Microwave Spectrum and Nuclear Quadrupole Coupling of 2-Chloropyridine

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Z. Naturforsch. **42 a**, 197–206 (1987); received October 9, 1986

The microwave spectrum of 2-chloropyridine, 2-Cl(C_5H_4N), has been studied to determine the ^{35}Cl, ^{37}Cl and ^{14}N nuclear quadrupole coupling constants. The results are discussed within a simple MO theory. We propose an approximate r_0-structure under certain assumptions. In addition to the ground state we observed one vibrationally excited state of both chlorine isotopic species of 2-chloropyridine.

Introduction

The chlorine nuclear quadrupole coupling of 2-chloropyridine has been reported by different authors [1, 2, 3]. The nitrogen hyperfine structure (hfs) has not been resolved so far. One aim of this work was the analysis of the ^{14}N-hfs and a comparison to that of pyridine to detect possible changes by the chlorine substitution. In the course of this work we examined if a change of the ring structure by substitution can be noticed. We further determined the rotational and centrifugal distortion constants, the former more precisely.

Experimental Details and Analysis

2-chloropyridine was purchased from Merck-Schuchardt, Hohenbrunn, and used without further purification. The spectra were measured with a microwave Fourier transform (MWFT) spectrometer constructed in Kiel in X [4], Ku [5] and K [6] band from 8 to 26.5 GHz at sample pressures of about 0.5 mTorr (0.07 Pa) and temperatures between $-16\,°C$ and $-35\,°C$. Figure 1 shows an example of the MWFT spectra. The multiplets used for the hfs analysis were evaluated by a lineshape analysis [7] to account for the interference of neighbouring lines. The Tables 1 a–d contain a selection of the measured transitions. The complete list has been deposited at the Universitätsbibliothek * Kiel and is available under the number TNA 8.

The spectrum of 2-chloropyridine consists of a- and b-type transitions according to the dipole moments $\mu_a = 3.3$ D and $\mu_b = 1.9$ D, which were calculated with the CNDO/2 method [8] assuming the r_0-structure (see below). The spectra were analysed in the following manner: For the transitions which show quadrupole hfs we subtracted the calculated frequency shifts obtained by the hfs analysis from the frequency of the components. For the hypothetical unsplit line frequency the arithmetic mean is taken. This was used as input data for the fourth order centrifugal distortion analysis [9] according to Watson's A reduction [10].

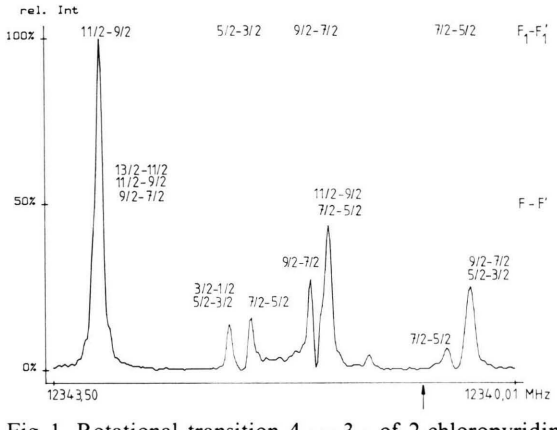

Fig. 1. Rotational transition $4_{13} - 3_{12}$ of 2-chloropyridine-(^{35}Cl). F and F_1 quantum numbers are given. The ^{14}N hfs has not been resolved completely in this example. Range of 3.49 MHz out of a 25 MHz scan. Power spectrum, sample interval 20 ns, 2560 k averaging cycles, 1024 data points supplemented by 3072 zeros, microwave polarising frequency (↑) 12340.8 MHz, sample gas pressure 0.4 mTorr, (0.05 Pa) temperature in the waveguide cell $-22\,°C$.

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Table 1. Selection of the measured transitions of 2-chloropyridine ν: measured frequency; $\Delta\nu_{hfs}$: frequency shift from the component of reference; ν_0: hypothetical unsplit line frequency; δ_{hfs}: difference between calculated and experimental hfs shift; δ_r: difference between calculated and observed centre frequency with respect to the rigid rotor; δ_{cd}: difference between calculated and observed center frequency with respect to the distorted rotor; * transition not used for hfs analysis. Frequencies and frequency shifts in MHz, deviations in kHz. The numbers given for F_1 and F are twice the quantum numbers. Table 1a. 2-chloropyridine-(^{35}Cl), vibrational ground state.

