The Bond N−Cl. A Spectroscopic (^{35}Cl-NQR, IR) Investigation

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Chlorine bound to nitrogen is an interesting oxidizing agent in aqueous, partial aqueous and non-aqueous media. One can assume that the oxidizing action of the chlorine depends on the polarization of the Cl atom in the bond N−Cl which will depend on the electron distribution in the ligands R and R″ of the configuration R−NCl−CO−R″. 17 compounds were synthesized with R = substituted phenyl radical $C_6H_{5-y}X_y$, X = Cl, NO_2, R″ = CH_2Cl. The ^{35}Cl NQR frequencies are observed in the range 52 to 54 MHz (T = 77 K) for the $Cl^{(N)}$, 34 to 37 MHz for the phenyl chlorines and the CH_2Cl group. Their temperature dependence was followed up to 300 K. Therefrom the assignment of the resonance to certain Cl-atoms in the molecules is possible. Generally, the substitution of a negative substituent X (Cl, NO_2) in the phenyl ring raises the resonance frequencies; the influence of the CH_2Cl group on the N−Cl bond is weak. Strong is the influence of the carbonyl group on the N−Cl bond. The IR group frequencies ν(C=O) are found in the range $1680 \leq \nu\,(C{=}O)/cm^{-1} \leq 1717$, shifted up by $\leq 20\ cm^{-1}$ compared to the corresponding acetamide R−NH−CO−R″. Influence of the phenyl ring substitution on ν (C=O) does not follow a simple law of inductive effect. Also a correlation between the vibration frequencies of the N−Cl group and the phenyl group substitution is not found.

Introduction

N−Cl compounds are of interest in synthetic, analytical and biological chemistry, because of their oxidizing action in aqueous, partial aqueous and non-aqueous media. Their oxidizing power depends on the ease with which the halogen is released as positive ion in the reaction system, which in turn depends on the electron environment around the N−X bond. In recent years one of us [1] has followed up oxidation reactions in solution with N-halogen. A sensitive measure for the polarization of the N-halogen bond is the halogen nuclear quadrupole resonance (NQR). The ^{35}Cl NQR at 77 K of several compounds with N−Cl bond was studied in the past. For the configuration R=N−Cl, Segel et al. [2] observed for N-chloro-p-benzoquinoneimine a ^{35}Cl NQR singlet at 45.0 MHz, and Hart and Whitehead [3] observed a singlet at 46.3 MHz on 2,6-dibromo-N-chloro-p-benzoquinoneimine. At the lower end of the frequency scale for ^{35}Cl NQR in N−Cl bonds one finds also N-chloropiperidine (Kashiwagi et al. [4]) with 43.9 MHz. In the 44−46 MHz range the resonances of $(R-S)(O_2)-N-Cl)^- \cdot Na^+ \cdot 3H_2O$ (chloramine B, R = C_6H_5) [3] and chloramine T, R = $H_3CC_6H_4$) (Hooper and Bray [5]) have been observed. N-chloroethyleneimine (45.6 MHz) is in this range (Osokin et al. [6]) as is N-chloro-N-methyl-methanamine (Schempp [7]). The dichloramines B and T with the configuratioan $R-S(O)_2-NCl_2$ have been studied [3, 5] and the ^{35}Cl NQR frequencies are considerably higher, between 51.6 and 52.6 MHz. The ^{35}Cl NQR spectrum of N-chlorosuccinimide [3, 5], N-chlorophthalimide [3], 1,3-dichloro-5,5-dimethylhydantoin [3, 5], N,N-dichlorourethane and 1-chlorobenzotriazole [3] are still up in the frequency scale with the highest resonance found at 56.7 MHz. The $^{35}Cl^{(N)}$ resonance frequencies may go up higher; 1,3,5-trichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione has its $^{35}Cl^{(N)}$ at 58.9 MHz (77 K) (Nagao and Katagiri [8−10]). For this compound the ^{37}Cl NQR was reported too (Fitzky et al. [11]). The salts $[(CH_3)_3NCl]^+ClO_4^-$ and $[(CH_3)_3NCl]^+BF_4^-$ were studied by Lynch and Waddington [12] and by Cowan et al. [13]. An upshift of the ^{35}Cl frequencies into the range of 52−54 MHz occurs in configurations $R-NCl(NO_2)$ as shown by Fridman et al. [14].

