NQR and Crystal Structure of 4,5-Dichloroimidazole, $C_3H_2N_2Cl_2$*

Shi-Qi Dou and Alarich Weiss

Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, Darmstadt, Germany

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The two line ^{35}Cl NQR spectrum of 4,5-dichloroimidazole was measured in the temperature range $77 \leqq T/K \leqq 389$. The temperature dependence of the NQR frequencies conforms with the Bayer model and no phase transition is indicated in the curves $\nu(^{35}Cl) = f(T)$. Also the temperature coefficients of the ^{35}Cl NQR frequencies are "normal". At 77 K the ^{35}Cl NQR frequencies are 37.409 MHz and 36.172 MHz and at 389 K 35.758 MHz and 34.565 MHz.

The compound crystallizes at room temperature with the tetragonal space group D_4^4-$P4_12_12$, $Z = 8$ molecules per unit cell; at 295 K: $a = 684.2(5)$ pm, $c = 2414.0(20)$ pm. The relations between the crystal structure and the NQR spectrum are discussed.

Introduction

Imidazole is a weak base, pK = 6.95, and in the protonated form two resonance structures can be formulated which may be written for the molecule itself, too. Substitution of the hydrogen at the carbon atoms by chlorine should change this property only little. Therefore we became interested to study the ^{35}Cl NQR spectrum and the structure of 4,5-dichloroimidazole for comparison of NQR frequencies and bond lengths C–Cl in the configuration ClC=CCl [1, 2]. In the following, we report on the results of the crystal structure determination and on the ^{35}Cl NQR spectrum in the range $77 \leqq T/K \leqq 389$.

Experimental

4,5-Dichloroimidazole, commercially available from Fluka, Neu-Ulm, Germany, was used after recrystallization from hot water (colorless small prisms) [3] for both experiments, ^{35}Cl NQR and X-ray diffraction.

The crystal structure was determined with a 4-circle X-ray goniometer; in Table 1 the experimental details are given together with some crystallographic data of the compound. The structure was determined from the reflexion intensities, after appropriate corrections for absorption and LP-factor, by direct methods, SHELX 86 [4]. The final atomic positions and thermal parameters, including the hydrogen positions, were found by least squares refinement, SHELX 76 [5].

For the ^{35}Cl NQR measurements a superregenerative spectrometer with lock in technique, time constant 10 s, and recorder was used. The temperatures at

Table 1. Crystal structure of 4,5-dichloroimidazole, $C_3H_2N_2Cl_2$; experimental conditions for the structure determination and crystal structure data.

Formula		$C_3H_2N_2Cl_2$; $M = 136.95$
Crystal habitus		Colorless prism $(0.15 \times 0.18 \times 0.65)$ mm^3
Diffractometer		Stoe-Stadi 4
Wavelength λ/pm		71.069 (MoKα)
Monochromator		Graphite (002)
T/K		290
Scan		$\omega/2\theta$
Absorption coefficient μ/m^{-1}		938
F (000)		544.00
$(\sin\theta/\lambda)_{max}$/pm^{-1}		0.005385
Number of reflexions measured		1419
Independent reflexions		744
Reflexions considered		660
Number of free parameters		71
$R(F)$		0.060
$F_w(F)$		0.056
Lattice constants	a/pm	684.2(5)
	b/pm	684.2(5)
	c/pm	2414.0(20)
	$V \cdot 10^{-6}$/pm^3	1130.06(259)
Space group		D_4^4-$P4_12_12$
Formula units/unit cell Z		8
ϱ_c/(Mg · m^{-3})		1.609(3)
ϱ_x/(Mg · m^{-3})		1.577 (with Nonane as liquid)

Point positions: all atoms in 8 b:

x, y, z; $\bar{x}, \bar{y}, \frac{1}{2}+z$; $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{4}+z$; $\frac{1}{2}+y, \frac{1}{2}-x, \frac{3}{4}+z$;
$y, x, \bar{z}$; $\bar{y}, \bar{x}, \frac{1}{2}-z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}-z$

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Reprint requests to Prof. Dr. Al. Weiss, Institut für Physikalische Chemie, Petersenstraße 20, W-6100 Darmstadt, FRG.

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Table 2. Atomic coordinates and thermal parameters of 4,5-dichloroimidazole, $C_3H_2N_2Cl_2$; the temperature factor is of the form: $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} - 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$. The U_{ij} are given in $(pm)^2$; U is isotropic mean for the hydrogen atoms.

