Nitrogen and Chlorine Hyperfine Structure in the Rotational Spectra of 4-Chloropyridine

N. Heineking and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

Z. Naturforsch. **41a**, 1297–1301 (1986); received July 3, 1986

We resolved and analysed the ^{14}N hyperfine structure in addition to the ^{35}Cl and ^{37}Cl hyperfine structure of 4-chloropyridine- ^{35}Cl and - ^{37}Cl to investigate substitutional effects.

The ^{14}N , ^{35}Cl , and ^{37}Cl hyperfine structure in the rotational spectra of 4-chloropyridine- ^{35}Cl and - ^{37}Cl has been investigated by microwave Fourier transform (MWFT) spectroscopy [1]. The aim was to study the substitutional effect produced by the chlorine atom reflected by the ^{14}N quadrupole coupling. This paper is the second in a series. In the first we presented results for pyridine and [4-D]pyridine [2], which were investigated to provide a reference.

4-Chloropyridine was first investigated by Caminati and Forti [3]. They reported the rotational constants of both isotopic forms and the ^{35}Cl quadrupole coupling constants.

Our MWFT spectrometers in the range from 5.3 to 18 GHz described elsewhere [4–6] were used.

The substance, which at room temperature tends to dimerize, was prepared by neutralisation of 4-chloropyridine hydrochloride (Fluka). It was purified by sublimation and stored below its freezing point of -42.5°C .

The spectra were recorded at temperatures of approximately -35°C and pressures between 0.2 and 1 Pa (1.5 and 7.5 mTorr).

Part of the measurements are given in Tables 1a and 1b. The complete list is available under the number TNA5 from the Universitätsbibliothek, D-2300 Kiel. The multiplets were simulated by a line contour analysis [7] to account for interference of neighbouring lines. A sample of a multiplet is presented in Fig. 1, showing the Cl and N hfs of the $4_{23}-3_{22}$ rotational transition of the ^{37}Cl -species.

A first order hfs analysis [8] proved to be sufficient as the hfs patterns could be calculated near to the experimental uncertainty. A coupled basis $F_1 = J + I$ (chlorine), $F = F_1 + I$ (nitrogen), (J angular momentum, I spin operator), was used. The hypothetical unsplit transitions were calculated by

Fig. 1. Rotational transition $J_{K_-K_+} = 4_{23} - 3_{22}$ of 4-chloropyridine- ^{37}Cl showing both chlorine and nitrogen hfs. F_1 quantum numbers are given. The components with $F_1 = 5/2 - 3/2$ could not be detected. They are overlaid by an unassigned line. In the lower trace the result of a theoretical line pattern is given. The intensities are not reproduced as the polarization conditions vary over the range of the multiplet. Range 10971–10980 MHz out of a 25 MHz recording, sampling interval 20 ns, polarizing frequency 10974 MHz (↑), temperature -30°C , pressure 2.7 mTorr, 10^7 averaging cycles, 1024 data points supplemented by 3072 zeros prior to Fourier transformation.

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

Table 1a. Selection of measured rotational transitions of 4-chloropyridine- ^{35}Cl showing ^{35}Cl (F_1 quantum numbers) and ^{14}N (F quantum numbers) hyperfine structure. The F and F_1 quantum numbers are multiplied by 2. ν measured and improved frequencies, $\Delta\nu$ hfs splittings referred to the strongest component, ν_0 hypothetical unsplit lines, $\Delta(\Delta\nu) = \Delta\nu - \Delta\nu_{\text{calc}}$ deviations of the splittings, $\Delta\nu_{\text{calc}}$ splittings calculated with the constants of Table 2, $\Delta\nu_0$ deviations from the rigid rotor spectrum calculated with the rotational constants of Table 2, determined from transitions marked with *.