Hart and Whitehead have analysed theoretically and classified the chlorine NQR spectra of the compounds given above. A comprehensive report on ^{35}Cl NQR data of chlorine in bonds N−Cl (also of ^{14}N-NQR in these bonds) is due to Chihara and Nakamura [15].

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Several years ago we have studied the ^{35}Cl NQR spectra of a number of ring chlorinated anilines, anilinium salts (Pies and Weiss [16]) and acetanilides $Cl_nC_6H_{5-n}NHC(O)CH_{3-x}Cl_x$ (Pies et al. [17]). At present the chemistry of acetanilides has found considerable interest because of their use as fungicides and pesticides. Recently we have determined the crystal structure of N-[2,6 dichlorophenyl]-2-chloroacetamide and of N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide. As a function of temperature the ^{35}Cl-NQR spectrum of these two compounds and of N-[2,6-dichlorophenyl]-2,2-dichlo-roacetamide and the phase transitions in these solid compounds were investigated (Groke et al. [18]), $2,6\text{-}Cl_2C_6H_3NHCOCCl_3$ by neutron diffraction and T_1 (^{35}Cl) measurements (Groke et al. [19]). Nagao and Katagiri have studied ^{35}Cl NQR resonances at 77 K of N–Cl in N-[2,6-dichlorophenyl]-acetamide, N-[2,5-dichlorophenyl]-acetamide, and N-[2-chlorophenyl]-acetamide including the ring-chloro resonances. The $Cl^{(N)}$ frequencies are in the range 52.6–53.4 MHz [8].

In the following we report on ^{35}Cl NQR in N–Cl bonds of N-[chloro- and nitrophenyl]-N(Cl)-2-chloroacetamides and the C=O and N–Cl IR wave numbers. We shall discuss the influence of the substitution on the phenyl ring and of the CH_2Cl group on the ^{35}Cl NQR in the bond N–Cl and on ν (C=O) and ν (N–Cl).

Experimental

The Preparation of the Compounds

The acetanilides were prepared from commercial anilines and chloroacetylchloride, respectively, following the methods given in [17]. The compounds were purified by either zone refining or by double distillation. The compounds were recrystallized from ethanol. The purity of the reported acetanilides was checked by measuring the melting points T_m and the ^{35}Cl NQR frequencies known from [17], see Table 1. New acetanilides were analysed by chemical analysis (C, N, H). N-chloro-N-[chlorophenyl]-2-chloroacetamides were prepared as follows by procedures similar to those of N-chloro-N-[chlorophenyl]acetamides [20–23].

a) N-chloro-N-[phenyl or monochlorophenyl]-2-chloroacetamides were prepared by treating the finely powdered corresponding acetanilides, suspended in aqueous solution of $NaHCO_3$, with an excess of sodium hypochlorite solution under vigorous stirring (3 h). The organic matter was extracted with $HCCl_3$. The $HCCl_3$-solution was further treated with a fresh mixture of solutions of $NaHCO_3$ and NaOCl (30′). For complete chlorination the latter step was repeated once more. The solution was dried with Na_2SO_4, filtered, and $HCCl_3$ was evaporated under reduced pressure to obtain the desired N–Cl compound.

b) N-chloro-N-[dichlorophenyl]-2-chloroacetamides were prepared by treating the corresponding acetanilides with a calcium hypochlorite solution, acidified with acetic acid (30′). After extraction with $HCCl_3$, the chloroform solution was again treated with aqueous acetic acid solution of $Ca(OCl)_2$ 2–3 times. The chloroform solution was freed from acetic acid with $NaHCO_3$ and then dried with Na_2SO_4. $HCCl_3$ was evaporated and the nitrogen chlorides solidified on cooling. The 2,4- and 2,6-dichlorophenyl compounds solidified after 2–4 weeks.

c) N–Cl–N-[nitrophenyl]-2-chloroacetamides were prepared by treating the corresponding acetanilides in pure acetic acid with aqueous acetic acid solutions of $Ca(OCl)_2$. The rest of the procedure was similar to (b).

All the N-chloro-compounds were recrystallized either from a mixture $HCCl_3$/light petrolether or from cyclohexane, toluene, and mixtures of the two solvents, respectively. The purity of the compounds was checked by estimating the active chlorine content by iodometric titration. In Table 1 we list the compounds synthesized, analysed, and investigated spectroscopically, their crystal habitus, color, melting point T_m, and the results of the chemical analysis.