J'	K'_-	$K'_+ - J''$	K''_-	K''_+	$2F'_1$	$2F'$,	$2F''_1$	$2F''$	ν	$\Delta\nu_{hfs}$	δ_{hfs}	ν_0	δ_{cd}
4	1	3 − 3	1	2	7	9, 5		7	12 340.349	−2.797	6	12 342.100	−2
					7	5, 5		3					
					7	7, 5		5	12 340.519	−2.627	13		
					9	11, 7		9	12 341.420	−1.726	−10		
					9	7, 7		5					
					9	9, 7		7	12 341.547	−1.599	13		
					5	7, 3		5	12 342.006	−1.140	−14		
					5	3, 3		1	12 342.164	−0.982	−6		
					5	5, 3		3					
					11	13, 9		11	12 343.146				
					11	11, 9		9					
					11	9, 9		7					
4	1	4 − 3	1	3	7	7, 5		5	10 916.057	−1.043	6	10 917.757	−2
					7	9, 5		7	10 916.329	−0.771	9		
					7	5, 5		3					
					9	9, 7		7	10 916.911	−0.189	−4		
					9	11, 7		9	10 917.100				
					9	7, 7		5					
					5	5, 3		3	10 917.751	0.651	−15		
					5	7, 3		5	10 918.013	0.913	−4		
					11	11, 9		9	10 918.683	1.583	0		
					11	9, 9		7	10 918.783	1.683	23		
					11	13, 9		11					
4	2	2 − 3	2	1	9	7, 7		5	11 863.912	−9.878	2	11 868.562	7
					9	11, 7		9					
					9	9, 7		7	11 864.099	−9.691	13		
					7	5, 5		3	11 866.412	−7.378	4		
					7	9, 5		7					
					7	9, 7		7	11 866.553	−7.237	21		
					7	7, 5		5					
					11	9, 9		7	11 871.107	−2.683	7		
					11	13, 9		11	11 871.182	−2.608	18		
					11	11, 9		9	11 871.312	−2.478	25		
					5	7, 3		5	11 873.653	−0.137	−1		
					5	3, 3		1					
					5	5, 3		3	11 873.790				
5	1	5 − 4	0	4	7	7, 5		5	16 500.926	−1.845	−3	16 503.888	0
					7	9, 5		7	16 501.641	−1.130	11		
					13	13, 11		11	16 502.771				
					9	9, 7		7	16 503.444	0.673	−15		
					13	15, 11		13	16 503.520	0.749	−1		
					13	11, 11		9	16 503.630	0.859	−2		
					9	11, 7		9	16 504.095	1.324	−5		
					9	7, 7		5	16 504.196	1.425	−16		
					11	11, 9		9	16 505.257	2.486	−3		
					11	13, 9		11	16 505.965	3.194	5		
					11	9, 9		7	16 506.028	3.257	−12		

Table 1a continued. 2-chloropyridine-(^{35}Cl), vibrational ground state.