Atom	x/a	b/y	z/c	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Cl^{(4)}$	0.3392(4)	0.5888(4)	0.1551(1)	1125(20)	837(17)	1356(24)	215(13)	−103(18)	392(14)
$Cl^{(5)}$	0.7021(3)	0.2261(4)	0.1627(1)	743(14)	1161(19)	1143(19)	230(12)	233(13)	25(15)
$N^{(1)}$	0.4327(9)	0.1190(10)	0.2361(3)	715(46)	719(43)	746(46)	397(36)	−5(35)	38(39)
$C^{(2)}$	0.2603(13)	0.1774(13)	0.2554(4)	870(60)	906(65)	768(35)	431(52)	127(54)	127(48)
$N^{(3)}$	0.2054(9)	0.3447(9)	0.2327(3)	700(39)	786(43)	780(43)	415(36)	47(38)	46(37)
$C^{(4)}$	0.3477(10)	0.3880(10)	0.1963(3)	643(43)	513(42)	668(45)	121(40)	−179(44)	−27(37)
$C^{(5)}$	0.4898(10)	0.2521(11)	0.1982(3)	606(42)	634(45)	592(46)	163(43)	−48(40)	−68(45)
$H(N^{(1)})$	0.5065(127)	0.0321(113)	0.2466(31)	900					
$H(C^{(2)})$	0.2201(127)	0.1084(120)	0.2817(30)	900					

Table 3. Crystal structure of 4,5-dichloroimidazole, $C_3H_2N_2Cl_2$; intra- and intermolecular distances (d/pm) and angles (°).

Atoms	d/pm	Atoms	Angle/°
$Cl^{(4)}-C^{(4)}$	169.6(7)	$Cl^{(5)}-C^{(5)}-C^{(4)}$	132.3(7)
$Cl^{(5)}-C^{(5)}$	169.6(7)	$Cl^{(5)}-C^{(5)}-N^{(1)}$	121.3(5)
$N^{(1)}-C^{(2)}$	133.1(10)	$C^{(4)}-C^{(5)}-N^{(1)}$	106.3(7)
$C^{(2)}-N^{(3)}$	132.4(9)	$Cl^{(4)}-C^{(4)}-C^{(5)}$	127.2(7)
$N^{(3)}-C^{(4)}$	134.5(9)	$Cl^{(4)}-C^{(4)}-N^{(3)}$	122.4(5)
$C^{(4)}-C^{(5)}$	134.6(9)	$C^{(5)}-C^{(4)}-N^{(3)}$	110.3(7)
$C^{(5)}-N^{(1)}$	134.7(9)	$C^{(4)}-N^{(3)}-C^{(2)}$	104.9(6)
$N^{(1)}-H(N^{(1)})$	82.0(74)	$N^{(1)}-C^{(2)}-N^{(3)}$	111.4(7)
$C^{(2)}-H(C^{(2)})$	83.7(76)	$C^{(5)}-N^{(1)}-C^{(2)}$	107.0(6)
$N^{(1)}\cdots N'^{(3)}$	279.5(7)	$N'^{(3)}\cdots H(N^{(1)})-N^{(1)}$	
$N'^{(3)}\cdots H(N^{(1)})$	198.2(79)		172.4(9)
$Cl^{(5)}\cdots Cl'^{(4)}$	366.3(3)		

	a/x	b/y	c/z
$N'^{(3)}$	0.6554	−0.2054	0.2673
$Cl'^{(4)}$	0.1608	0.0888	0.0949

the sample site were produced in the usual way, see e.g. [2]. Frequency and temperature measurements are accurate to ±5 kHz and 0.5 K, respectively.

Results

In Table 1 some crystallographic data of 4,5-dichloroimidazole are given, together with the experimental conditions for the crystal structure determination. Table 2 lists the atomic coordinates and the thermal parameters, and in Table 3 intra- and intermolecular coordinates are presented. The calculated and observed structure factors are available on request [15].