^{35}Cl NQR Spectroscopy

Polycrystalline samples of the title compounds were studied as function of temperature T in the range $77 \leq T/K \leq 300$, or up to the fade out temperature T_f of the ^{35}Cl NQR signals (Table 2). The spectra were registered by the continuous wave method with a superregenerative spectrometer. T at the sample site was produced by a stream of temperature and flow regulated nitrogen gas and with a liquid nitrogen bath at 77 K. The temperatures at the sample site were measured by copper-constantan thermocouples to ±1 K, the resonance frequency via a frequency counter to ±5 kHz, the latter accuracy is determined by the line width of the resonances, which is between 15 and 20 kHz. The $^{37}Cl^{(N)}$ NQR was also registered for the N–Cl compounds at 77 K.

Table 1. Compounds (acetanilides and Cl$^{(N)}$-acetanilides), synthesized, analysed, and studied. Given is for the newly synthesized compounds in weight% (calc./found): C, H, N, $(Cl)_{act.}$, the habitus, color, melting point T_m (in °C).

The acetanilides (N–H) of (**7**), (**9**)–(**14**), i.e., (**7a**), (**9a**)–(**14a**), have not been analysed chemically. The identification of the compounds was done by measuring their melting points and ^{35}Cl-NQR of w-Cl and ring-Cl, respectively, at 77 K and comparing the data with literature data reported in [17].

I. Compounds

(**1**): N-phenyl-2-chloroacetamide, C_8H_8ClNO; prisms, white, $T_m = 134\,°C$;
(**2**): N-[3-chlorophenyl]-2-chloroacetamide, $C_8H_7Cl_2NO$; needles, transparent, $T_m = 100\,°C$;
(**3**): N-[2-nitrophenyl]-2-chloroacetamide, $C_8H_7ClN_2O_3$; needles, greenish yellow, $T_m = 88\,°C$;
(**4**): N-[3-nitrophenyl]-2-chloroacetamide, $C_8H_7ClN_2O_3$; prisms, grey, $T_m = 115\,°C$;
(**5**): N-[4-nitrophenyl]-2-chloroacetamide, $C_8H_7ClN_2O_3$; prisms, yellow, $T_m = 182\,°C$;
(**6**): N–Cl–N-[phenyl]-2-chloroacetamide, $C_8H_7Cl_2NO$; prisms, white, $T_m = 75\,°C$;
(**7**): N–Cl–N-[2-chlorophenyl]-2-chloroacetamide, $C_8H_6Cl_3NO$; prisms, transparent, $T_m = 76\,°C$;
(**8**): N–Cl–N-[3-chlorophenyl]-2-chloroacetamide, $C_8H_6Cl_3NO$; prisms, transparent, $T_m = 81\,°C$;
(**9**): N–Cl–N-[4-chlorophenyl]-2-chloroacetamide, $C_8H_6Cl_3NO$; prisms, white, $T_m = 72\,°C$;
(**10**): N–Cl–N-[2,3-dichlorophenyl]-2-chloroacetamide, $C_8H_5Cl_4NO$; prisms, pale yellow, $T_m = 65\,°C$;
(**11**): N–Cl–N-[2,4-dichlorophenyl]-2-chloroacetamide, $C_8H_5Cl_4NO$; prisms, transparent, $T_m = 48\,°C$;
(**12**): N–Cl–N-[2,5-dichlorophenyl]-2-chloroacetamide, $C_8H_5Cl_4NO$; prisms, white, $T_m = 75\,°C$;
(**13**): N–Cl–N-[2,6-dichlorophenyl]-2-chloroacetamide, $C_6H_5Cl_4NO$; prisms, pale orange, $T_m = 48\,°C$;
(**14**): N–Cl–N-[3,4-dichlorophenyl]-2-chloroacetamide, $C_8H_5Cl_4NO$; plate like prisms, pale yellow, $T_m = 84\,°C$;
(**15**): N–Cl–N-[2-nitrophenyl]-2-chloroacetamide, $C_8H_6Cl_2N_2O_3$; plates, pale yellow, $T_m = 97\,°C$;
(**16**): N–Cl–N-[3-nitrophenyl]-2-chloroacetamide, $C_8H_6Cl_2N_2O_3$; prisms, pale yellow, $T_m = 87–92\,°C$ (decomp);
(**17**): N–Cl–N-[4-nitrophenyl]-2-chloroacetamide, $C_8H_6Cl_2N_2O_3$; prisms, pale yellow, $T_m = 89\,°C$;
(**18**): N–Cl–N-[phenyl]-acetamide, C_8H_8ClNO; prisms, white, $T_m = 90\,°C$ (91°C)