J'	K'_-	$K'_+ - J''$	K''_-	K''_+	$2F'_1$	$2F'$,	$2F''_1$	$2F''$	ν	$\Delta\nu_{\mathrm{hfs}}$	δ_{hfs}	ν_0	δ_{cd}
6	1	6 − 5	0	5	9	9,	7	7	18 607.802	−1.159	13	18 609.854	2
					9	11,	7	9	18 608.412	−0.549	7		
					15	15,	13	13	18 608.961				
					11	11,	9	9 }	18 609.594	0.633	−3		
					15	17,	13	15 }					
					15	13,	13	11	18 609.679	0.718	3		
					11	13,	9	11	18 610.158	1.197	−8		
					11	9,	9	7	18 610.239	1.278	1		
					13	13,	11	11	18 610.723	1.762	−2		
					13	15,	11	13	18 611.338	2.377	−3		
					13	11,	11	9	18 611.393	2.432	3		
6	3	3 − 6	2	4	9	9,	9	9	21 093.759	−9.085	17	21 098.518	−2
					9	11,	9	11	21 094.164	−8.680	−3		
					9	7,	9	7	21 094.272	−8.572	8		
					15	15,	15	15	21 095.390	−7.454	1		
					15	17,	15	17	21 095.831	−7.013	−12		
					15	13,	15	13	21 095.901	−6.943	−2		
					11	11,	11	11	21 100.785	−2.059	13		
					11	13,	11	13	21 101.169	−1.675	−5		
					11	9,	11	9	21 101.252	−1.592	−2		
					13	13,	13	13	21 102.449	−0.395	16		
					13	15,	13	15	21 102.844				
					13	11,	13	11	21 102.921	0.077	8		
5	0	5 − 4	0	4								14 180.441	3
5	1	5 − 4	0	4								16 503.888	0
5	2	3 − 4	2	2								14 954.621	2
6	0	6 − 5	0	5								16 826.121	−3
6	1	6 − 5	1	5								16 286.400	−3
6	3	3 − 5	3	2		*						17 652.761	−3
7	1	7 − 6	0	6		*						20 724.784	3
7	2	6 − 7	1	7								18 440.242	−7
8	3	5 − 8	2	6								19 728.434	−2
9	0	9 − 8	0	8		*						24 485.028	1
10	1	9 − 10	0	10		*						18 809.868	−9
10	3	7 − 10	2	8		*						18 073.814	−2
10	3	8 − 10	2	9		*						24 500.619	−1
11	1	10 − 11	0	11		*						21 741.552	3
12	1	11 − 12	0	12		*						24 724.788	2
13	2	11 − 13	1	12		*						18 318.033	6
14	2	12 − 14	1	13		*						20 948.478	−4
15	3	12 − 15	2	13		*						17 678.705	1
15	4	11 − 15	3	12		*						24 754.120	−1
16	3	13 − 16	2	14		*						18 859.474	3
16	4	12 − 16	3	13		*						23 674.075	0
17	3	14 − 17	2	15		*						20 543.506	3
17	4	13 − 17	3	14		*						22 802.556	9
18	3	15 − 18	2	16		*						22 717.704	4
18	4	14 − 18	3	15		*						22 252.413	−1
19	3	16 − 19	2	17		*						25 336.107	−2
19	4	15 − 19	3	16		*						22 118.777	−5
20	4	16 − 20	3	17		*						22 474.152	−2
21	4	17 − 21	3	18		*						23 367.409	−2
22	4	18 − 22	3	19		*						24 822.685	0
25	6	19 − 24	7	18		*						21 378.120	0

Table 1 b. 2-chloropyridine-(^{37}Cl), vibrational ground state.

J'	K'_-	K'_+	$-J''$	K''_-	K''_+	$2F'_1$	$2F'$,	$2F''_1$	$2F''$	ν	$\Delta\nu_{\mathrm{hfs}}$	δ_{hfs}	ν_0	δ_{cd}
4	0	4	−3	0	3	5	7, 3	5		11 184.207	−1.649	−4	11 185.451	1
						5	3, 3	1						
						7	7, 5	5						
						7	9, 5	7		11 184.390	−1.466	3		
						7	5, 5	3						
						11	11, 9	9		11 185.696	−0.160	5		
						11	13, 9	11		11 185.856				
						11	9, 9	7						
						9	9, 7	7						
						9	11, 7	9		11 186.031	0.175	1		
						9	7, 7	5						
4	1	3	−3	1	2	7	9, 5	7		12 012.692			12 014.087	−4
						7	5, 5	3						
						9	11, 7	9		12 013.550	0.858	−1		
						9	7, 7	5						
						9	9, 7	7		12 013.667	0.975	7		
						5	7, 3	5		12 014.009	1.317	−4		
						5	3, 3	1		12 014.158	1.466	−7		
						5	5, 3	3						
						11	13, 9	11		12 014.918	2.226	6		
						11	11, 9	9						
						11	9, 9	7						
4	1	4	−3	1	3	7	7, 5	5		10 568.482			10 659.868	−4
						7	9, 5	7		10 658.750	0.268	−5		
						7	5, 5	3						
						9	9, 7	7		10 659.179	0.697	−1		
						9	11, 7	9		10 659.365	0.883	1		
						9	7, 7	5						
						5	5, 3	3		10 659.830	1.348	−5		
						5	7, 3	5		10 660.097	1.615	6		
						11	11, 9	9		10 660.591	2.109	4		
						11	13, 9	11		10 660.687	2.205	9		
4	2	2	−3	2	1	9	9, 9	7		11 547.532			11 551.193	−2
						9	7, 7	5						
						9	11, 7	9						
						7	5, 5	3		11 549.510	1.978	5		
						7	9, 7	7						
						7	9, 5	7		11 549.632	2.100	18		
						7	7, 5	5						
						11	9, 9	7		11 553.150	5.618	0		
						11	13, 9	11		11 553.243	5.711	−3		
						11	9, 7	7						
						11	11, 9	9		11 553.362	5.830	8		
						5	7, 3	5		11 555.193	7.661	7		
						5	3, 3	1						
						5	5, 3	3		11 555.306	7.774	−15		
4	2	3	−3	2	2								11 360.784	11
6	1	5	−5	1	4		*						17 907.297	−2
7	1	7	−6	1	6		*						18 504.910	1
7	2	5	−6	2	4		*						20 681.521	3
7	2	5	−7	1	6								11 120.438	−1
8	2	6	−8	1	7								11 270.731	1
9	0	9	−8	0	8								23 952.985	0