The ^{35}Cl NQR frequencies are listed for 77 K and 290 K in Table 4, which contains also the parameters describing the temperature dependence of the frequencies. The parameters are the coefficients of the polynomial

$$\nu = \sum_{i=-1}^{2} a_i T^i . \quad (1)$$

Discussion

In Fig. 1 the projection of the unit cell of 4,5-dichloroimidazole along [100] onto the (bc)-plane is shown. One recognizes immediately zig-zag chains of the molecules running in the direction [010] at $z = 0$, 0.25, 0.5, and 0.75. Hydrogen bonds $N^{(1)}-H\cdots N^{(3)}$ connect the molecules within a chain. One can also speak about layers, parallel to (ab), and the layers are bond together by van der Waals forces between the chlorine atoms forming the surfaces of the layers. The intermolecular bond distance we observe, $N^{(1)}\cdots N^{(3)}$ is 279.5(7) pm, see Table 3; this value compares well with the intermolecular distance $N^{(1)}\cdots N^{(3)}$ observed for imidazole, for which compound several crystal structure determinations have been reported [6–9]. The layer distances, determined by the intermolecular distance $Cl^{(5)}\cdots Cl'^{(4)} = 366.3$ pm, compare favorably with the van der Waals diameter of the chlorine atom (360 pm).

It is worthwhile to compare imidazole, $C_3N_2H_4$, with the present derivative, 4,5-dichloroimidazole. Imidazole crystallizes with a structure basically similar to the structure of the 4,5-dichloro compound. In both cases the significant structural property is the chain structure, formed by intermolecular hydrogen bonds. The interesting features of the hydrogen bonded chain system of imidazole were found by Zimmermann and his coworkers [10–12]. By spectroscopic methods (IR-, Raman- and ^1H-NMR spectroscopy) and by X-ray diffraction on solutions they observed a strong intermolecular hydrogen bond

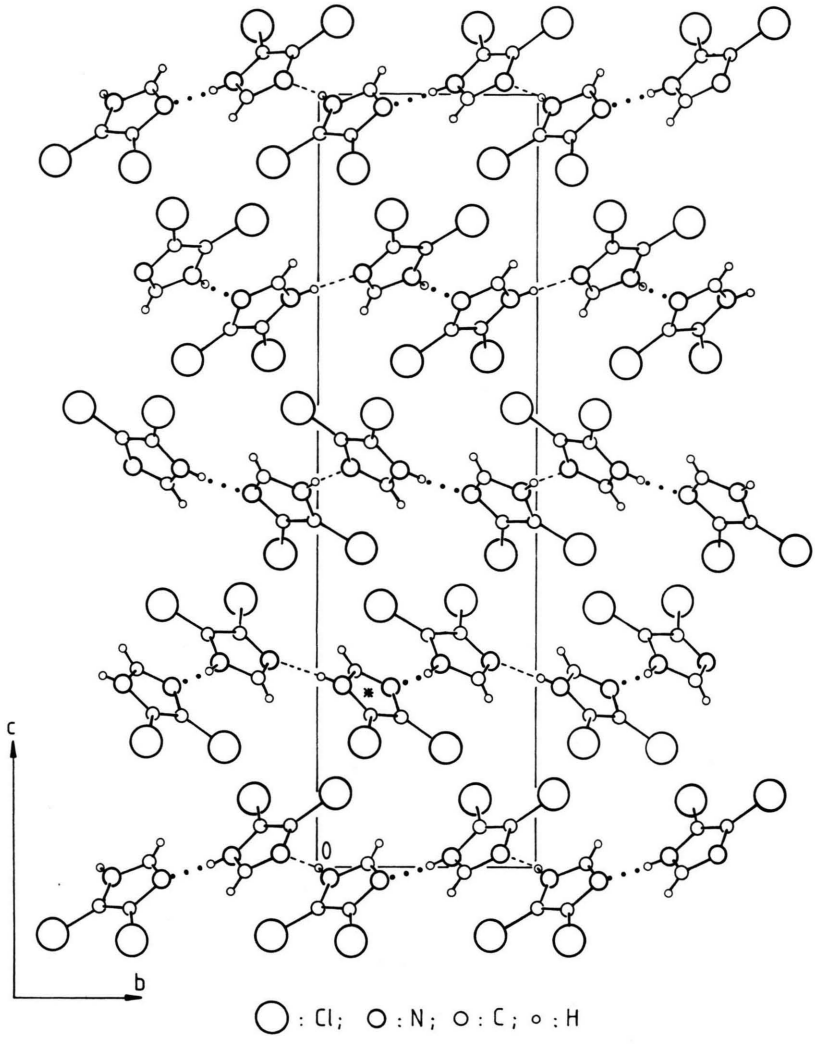

Fig. 1. Projection of the unit cell of 4,5-dichloroimidazole, $C_3H_2Cl_2N_2$ along [100] onto the (bc)-plane. The molecule marked by * is the one for which the coordinates are given in Table 2.

