaluated to $a_s^2 = 0.312$ [14]. The normalized valence orbitals of the nitrogen atom are

$$\begin{aligned} \psi_1 &= (1-2a_s^2)^{1/2}\,\psi_s + (2a_s^2)^{1/2}\,\psi_{Pz} \text{ (lone pair)},\\ \psi_{2,3} &= (a_s^2)^{1/2}\,\psi_s - (1/2-a_s^2)^{1/2}\,\psi_{Pz}\\ &\quad \pm (1/2)^{1/2}\,\psi_{Px} \ (\sigma \text{ bonds}),\\ \psi_4 &= \psi_{Py} \ (\pi \text{ bond}) \end{aligned} \tag{1}$$

with a_s^2 = amount of s character in the C−N bond, z = symmetry axis of the pyridine moiety, y = axis perpendicular to molecular plane, x = in-plane-axis.

If we assume that ψ_1 is occupied by the lone pair, then the population numbers of the orbitals ψ_1 to ψ_4, are as follows:

$$\begin{aligned} &n(\psi_1) = 2;\quad n(\psi_2) = n(\psi_3) = 1 + i_\sigma;\\ &n(\psi_4) = 1 + i_\pi\ . \end{aligned} \tag{2}$$

Table 4. Ring nitrogen quadrupole coupling constants and derived electronic parameters of pyridine compounds. i_π, i_σ polarisation of π and σ bond respectively.

Compound	Coupling constants [MHz]	Derived parameters
pyridine [2]	$\chi_{xx} = \chi_{bb} = +1.434\ (3)$ $\chi_{zz} = \chi_{aa} = -4.908\ (3)$ $\chi_{cc} = +3.474\ (3)$	$i_\pi = 2.70\%$ $i_\sigma = 18.96\%$
4-cyanopyridine [3]	$\chi_{xx} = \chi_{bb} = +1.41\ (11)$ $\chi_{zz} = \chi_{aa} = -5.02\ (4)$ $\chi_{cc} = +3.61\ (12)$	$i_\pi = 1.0\%$ $i_\sigma = 18.4\%$
4-pyridinecarbaldehyde	$\chi_{bb} = +1.179\ (9)$ $\chi_{aa} = -4.900\ (8)$ $\chi_{cc} = +3.721\ (9)$ $\chi_{xx} = +1.37$ $\chi_{zz} = -5.09$	$i_\pi = -0.2\%$ $i_s = 18.4\%$
3-pyridinecarbaldehyde	$\chi_{bb} = -2.306\ (25)$ $\chi_{aa} = -1.156\ (10)$ $\chi_{cc} = +3.462\ (25)$ $\chi_{xx} = +1.58$ $\chi_{zz} = -5.04$	$i_\pi = 2\%$ $i_\sigma = 17\%$

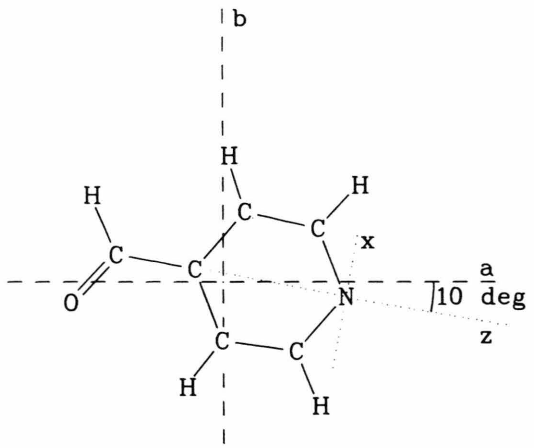

Fig. 1. The molecular geometry of 4-pyridinecarbaldehyde. The molecular geometry yields an angle Θ of 10° between the a axis and the C_7-C_4-N line of the molecule [4].