Table 1 c. 2-chloropyridine-(^{35}Cl), excited state.

J'	K'_-	K'_+	$-J''$	K''_-	K''_+	$2F'_1$	$2F'$,	$2F''_1$	$2F''$	ν	$\Delta\nu_{hfs}$	δ_{hfs}	ν_0	δ_r
4	0	4	−3	0	3	5	7, 3	5		11 469.456	−2.356	−14	11 471.077	3
						5	3, 3	1						
						7	9, 5	7		11 469.727	−2.085	−4		
						7	5, 5	3						
						11	11, 9	9		11 471.405	−0.407	16		
						11	13, 9	11		11 471.560	−0.252	4		
						11	9, 9	7						
						9	9, 7	7		11 471.394	−0.150	17		
						9	11, 7	9		11 471.812				
						9	7, 7	5						
4	1	3	−3	1	2	7	9, 5	7		12 350.139	−2.785	8	12 351.876	−1
						7	5, 5	3						
						7	7, 5	5		12 350.278	−2.646	−15		
						9	11, 7	9		12 351.215	−1.709	−5		
						9	7, 7	5						
						9	9, 7	7		12 351.330	−1.594	8		
						5	7, 3	5		12 351.776	−1.148	−22		
						5	3, 3	1		12 351.933	−0.991	−12		
						5	5, 3	3						
						11	13, 9	11						
						11	11, 9	9		12 352.924				
						11	9, 9	7						
4	1	4	−3	1	3	7	7, 5	5		10 927.342	−2.621	−8	10 929.040	−3
						7	9, 5	7		10 927.612	−2.351	−11		
						7	5, 5	3						
						9	9, 7	7		10 928.196	−1.767	−10		
						9	11, 7	9		10 928.381	−1.582	12		
						9	7, 7	5						
						5	7, 3	5		10 929.306	−0.657	−3		
						11	11, 9	9		10 929.963				
						11	9, 9	7		10 930.070	0.102	22		
						11	13, 9	11						
4	2	2	−3	2	1	9	7, 7	5		11 875.541			11 880.172	−1
						9	11, 7	9						
						7	9, 5	7		11 878.029	2.488	1		
						7	5, 5	3						
						7	9, 7	7		11 878.178	2.637	26		
						7	7, 5	5						
						11	9, 9	7		11 882.712	7.171	6		
						11	13, 9	11		11 882.777	7.236	8		
						11	9, 5	7		11 882.903	7.362	18		
						11	11, 9	9						
						5	7, 3	5		11 885.245	9.704	−4		
						5	3, 3	1						
						5	5, 3	3		11 885.379	9.838	−3		
4	2	3	−3	2	2								11 667.163	3
8	2	6	−8	1	7								11 191.983	0

Both analyses were treated in an iterative manner until the coupling constants on one hand and the rotational and centrifugal distortion constants on the other hand converged to final values. The results of the centrifugal distortion analysis are shown in Table 2. We transferred the distortion constants Δ_K and δ_K from the ^{35}Cl species as fixed values to the ^{37}Cl species as we measured not a sufficient number of ^{37}Cl species transitions.

Molecular Structure

The small values of the inertial defects Δ = 0.03816(4) amuÅ^2 and 0.03905(43) amuÅ^2 for 2-^{35}Cl(C_5H_4N) and 2-^{37}Cl(C_5H_4N) derived from the rotational constants indicate that the molecule is planar. Since only two isotopic species have been studied accurate structural information is difficult to obtain. However, we propose a r_0-structure trans-

Table 1 d. 2-chloropyridine-(^{37}Cl), excited state.