Table 4. Power series expansion $\nu(^{35}Cl) = \sum a_i T^i$ for 4,5-dichloroimidazole, $C_3H_2N_2Cl_2$. N = number of experimental points used for fitting, σ the standard deviation and $\delta T = T_2 \ldots T_1$, the temperature range for which the polynomial $\nu(T) = \sum a_i T^i$ was fitted to the experimental ν_1 and ν_2. The compound shows ^{35}Cl NQR frequencies in the whole range covered. The signal to noise ratio, S/N, measured with a time constant 10 s and recorder is given in parentheses.

Line	(^{35}Cl) NQR line at 77 K	(^{35}Cl) NQR line at 389 K	$\sigma \cdot 10^3$ / MHz	a_{-1} / MHz · K	a_0 / MHz	$a_1 \cdot 10^3$ / MHz · K^{-1}	$a_2 \cdot 10^6$ / MHz · K^{-2}	N	$\delta T = T_2 \ldots T_1$
1	37.409(5)	35.760(5)	4	−11.844	37.935	−4.663	−2.209	16	77 ... 388
2	36.172(5)	34.564(5)	7	−17.710	36.852	−5.773	0.015		

which leads to a proton transfer even in the solid state, and there down to 120 K. For the molecule in the solid this means the realisation of the two tautomeric forms.

An important contribution to the imidazole problem is provided by the ^{14}N-NQR experiments of Koo and Hsieh [13]. By double resonance experiments the authors determined the ^{14}N nuclear quadrupole coupling constants, $e^2 Q q h^{-1}(^{14}N)$, and the asymmetry parameters, $\eta(^{14}N)$ at 77 K. 3.2714 MHz and 0.128 have been found for $e^2 Q q h^{-1}$ and η for one nitrogen

and 1.4245 MHz and 0.98 for the other one, respectively. These results show that at 77 K the two nitrogen atoms are distinctly different and the hydrogen is fixed to one position in the molecule at least in the time scale of the NQR experiment. Also $e^2Qqh^{-1}(^2H)$ and $\eta(^2H)$ measured on monodeuteroimidazole by Hunt et al. [14] points toward a fixed hydrogen atom at 77 K. In [14], the assignment of the ^{14}N NQR parameters to the tri-coordinated nitrogen, respectively to the two-coordinated one, is discussed in detail.

A consequence of a rapid proton exchange between the two possible positions of the imino hydrogen is the averaging of the intramolecular distances within the ring C_3N_2. For imidazole the reported distances are between 132.0 pm and 137.5 pm [9] at room temperature and between 132.6 pm and 137.8 pm at 120 K [8]. We find these intramolecular ring distances between 132.4 pm and 134.7 pm (Table 3). One significant difference between imidazole and the 4,5-dichloro derivative is the slight overall shortening of the intermolecular distances in the Cl-substituted compound compared with imidazole. An other characteristic of the molecules in the solid is the planarity of the rings. [8] reports a maximum deviation of the atoms from the optimum plane through the five atom rings of 0.4 pm and [9] finds 0.4 pm, too. The best plane through the ring N_2C_3 of 4,5-dichloroimidazole is given by

$$0.4702\,x + 0.5058\,y + 0.7160\,z = 5.8889, \qquad (2)$$

the deviations being (in pm): ($Cl^{(4)}$: −3.8; $Cl^{(5)}$: −1.9; $N^{(1)}$: 0.4; $C^{(2)}$: −0.9; $N^{(3)}$: 1,1; $C^{(4)}$: −0.9; $C^{(5)}$: 0.3. The substitution apparently slightly disturbes the planarity of the ring.