$J'K'_1K'_2 - J''K''_1K''_2$	$F'_1 - F''_1, F' - F''$ *2	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ $\Delta\nu_0$ [kHz][kHz]	$J'K'_1K'_2 - J''K''_1K''_2$	$F'_1 - F''_1, F' - F''$ *2	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ $\Delta\nu_0$ [kHz][kHz]
2 0 2 - 1 0 1	5-3, 5-3 7-5, 7-5 7-5, 9-7 7-5, 5-3 5-3, 7-5	5621.964 5622.785 5623.113 5623.203 5623.410	-1.149 -0.328 +0.090 +0.297		+ 4 + 7 + 30 - 14		7-5, 9-7 7-5, 5-3 9-7, 9-7 9-7, 11-9 9-7, 7-5	8933.476 8933.568 8937.545 8937.957 8938.022		8935.858*	- 13 + 3 + 36 + 28 + 32
2 1 1 - 1 1 0	5-3, 3-1 5-3, 7-5 5-3, 5-3 7-5, 7-5 7-5, 9-7 7-5, 5-3	5950.687 5951.081 5951.455 5968.287 5969.363 5969.741	-18.676 -18.282 -17.908 -1.076 +0.378		+ 55 + 19 + 1 + 13 - 24	3 1 3 - 2 1 2	5-3, 5-3 7-5, 7-5 7-5, 9-7 7-5, 5-3 5-3, 7-5 9-7, 9-7 9-7, 11-9 9-7, 7-5 3-1, 5-3	7955.721 7956.344 7956.489 7960.320 7960.801 7960.89	-5.080 -4.457 -4.312 -0.481 +0.089		- 41 - 28 + 9 - 5 - 11
2 1 2 - 1 1 1	5-3, 3-1 5-3, 5-3 5-3, 7-5 7-5, 7-5 7-5, 9-7 7-5, 5-3	5299.115 5299.283 5316.248 5317.477 5317.935	-18.362 -18.194 -1.229 +0.458		+ 47 + 58 - 34 + 17 - 2	3 2 1 - 2 2 0	7-5, 7-5 7-5, 9-7 7-5, 5-3 5-5, 7-7 5-3, 3-1 5-3, 7-5 5-3, 5-3 9-7, 9-7 9-7, 11-9 9-7, 7-5 3-1, 5-3	8513.565 8514.065 8514.229 8526.706 8526.821 8526.942 8531.097 8532.375 8532.827 8544.935	-18.810 -18.310 -18.146 -5.669 -5.554 -5.433 -1.278 +0.452 +12.560		+ 19 - 21 + 11 - 20 + 9 + 34 + 7 - 5 + 45
3 0 3 - 2 0 2	5-3, 5-3 3-1, 5-3 5-3, 7-5 5-3, 3-1 7-5, 7-5 9-7, 9-7 9-7, 7-5 9-7, 11-9 7-5, 9-7 7-5, 5-3	8385.237 8385.934 8386.088 8386.420 8389.973 8390.103 8390.194 8390.290 8390.491 8390.592	-0.851 -0.154 +0.332 +3.885 +4.015 +4.106 +4.202 +4.403 +4.504		- 15 + 18 - 19 + 8 + 10 + 25 + 25 - 4 + 16	3 2 2 - 2 2 1	7-5, 7-5 7-5, 9-7 7-5, 5-3 9-7, 9-7 9-7, 11-9 9-7, 7-5	8444.907 8445.450 8445.623 8462.295 8463.607 8464.073	-0.543 +0.173 +16.845 +18.157 +18.623		+ 14 + 23 + 2 + 7 + 14

Table 1b. Selection of measured rotational transitions of 4-chloropyridine-[^{37}Cl] showing ^{37}Cl (F_1 quantum numbers) and ^{14}N (F quantum numbers) hyperfine structure. See also Table 1a.