J'	K'_-	K'_+	$-J''$	K''_-	K''_+	$2F'_1$	$2F'$,	$2F''_1$	$2F''$	ν	$\Delta\nu_{hfs}$	δ_{hfs}	ν_0	δ_r
4	0	4	−3	0	3	5	7,	3	5				11 195.098	1
						5	3,	3	1	11 193.847	−1.828	−14		
						7	7,	5	5					
						7	9,	5	7					
						7	5,	5	3	11 194.052	−1.623	15		
						11	11,	9	9	11 195.333	−0.342	0		
						11	13,	9	11					
						11	9,	9	7	11 195.508	−0.167	8		
						9	9,	7	7					
						9	11,	7	9					
						9	7,	7	5	11 195.675				
4	1	3	−3	1	2	7	9,	5	7				12 023.710	4
						7	5,	5	3	12 022.329	−2.200	15		
						7	7,	5	5	12 022.494	−2.035	8		
						9	11,	7	9					
						9	7,	7	5	12 023.168	−1.361	−5		
						9	9,	7	7	12 023.281	−1.248	−6		
						5	7,	3	5	12 023.635	−0.894	6		
						5	3,	3	1					
						5	5,	3	3	12 023.785	−0.744	−1		
						11	13,	9	11					
						11	11,	9	9	12 024.529				
						11	9,	9	7					
4	2	2	−3	2	1	9	9,	9	7				11 562.496	−5
						9	7,	7	5	11 558.836	−7.634	−5		
						9	11,	7	9					
						7	5,	5	3					
						7	9,	7	7	11 560.817	−5.653	10		
						7	9,	5	7					
						7	7,	5	5	11 560.931	−5.539	8		
						11	13,	9	11					
						11	9,	7	7	11 564.560	−1.910	23		
						11	11,	9	9	11 564.670	−1.800	15		
						5	7,	3	5					
						5	3,	3	1	11 566.470				
4	2	3	−3	2	2	7	7,	5	5				11 371.217	0
						7	9,	5	7	11 369.646				
						7	5,	5	3					
						11	11,	9	9					
						11	13,	9	11	11 373.234	3.588	13		
						11	9,	9	7					
						5	5,	3	3					
						5	7,	3	5	11 375.134	5.488	−18		
						5	3,	3	1					
8	2	6	−8	1	7								11 201.761	0

ferring structural parameters from pyridine, and hence, hope to get some idea whether any ring distortion needs to be considered to explain the rotational constants. Sørensen [11] and Mata [12] have determined complete r_s-structures of pyridine. Since r_s-structures do not reproduce rotational constants very well, we fitted the structural parameters of pyridine using the programm MWSTR [13] to the known rotational constants in order to discuss the structure of 2-chloropyridine with reasonable assumptions. Table 3 contains the coordinates of pyridine obtained this way. Compared to the r_s-structures the ring is slightly expanded. This structure can reproduce the rotational constants of all isotopic pyridine species very well as shown in Table 4 a. With the assumption of this undisturbed pyridine ring the C−Cl bond length and the angle $\measuredangle NC_2Cl$ of 2-chloropyridine were fitted to the observed rotational constants of both species yielding

$$r_{C_2-Cl} = 1.718\ \text{Å} \quad \text{and} \quad \measuredangle NC_2Cl = 114.86°\,.$$

Table 2. Rotational [MHz] and centrifugal distortion [kHz] constants of 2-chloropyridine in the vibrational ground state. A, B, C: rotational constants, Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K fourth order centrifugal distortion constants according to Watson's A reduction, N: number of transitions, σ: standard deviation of the fit [MHz], $|(\ ,\ )|$: maximum correlation coefficient, $\Delta = I_c - I_b - I_a$: inertial defect [amu Å^2], I: moment of inertia [amu Å^2] (conversionfactor 505 376 MHz amu Å^2). Fixed values in square brackets, standard errors in units of the last digit in brackets, derived parameters below the line.