II. Chemical Analysis

(**1**): C (56.65/56.56), H (4.75/4.70), N (8.26/8.23); (**2**): C (47.09/47.0), H (3.46/3.42), N (6.86/6.84);
(**3**): C (44.77/44.65), H (3.29/3.16), N (13.05/13.12); (**4**): C (44.77/44.73), H (3.29/3.20), N (13.05/13.16);
(**5**): C (44.77/44.68), H (3.29/3.18), N (13.05/13.16); (**6**): Cl (17.37/17.12); (**7**): Cl (14.87/14.67); (**8**): Cl (14.87/14.58);
(**9**): Cl (14.87/14.51); (**10**): Cl (12.99/12.82); (**11**): Cl (12.99/12.86); (**12**): Cl (12.99/12.77); (**13**): Cl (12.99/12.87);
(**14**): Cl (12.99/12.79); (**15**): Cl (14.24/14.16); (**16**): Cl (14.24/14.03); (**17**): Cl (14.24/13.93); (**18**): Cl (20.90/20.59).

Acetanilides synthesized and identified by comparing melting points T_m (in °C) and ^{35}Cl NQR in frequencies (in MHz) with the data reported by Pies et al. [17]. The data of [17] are in parentheses; the sequence is (Compound); T_m: $\nu^{(1)}$.

(**7a**): T_m 75 (75–76), $\nu(Cl^{(2)})$ 35.342 (35.351), $\nu(Cl^{(W)}$ 36.155 (36.278); (**9a**): T_m 169 (168), $\nu(Cl^{(4)})$ 35.752 (35.745), $\nu(Cl^{(W)})$ 34.954 (34.962); (**10a**): T_m 111 (111–112); (**11a**): T_m 103 (102–103), $\nu(Cl^{(2)})$ 36.112, 36.164 (36.138, 36.159), $\nu(Cl^{(4)})$ 35.306, 35.551 (35.310, 35.588); (**12a**): T_m 116 (116.5); (**13a**): T_m 176 (177–178), $\nu(Cl^{(2,6)})$ 35.746 (35.754), 36.168 (36.180), $\nu(Cl^{(W)})$ 36.616 (36.674); (**14a**): T_m 107 (108).

IR-Spectroscopy

The IR spectra of the compounds were taken at room temperature, with compounds immersed in Nujol (Perkin-Elmer Model 325 Infrared Spectrophotometer). For comparison, both the basic acetanilides and the N-chlorinated compounds were studied in the range, $4000 \geq \nu/\text{cm}^{-1} \geq 400$.

Results

In Table 2 we have listed the ^{35}Cl NQR frequencies at selected temperatures for the title compounds. From this table one recognises that there is no change in the multiplicity of the spectrum from 77 K up to room temperature (besides a dynamical fade out of $\nu(Cl^{(W)})$. We can safely conclude that there is no phase transition of first order in the title compounds in the range $77 \leq T/K \leq 300$. In a few cases not all resonances could be observed and also the temperature dependent measurements are some times incomplete because of very low signal to noise ratio, S/N. It may be difficult to assign the Cl$^{(W)}$ NQR frequencies and the phenyl ring ones if they are close together. A measurement of $\nu(^{35}Cl) = f(T)$ is often a solution of the problem as shown some time ago (Biedenkapp and Weiss [24]). Therefore we have measured $\nu(^{35}Cl) = f(T)$ for some compounds with a more dense net of points. In Figs. 1, 2, and 3, the ^{35}Cl NQR frequencies of (**6**) and (**10**), of (**7**) and (**11**), and of (**12**) and (**13**) are plotted as function of T. The functions shown in these figures are rationalised by a power series expansion

$$\nu = \sum (a_i T^i), \quad -1 \leq i \leq 2 \qquad (1)$$

and the coefficients a_i are listed in Table 3.