$J'K'_L - J''K''_L$	$F'_1 - F''_1, F' - F''$ *2	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ [kHz]	$\Delta\nu_0$ [kHz]	$J'K'_L - J''K''_L$	$F'_1 - F''_1, F' - F''$ *2	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ [kHz]	$\Delta\nu_0$ [kHz]
2 0 2 - 1 0 1	7-5, 7-5 7-5, 9-7 7-5, 5-3 5-3, 7-5	5479.261 5479.581 5479.757 5479.964	-0.320 +0.176 +0.383	5478.287*	+ 10 + 95 +103	+ 8		9-7, 9-7 11-9, 11-9 11-9, 9-7 11-9, 13-11	10835.499 10835.628		10835.169*	- 8	
2 1 1 - 1 1 0	5-3, 3-1 5-3, 7-5 5-3, 5-3 7-5, 7-5 7-5, 9-7 7-5, 5-3	5792.165 5792.586 5792.98 5806.045 5807.075 5807.416	-14.910 -14.489 -14.095 -1.030 +0.341		+ 20 + 4 + 1 + 19 - 41	+ 41	4 1 3 - 3 1 2	7-5, 7-5 7-5, 9-7 7-5, 5-3 9-7, 9-7 9-7, 11-9 9-7, 7-5	11572.598 11572.953 11573.486 11573.691	-2.471 -2.116 -1.583 -1.378		- 3 + 31 + 44 - 22	
2 1 2 - 1 1 1	5-3, 7-5 7-5, 7-5 7-5, 9-7 7-5, 5-3	5173.504 5186.750 5187.914 5188.299	-14.410 -1.164 +0.385	5184.242*	0 + 4 + 57 - 77	+ 57		5-3, 5-3 5-3, 7-5 5-3, 3-1 11-9, 11-9 11-9, 13-11 11-9, 9-7	11573.947 11574.249 11574.860 11575.069	-1.122 -0.820 -0.209		- 23 - 20 - 4	- 2
3 0 3 - 2 0 2	5-3, 5-3 5-3, 7-5 7-5, 7-5 9-7, 9-7 9-7, 7-5 9-7, 11-9 7-5, 9-7 7-5, 5-3	8175.635 8176.482 8179.378 8179.529 8179.646 8179.763 8179.916 8180.049	-4.281 -3.434 -0.538 -0.387 -0.270 -0.153 +0.133		- 13 + 14 - 17 - 28 + 15 + 31 + 59	- 3	4 2 2 - 3 2 1	9-7, 9-7 9-7, 11-9 9-7, 7-5 7-5, 7-5 7-5, 9-7 7-5, 5-3 11-9, 11-9 11-9, 13-11	11123.715 11124.153 11124.265 11125.763 11126.157 11126.31 11129.398 11129.866	-5.683 -5.245 -5.133 -3.635 -3.241 -3.088		0 - 34 - 8 - 9 - 16 + 23	- 12
3 1 3 - 2 1 2	5-3, 5-3 7-5, 7-5 7-5, 9-7 5-3, 7-5 7-5, 5-3 9-7, 9-7 9-7, 11-9 9-7, 7-5 3-1, 5-3	7764.359 7764.966 7765.083 7768.025	-4.100 -3.493 -3.376 -0.434		+ 16 - 38 + 18 + 48		4 2 3 - 3 2 2	9-7, 9-7 9-7, 11-9 9-7, 7-5 7-5, 7-5 7-5, 9-7 7-5, 5-3 11-9, 11-9 11-9, 13-11 11-9, 9-7	10971.456 10971.977 10972.065 10973.540 10973.956 10974.074 10977.050 10977.653 10977.779	-0.521 +0.088 +1.563 +1.979 +2.097 +5.073 +5.676 +5.802		- 5 + 12 + 21 + 10 + 19 + 14 + 11 + 18	- 19
4 0 4 - 3 0 3	5-3, 5-3 5-3, 3-1 7-5, 7-5 5-3, 7-5 7-5, 5-3 7-5, 9-7	10833.800 10834.150	-1.699 -1.349		+ 82 + 60								

Table 2. Rotational and quadrupole coupling constants [MHz] of 4-chloropyridine- ^{35}Cl and ^{37}Cl determined from all measured transitions. σ standard deviation of the fit in kHz, $|(B, C)|$ maximum correlation coefficient. Single standard errors in brackets. Derived parameters below the line.