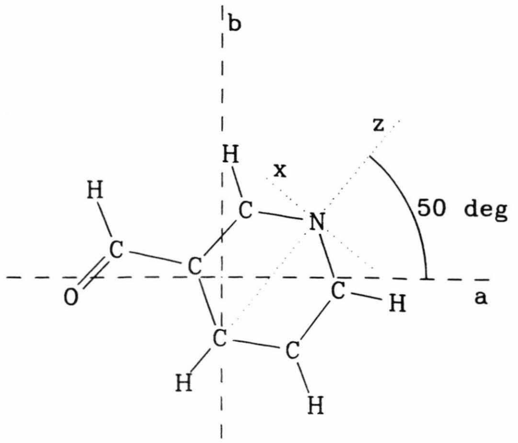

Fig. 2. The molecular geometry of 3-pyridinecarbaldehyde. Here the geometry yields an angle Θ between the a axis and the C_4-N line of 50°, calculated with the structural data given in [5].

We can then calculate i_σ and i_π as described in [15]. With our experimental data for χ_{gg}, $g = x, z$, we have obtained the results given in Table 4, wherein χ_{xx} and χ_{zz} have been calculated by the assumption that the molecular geometry of 4-pyridinecarbaldehyde yields an angle of $\theta = 10°$ between the a axis and the C_7-C_4-N line, see Figure 1. The quadrupole coupling tensor is then transformed into the ring axis by a rotation of 10°. For 3-pyridinecarbaldehyde this transformation is given by a rotation of $\theta = 50°$, see Figure 2. With the unsubstituted pyridine chosen as a standard, the polarisation of the π bond becomes obvious due to the well known withdrawing effect of the aldehyde-function (−M Effect). In the case of 4-aldehyde, the aldehyde-function lowers the π-electron density in the ring system in this substitution position more than the less attractive cyano-function, as seen in Table 4. The aldehyde-function in the 3-position cannot act in the same way, which is also indicated by the values of χ_{cc} in Table 4. This is well known in organic chemistry and described by the figurative description of mesomery. It is also noteworthy that no particular effect on i_σ in all substituted pyridines is shown; this is in good agreement with the localisation of the σ-bonds. Finally it should be stated that because of the simplifying assumptions of the model, the results are not very exact but give a good reproduction of the relationship between the electron excess i_π and acceptor influences related to the substitution position in aromatic ring systems.

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[1] H. Dreizler, J. Mol. Phys. **59**, 1 (1986).
[2] N. Heineking, H. Dreizler, and R. Schwarz, Z. Naturforsch. **41a**, 1210 (1986).
[3] N. Heineking and H. Dreizler, Z. Naturforsch. **42a**, 83 (1987).
[4] K. Georgiou and G. Roussy J. Mol. Spectrosc. **82**, 176 (1980).
[5] L. Haeck and G. Roussy, Chem. Phys. Lett. **52**, 512 (1982).
[6] G. Bestmann and H. Dreizler, Z. Naturforsch. **37a**, 58 (1982).
[7] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35 a**, 392 (1980).
[8] W. Stahl, G. Bestmann, H. Dreizler, U. Andresen, and R. Schwarz, Rev. Sci. Instrum. **56**, 1759 (1985).
[9] J. Haekel and H. Mäder, Z. Naturforsch. **43 a**, 203 (1988).
[10] Author: G. Herberich, Aachen.
[11] Author: H. Mäder, Kiel.
[12] W. Gordy and R. L. Cook, Microwave Molecular Spectra, John Wiley & Sons, New York 1984, 3rd edition, chapter 14.13
[13] G. O. Sørensen, L. Mahler, and N. Rastrup-Andersen, J. Mol. Struct. **30**, 119 (1974).
[14] P. W. Atkins, Molecular Quantum Mechanics, Oxford University Press, 1983, 2nd edition p. 270 (10.83).
[15] N. Heineking and H. Dreizler, Z. Naturforsch. **42a**, 207 (1987).