The IR wave numbers $\nu/c(C{=}O)$ and $\nu/c(N{-}Cl)$ are listed in Table 4. There is no problem in assignment of $\upsilon(C{=}O)$, but the assignment of $\nu(N{-}Cl)$ is

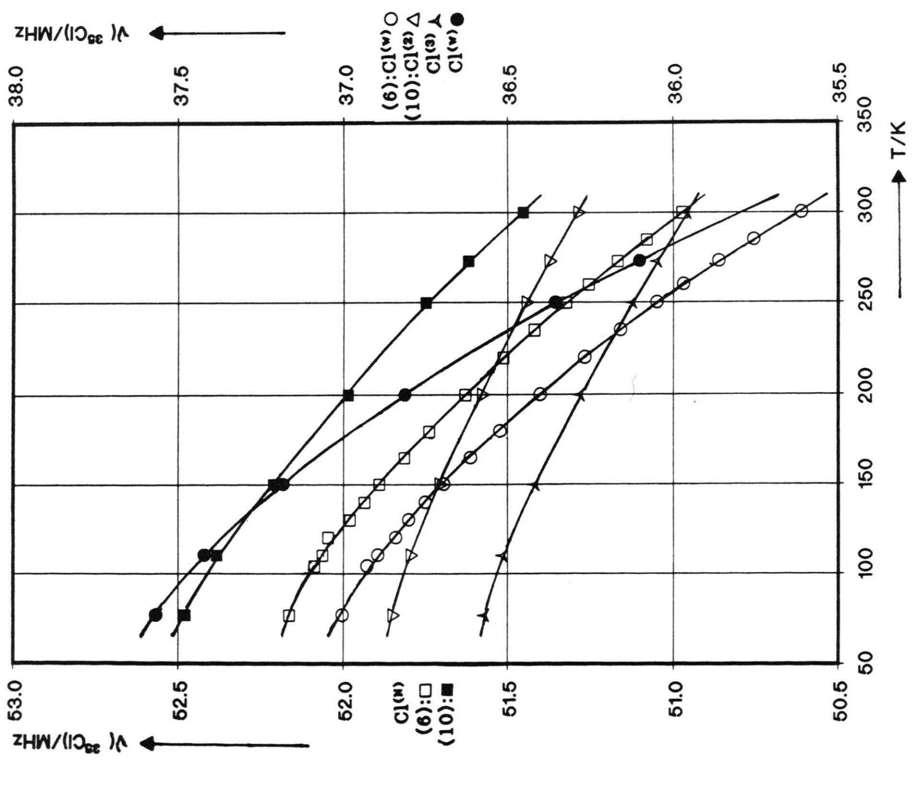

Fig. 1. ^{35}Cl NQR frequencies of N–Cl–N-[phenyl]-2-chloroacetamide (**6**) and N–Cl–N-[2,3-dichlorophenyl]-2-chloroacetamide (**10**) as function of temperature.

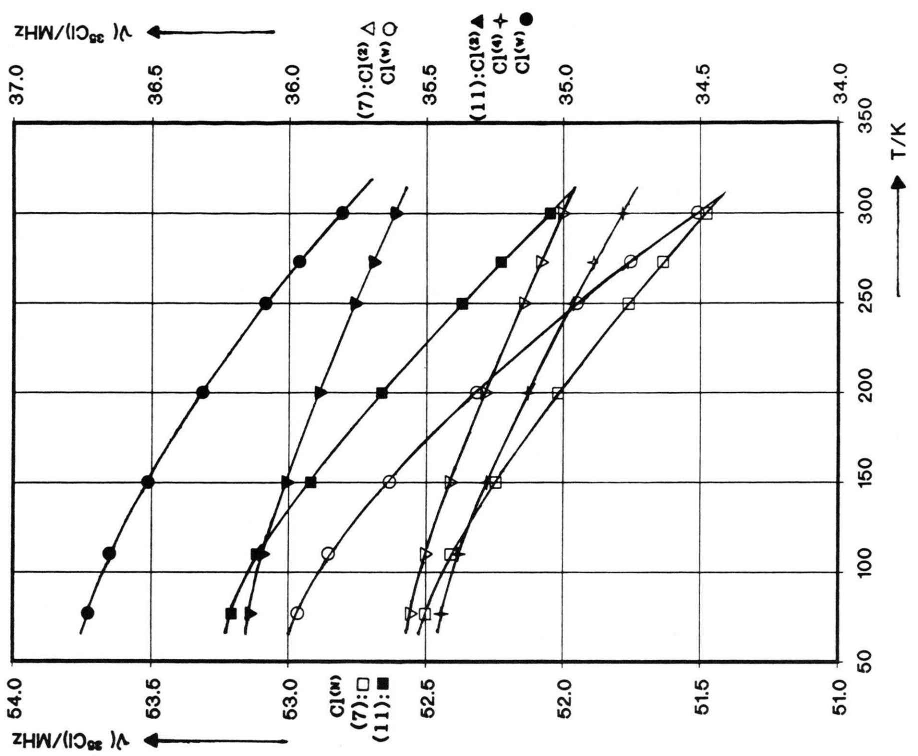

Fig. 2. ^{35}Cl NQR frequencies of N–Cl–N-[2-chlorophenyl]-2-chloroacetamide (**7**) and N–Cl–N-[2,4-dichlorophenyl]-2-chloroacetamide (**11**) as function of temperature.