4-chloropyridine- ^{35}Cl		4-chloropyridine- ^{37}Cl	
A	6019.0(4)	A	6019.1(7)
B	1572.631(2)	B	1528.210(5)
C	1246.748(2)	C	1218.659(6)
σ	14	σ	31
$ (B, C) $	0.792	$ (B, C) $	0.833
$\chi_{aa}(^{35}\text{Cl})$	- 71.65(2)	$\chi_{aa}(^{37}\text{Cl})$	- 56.4(1)
$\chi_{bb}(^{35}\text{Cl})$	+ 39.25(11)	$\chi_{bb}(^{37}\text{Cl})$	+ 30.8(3)
$\chi_{aa}(\text{N})$	- 4.81(1)	$\chi_{aa}(\text{N})$	- 4.7(1)
$\chi_{bb}(\text{N})$	+ 1.64(4)	$\chi_{bb}(\text{N})$	+ 1.5(1)
σ	15	σ	34
$ \chi_{aa}(\text{Cl}), \chi_{bb}(\text{Cl}) $	0.197	$ \chi_{aa}(\text{N}), \chi_{bb}(\text{N}) $	0.303
$\chi_{cc}(^{35}\text{Cl})$	+ 32.40(11)	$\chi_{cc}(^{37}\text{Cl})$	+ 25.6(3)
$\chi_{cc}(\text{N})$	+ 3.17(4)	$\chi_{cc}(\text{N})$	+ 3.2(1)

adding the hfs corrections to the frequencies of the strongest multiplet components. The transitions marked by asterisks were used for a rigid rotor analysis to refine the rotational constants. This refinement did not influence the hfs analysis.

The rotational and quadrupole coupling constants are given in Table 2. The standard errors of the rotational constants of the ^{37}Cl -species are higher as lines with higher J had to be included in the fit.

The coupling constants of the ^{37}Cl isotopomer are determined less precise. This reflects the lower isotopic abundance. Within the single standard error there is a rough agreement of the nitrogen coupling constants. We used the programs Q2SIM [9] and Q2FIT [10] for the hfs and DH9 [11] for the rotational analysis. The results for the nitrogen coupling will be discussed in a forthcoming paper.

Chlorine Coupling Discussion

The interpretation of the chlorine quadrupole coupling constants is guided by the Townes-Dailey approach [12]. It is assumed that the C-Cl bond is formed by a partially s-hybridized $3p_z$ orbital, the two counterhybridized lone pair orbitals in the molecular plane being equivalent. The p_y orbital perpendicular to the pyridine ring is further

supposed to interfere with the π orbitals of the aromatic system, lowering its occupation and forming a partial double bond.

The ionic character i_σ of the C-Cl bond and the double bond character i_π serve as determinable variables. The hybridization parameter a_s^2 is assumed to be 15% [13] for the C-Cl bond.

The four valence orbitals are described by

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

$$\psi_{2,3} (\text{lone pair orbitals})$$

$$= (\tfrac{1}{2} - \tfrac{1}{2} a_s^2)^{1/2} \psi_s \pm (\tfrac{1}{2})^{1/2} \psi_{p_z} - (\tfrac{1}{2} a_s^2)^{1/2} \psi_{p_x},$$

$$\psi_4 (\pi \text{ bonding orbital}) = \psi_{p_y}. \quad (1)$$

The occupation numbers are

$$\begin{aligned} n_1 &= 1 + i_\sigma, \\ n_2 &= n_3 = 2, \\ n_4 &= 2 - i_\pi. \end{aligned} \quad (2)$$

From (1) and (2)

$$\begin{aligned} n_x &= 2, \\ n_y &= 2 - i_\pi, \\ n_z &= 1 + i_\sigma + a_s^2 (1 - i_\sigma), \end{aligned} \quad (3)$$

result.