	2-^{35}Cl(C_5H_4N)		2-^{37}Cl(C_5H_4N)
A	5872.0279 (6)		5871.996(1)
B	1637.8348 (1)		1591.788 (1)
C	1280.5136 (1)		1252.189 (1)
Δ_J	0.06528 (69)		0.063 (6)
Δ_{JK}	0.2794 (41)		0.245 (68)
Δ_K	0.966 (56)		[0.966]
δ_J	0.01507 (13)		0.015 (7)
δ_K	0.3323 (52)		[0.3323]
N	45		12
σ	0.004		0.006
$\lvert(\delta_J, \delta_K)\rvert$	−0.946	$\lvert(A, \Delta_{JK})\rvert$	0.910
Δ	0.03816 (4)		0.03905 (43)

Figure 2 shows the molecule in its principal axis system. The bond length C−Cl is shorter than that of chlorobenzene (r_{C-Cl} = 1.7248(1) Å [14]), where a deformation of the benzene ring has been determined. For chlorobenzene the carbon atom bonded to the chlorine atom is shifted towards the centre of the ring by 0.015 Å.

We could not detect this effect in the case of 2-chloropyridine since the proposed structure of Fig. 2 is able to reproduce all observed rotational constants quoted in Table 4 b.

Quadrupole Interaction

A first order hfs analysis [15, 16] was carried out using the basis $\hat{F}_1 = \hat{J} + \hat{I}(\mathrm{Cl})$, $\hat{F} = \hat{F}_1 + \hat{I}(\mathrm{N})$ ($\hat{J}$ angular momentum, $\hat{I}$ spin operator). The coupling constants are given in Table 5. The ^{14}N coupling constants agree within single standard error. The off diagonal elements χ_{ab} of the coupling tensors do not contribute measurably to the quadrupole splittings. As the χ_{ab}'s are not known the tensors could not be diagonalized in order to determine the principal tensor elements. Therefore we give no discussion of the nitrogen coupling constants in terms of the electronic structure. We can only state that χ_{cc} varies from pyridine χ_{cc} = 3.474(3) MHz [17] to

Table 3. Atom coordinates (Å) of pyridine C_5H_5N in its principal axis system. The number of digits given do not reflect the errors. The structure based on these coordinates was used as input for the CNDO/2 calculations of 2-chloropyridine.

	a	b
N	−1.3939	0.0
C_2	−0.6942	1.1430
C_3	0.7017	1.1978
C_4	1.4140	0.0
H_2	−1.2753	2.0585
H_3	1.2049	2.1541
H_4	2.4951	0.0

Table 4. Experimental rotational constants [MHz] and the differences [MHz] to the calculated rotational constants based on the proposed structures. 4 a) Various isotopic pyridines. The structure of Table 3 was used.

Molecule	References	Rotational constants		Obs-calc
Pyridine	[12]	A	6039.2516 (6)	0.026
		B	5804.9116 (6)	−0.080
		C	2959.2117 (6)	−0.684
2-D-pyridine	[12]	A	5900.8828 (5)	0.136
		B	5558.5214 (5)	0.143
		C	2861.7137 (5)	−0.510
3-D-pyridine	[12]	A	5889.1923 (10)	0.135
		B	5555.0518 (10)	0.148
		C	2858.0310 (10)	0.520
4-D-pyridine	[12]	A	6038.9967 (10)	−0.229
		B	5420.0697 (9)	0.168
		C	2855.8194 (8)	−0.594
2-^{13}C-pyridine	[11]	A	5963.13 (4)	0.305
		B	5758.90 (3)	0.192
		C	2928.96 (1)	−0.535
3-^{13}C-pyridine	[11]	A	5956.57 (5)	0.243
		B	5756.00 (4)	0.236
		C	2926.63 (1)	−0.534
4-^{13}C-pyridine	[11]	A	6039.46 (3)	0.235
		B	5676.03 (2)	0.183
		C	2925.40 (1)	−0.550
^{15}-N-pyridine	[11]	A	6039.45 (8)	0.225
		B	5680.37 (6)	0.184
		C	2926.54 (2)	−0.562
4 b) 2-chloropyridine. Structure of Fig. 2 was used.				
2-^{35}Cl(C_5H_4N)		A	5872.0279 (6)	0.005
		B	1637.8348 (1)	0.101
		C	1280.5136 (1)	−0.061
2-^{37}Cl(C_5H_4N)		A	5871.996 (4)	0.004
		B	1591.788 (1)	0.007
		C	1252.189 (1)	−0.117