From the Fourier synthesis we have been able to locate the hydrogen at the nitrogen $N^{(1)}$. Therefore we must assume that the tautomerism is at least partially suppressed by the substitution of H by Cl in the positions 4 and 5. This assumption is supported by our ^{35}Cl NQR data. In Fig. 2 the frequencies are plotted vs. temperature. As already mentioned, the two simple conclusions are: The ^{35}Cl NQR spectrum is in agreement with the symmetry properties of the crystal and there is no phase transition in the temperature range covered by the NQR measurements. Following the rule, $\nu(^{35}Cl) = c \cdot (1/(d(C-Cl)^{-3})$, ν_1 and ν_2 should be nearly equal in frequency. This is by no means so. Also

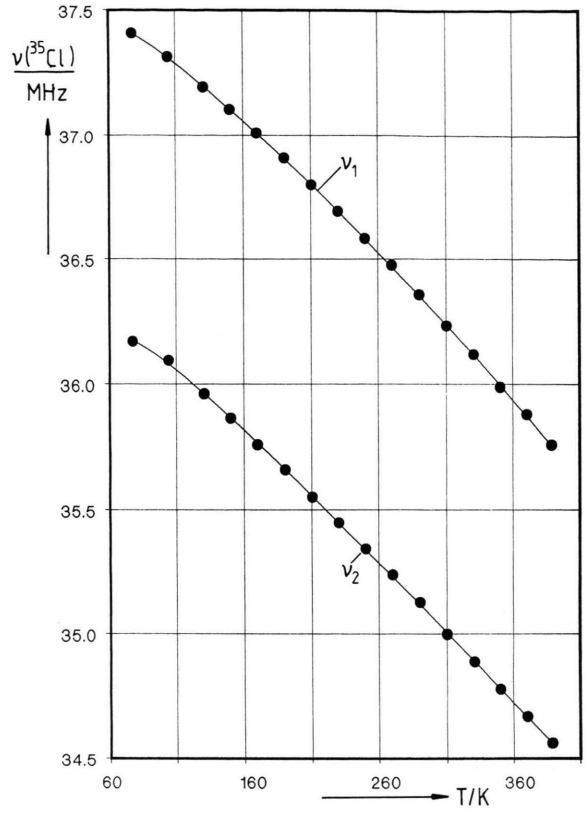

Fig. 2. ^{35}Cl NQR frequencies of 4,5-dichloroimidazole as functions of temperature.

the mean of the two frequencies (at 77 K) is much lower than expected from the $\nu(^{35}Cl) = f(C-Cl)$ relation given in [1] for bonds $C(sp^2)-Cl$. One may find several arguments for these discrepancies. The double bond C=C may be partially delocalized, the clamping of the C=C bond betwen two nitrogen atoms may change the hybrid character at the carbons, the Hammett parameter on the Cl site may be changed by the two nitrogens. Experiments with imidazoles of different substitution pattern and a precise location of the hydrogen position by neutron diffraction will be helpful for solving the problem.

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[1] St. Brummer, H. Paulus, and Al. Weiss, Z. Naturforsch. **43a,** 873 (1988).
[2] St. Brummer and Al. Weiss, Ber. Bunsenges. Phys. Chem. **94,** 497 (1990).
[3] A. W. Lutz and S. DeLorenzo, J. Heterocycl. Chem. **4,** 399 (1967).
[4] G. M. Sheldrick, Program for Crystal Structure Determination, Univ. of Göttingen, Germany 1986.
[5] G. M. Sheldrick, Program for Crystal Structure Determination, University of Cambridge, England 1976.
[6] G. Will, Nature London **198,** 575 (1963).
[7] G. Will, Z. Kristallogr. **119,** 1 (1963).
[8] S. Martinez-Carrera, Acta Cryst. **20,** 783 (1966).
[9] Yu. A. Omel'chenko and Yu. D. Kondrashev, Kristallografiya **16,** 115 (1970); Soviet Phys.-Cryst. **16,** 88 (1971).
[10] H. Zimmermann, Z. Elektrochem., Ber. Bunsenges. Phys. Chem. **63,** 601 (1959).
[11] H. Zimmermann, Z. Elektrochem., Ber. Bunsenges. Phys. Chem. **65,** 821 (1961).
[12] N. Joop and H. Zimmermann, Z. Phys. Chem. N.F. **42,** 61 (1964).
[13] J. Koo and Y. N. Hsieh, Chem. Phys. Lett. **9,** 238 (1971).
[14] M. J. Hunt, A. L. Mackay, and D. T. Edmonds, Chem. Phys. Lett. **34,** 473 (1975).
[15] Further information on the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany. Inquiries should be accompanied by the depository number CSD-55446, the names of the authors, and the full literature reference.