The independent coupling constants may then be expressed by

$$\begin{aligned} \chi_{zz} &= \chi_{aa} = [(i_\sigma - 1)(1 - a_s^2) + \tfrac{1}{2} i_\pi] e Q q_{310}, \\ \chi_{xx} &= \chi_{bb} = [-\tfrac{1}{2} (i_\sigma - 1)(1 - a_s^2) + \tfrac{1}{2} i_\pi] e Q q_{310}. \end{aligned} \quad (4)$$

It should be noted that the C-Cl bond is parallel to the principal inertia axis a . From (4) we get

$$\begin{aligned} i_\pi &= \frac{2}{3} \frac{(\chi_{aa} + 2\chi_{bb})}{e Q q_{310}}, \\ i_\sigma &= 1 + \frac{2}{3} \frac{(\chi_{aa} - \chi_{bb})}{e Q q_{310} (1 - a_s^2)}. \end{aligned} \quad (5)$$

With the experimental data of Table 2 and

$$e Q q_{310}(^{35}\text{Cl}) = + 109.74 \text{ MHz}$$

and

$$e Q q_{310}(^{37}\text{Cl}) = + 86.51 \text{ MHz} \quad [14]$$

the double bond characters amount to

$$i_\pi = 4.2\% \quad \text{and} \quad i_\pi = 4.0\%$$

for the ^{35}Cl and ^{37}Cl species respectively. The ionic characters are

$$i_{\sigma} = 20.7\% \quad \text{and} \quad i_{\sigma} = 20.9\% .$$

As we are aware of the approximative nature of this model, no standard errors are given.

The corresponding mesomeric structures and their importance are:

The contribution of III is higher in 4-chloropyridine than in chlorobenzene (3.3% [15]) or 3-chloropyridine (2.9% [16]) but less than the value for 2-chloropyridine (5.4% [17]).

Acknowledgement

We thank M. Andolfatto for the preparation of the substance, the members of our group for help and discussion, the Deutsche Forschungsgemeinschaft and Fonds der Chemie for funds. The calculations were made at the computer center of the University of Kiel.

- [1] H. Dreizler, J. Mol. Phys. **57** (1986) to be published.
- [2] N. Heineking, H. Dreizler, and R. Schwarz, Z. Naturforsch. **41 a**, 1210 (1986).
- [3] W. Caminati and P. Forti, Chem. Phys. Lett. **38**, 222 (1976).
- [4] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35 a**, 392 (1980).
- [5] G. Bestmann and H. Dreizler, Z. Naturforsch. **37 a**, 58 (1982).
- [6] G. Bestmann, H. Dreizler, E. Fliege, and W. Stahl, J. Mol. Struct. **97**, 215 (1983).
- [7] E. Fliege and H. Dreizler, Z. Naturforsch. **39 a**, 630 (1984).
- [8] W. Gordy and R. L. Cook, Microwave Molecular Spectra, John Wiley, New York 1984, Chapt. IX, 5; XV, 3.
- [9] Authors: H. Günter, Tübingen and J. Reinstädter, Gießen.
- [10] Authors: D. Hübner and W. Stolze, Kiel.
- [11] Author: G. Herberich, Aachen.
- [12] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw Hill, 1955, p. 244.
- [13] l.c. [12], p. 237.
- [14] l.c. [8], Table 14.2.
- [15] W. Caminati and A. M. Mirri, Chem. Phys. Lett. **12**, 127 (1971).
- [16] R. D. Brown and J. Matouskova, J. Mol. Struct. **29**, 33 (1975).
- [17] M. Meyer, Diplom-Thesis, Kiel 1986.