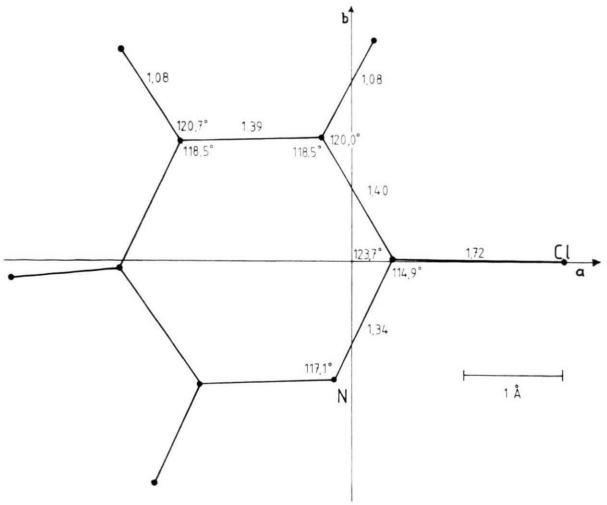

Fig. 2. 2-chloropyridine in the principal axis system. Structural parameters of the pyridine ring given in Table 3 were transferred. The values of the bond length and angles were rounded.

Table 5. Quadrupole coupling constants of 2-chloropyridine in the vibrational ground state. χ_{gg}: quadrupole coupling constants [MHz], σ: standard deviation [MHz], $|(,)|$: maximum correlation coefficient. Single standard errors in brackets, derived parameters below the line.

	2-^{35}Cl(C_5H_4N)	2-^{37}Cl(C_5H_4N)
χ_{aa}(Cl)	−70.42 (4)	−55.47 (5)
χ_{bb}(Cl)	39.69 (2)	31.23 (8)
χ_{aa}(N)	−0.09 (2)	−0.07 (4)
χ_{bb}(N)	−2.94 (2)	−2.99 (6)
σ	0.009	0.009
$\lvert(\chi_{aa}(\mathrm{Cl}), \chi_{aa}(\mathrm{N}))\rvert$	−0.72	−0.29
χ_{cc}(Cl)	30.73 (4)	24.24 (9)
χ_{cc}(N)	3.03 (3)	3.06 (7)

$\chi_{cc} = 3.03(3)$ indicating a substitutional effect. In the case of chlorine we make the usual assumption that the principal axis z of the coupling tensor coincides with the C−Cl bond. According to Fig. 2 the C−Cl bond coincides practically with the a principal axis of inertia. We define the principal coupling tensor axis y perpendicular to the molecular plane. Thus the principal elements of the coupling tensor and the coupling constants χ_{gg} ($g = a, b, c$) referred to the principal axes are assumed to be the same within the experimental errors. The ratios $C_g = \chi_{gg}(^{35}\mathrm{Cl})/\chi_{gg}(^{37}\mathrm{Cl})$ of the corresponding chlorine coupling constants $C_a = 1.2695(13)$, $C_b = 1.2709(33)$ and $C_c = 1.2672(50)$ are in good agreement with the ratio of the nuclear quadrupole moments $Q(^{35}\mathrm{Cl})/Q(^{37}\mathrm{Cl}) = 1.26878(15)$ [18].

We take this as an indication that the electronic surrounding in both isotopes is equal and equally located in the principal axis systems.

Within a simple MO model [19] the chlorine coupling constants depend on the population of the valence shell p-orbitals and eQq_{310}, the coupling contribution of one electron in a chlorine p_z-orbital with the principal quantum number $n = 3$:

$$\chi_{zz} = -\left(\frac{n_x + n_y}{2} - n_z\right) eQq_{310}$$

and cyclic permutations. (1)

Identifying the p-orbital populations n_g, $g = x, y, z$, with the bond order matrix elements $P_{P_zP_z}$, $P_{P_yP_y}$ and $P_{P_xP_x}$ [20] resulting from a CNDO/2 procedure we calculated the coupling constants. With the values

$$P_{P_zP_z} = 1.9919\,, \quad P_{P_yP_y} = 1.9707\,, \quad P_{P_xP_x} = 1.1430$$

combined with the normally accepted values of eQq_{310} of 109.74 MHz and 86.51 MHz for ^{35}Cl and ^{37}Cl [21] the calculated χ_{gg} were in poor agreement with the experimental values χ_{gg}. However there is a better agreement using the calibrated values 84.00 MHz and 66.17 MHz for eQq_{310} obtained from the experimental $\chi_{aa} = \chi_{zz}$ and the bond order matrix elements $P_{P_gP_g}$ with Equation (1). This yields

^{35}Cl: $\chi_{xx} = 36.54$ $\chi_{yy} = 33.87$ $(\chi_{zz} = -70.42$ MHz),

^{37}Cl: $\chi_{xx} = 28.79$ $\chi_{yy} = 26.68$ $(\chi_{zz} = -55.47$ MHz).

The brackets indicate that the values were used for calibration.

The experimental data may be used for a further consideration. The difference of the populations $n_x - n_y$ of the p_x and p_y orbital calculated with equation (1) and the experimental coupling constants is 0.054 for both isotopes with eQq_{310} 109.74 MHz and 86.51 MHz whereas CNDO/2 predicts 0.0212. Following Gordy [22] the experimental population difference is equivalent to 5.4% double bond character. With the assumption that the C−Cl bond is formed by a partically s-hybridized $3p_z$ orbital [23] with 15% s-contribution [24] the ionic character was found to be 21.3%. Since the applied theory gives only a rough picture of the bond we give no standard errors. The corresponding meso-

Table 6. Rotational and quadrupole coupling constants χ_{gg} [MHz] of an excited vibrational state of 2-chloropyridine. See also Table 2. Single standard errors in brackets, derived parameters below the line.

	$2\text{-}^{35}Cl(C_5H_4N)$		$2\text{-}^{37}Cl(C_5H_4N)$
A	5843.516 (2)		5843.277 (4)
B	1638.991 (1)		1592.926 (1)
C	1282.037 (1)		1253.675 (1)
σ	0.003		0.005
$\lvert(A, C)\rvert$	0.77	$\lvert(B, C)\rvert$	−0.85
χ_{aa}(Cl)	−70.09 (8)		−55.30 (11)
χ_{bb}(Cl)	39.70 (11)		31.17 (17)
χ_{aa}(N)	−0.10 (6)		0.00 (11)
χ_{bb}(N)	−2.94 (8)		−3.05 (13)
σ	0.014		0.015
$\lvert(\chi_{aa}(N), \chi_{bb}(N))\rvert$	−0.34	$\lvert(\chi_{aa}(Cl), \chi_{bb}(Cl))\rvert$	−0.24
Δ	−0.633 (1)		−0.6355 (1)
χ_{cc}(Cl)	30.39 (14)		24.13 (2)
χ_{cc}(N)	3.04 (14)		3.05 (17)

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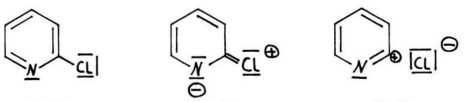

74% 5% 21%

The experimental double bond character is larger than that of 4-chloropyridine (4.2% [23]) and 3-chloropyridine (2.9% [25]). This sequence corresponds to that of the bromopyridines, whose double bond characters are somewhat smaller [26].

Excited Vibrational States

Walden [3] has observed vibrational satellites of 2-chloropyridine (^{35}Cl) and assigned them from considerations of intensity to the first excited vibrational state of the C−Cl out of plane vibration at 188 cm^{-1} [27]. We looked for the corresponding lines of the ^{37}Cl species, determined the rotational constants according to the rigid rotor model [28] and carried out a first order hfs analysis for both. The results summarized in Table 6 show a significant change of the rotational constant A whereas the nitrogen coupling constants are in rough agreement with the corresponding constants of the vibrational ground state. The chlorine coupling constants χ_{aa} and χ_{cc} seem to be slightly affected by the vibration. The vibrational assignment is consistent with the inertial defects $\Delta = -0.6331(1)$ amu Å^2 and $-0.6355(1)$ amu Å^2 for the ^{35}Cl and ^{37}Cl species respectively since out of plane vibrations show a negative change with vibrational quantum numbers contrary to in plane vibrations [29].

Acknowledgements

We thank the members of our group for help and discussions, especially Dr. W. Kasten for reading the manuscript, and the Deutsche Forschungsgemeinschaft and the Fonds der Chemie for funds. The calculations were carried out at the computer center of the University of Kiel.

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