Table 2. ^{35}Cl NQR frequencies (in MHz) of the title compounds at selected temperatures (in K). For the numbering of the compounds, see Table 1. The signal to noise (S/N) ratio determined with lock in technique, time constant 10 s, recorder, is given in parentheses. The numbering of the chlorines in the phenyl ring follows the rules of chemistry, Cl bounded to nitrogen is marked by $Cl^{(N)}$ the Cl of the CH_2Cl group by $Cl^{(W)}$.

Comp.	ν_i	Ass.	ν/MHz (S/N)						
			77 K	110 K	150 K	200 K	250 K	273 K	300 K
(1)	ν_1	$Cl^{(W)}$	35.333 (30)						
(2)	ν_1	$Cl^{(3)}$	No ^{35}Cl resonance found						
	ν_2	$Cl^{(W)}$	No ^{35}Cl resonance found						
(3)	ν_1	$Cl^{(W)}$	34.793 (15)						
(4)	ν_1	$Cl^{(W)}$	36.566 (15)						
(5)	ν_1	$Cl^{(W)}$	36.335 (5)						
(6)	ν_1	$Cl^{(N)}$	52.166 (60)	52.064 (50)	51.890 (50)	51.627 (35)	51.323 (30)	51.168 (30)	50.973 (30)
	ν_2	$Cl^{(W)}$	37.004 (50)	36.897 (50)	36.694 (50)	36.401 (30)	36.051 (20)	35.863 (20)	35.611 (15)
(7)	ν_1	$Cl^{(N)}$	52.502 (40)	52.408 (40)	52.246 (35)	52.018 (30)	51.761 (30)	51.635 (30)	51.477 (25)
	ν_2	$Cl^{(2)}$	35.560 (50)	35.505 (50)	35.415 (40)	35.289 (35)	35.148 (30)	35.086 (30)	35.005 (25)
	ν_3	$Cl^{(W)}$	35.969 (30)	35.857 (30)	35.637 (20)	35.319 (20)	34.952 (10)	34.756 (8)	34.511 (6)
(8)	ν_1	$Cl^{(N)}$	52.590 (10)	–	52.098 (5)				
	ν_2	$Cl^{(3)}$	35.048 (20)	35.007 (10)	34.944 (10)				
	ν_3	$Cl^{(W)}$	37.017 (10)	36.959 (10)	36.835 (5)				
(9)	ν_1	$Cl^{(N)}$	No ^{35}Cl resonance found						
	ν_2	$Cl^{(4)}$	35.686 (10)						
	ν_3	$Cl^{(W)}$	34.935 (15)						
(10)	ν_1	$Cl^{(N)}$	52.480 (15)	52.384 (15)	52.212 (15)	51.986 (10)	51.748 (10)	51.618 (4)	51.452 (3)
	ν_2	$Cl^{(2)}$	36.852 (25)	36.797 (25)	36.707 (25)	36.579 (20)	36.444 (15)	36.375 (15)	36.289 (10)
	ν_3	$Cl^{(3)}$	36.568 (25)	36.512 (25)	36.415 (20)	36.280 (15)	36.123 (10)	36.048 (10)	35.958 (10)
	ν_4	$Cl^{(W)}$	37.568 (15)	37.424 (15)	37.186 (15)	36.814 (10)	36.357 (3)	36.105 (2)	–
(11)	ν_1	$Cl^{(N)}$	53.209 (35)	53.116 (30)	52.922 (25)	52.663 (20)	52.371 (20)	52.229 (15)	52.049 (15)
	ν_2	$Cl^{(2)}$	36.144 (35)	36.097 (25)	36.012 (20)	35.893 (15)	35.763 (15)	35.697 (15)	35.616 (10)
	ν_3	$Cl^{(4)}$	35.441 (25)	35.381 (25)	35.279 (20)	35.129 (15)	34.963 (15)	34.886 (15)	34.782 (10)
	ν_4	$Cl^{(W)}$	36.728 (25)	36.652 (20)	36.515 (20)	36.320 (15)	36.089 (15)	35.966 (10)	35.809 (10)
(12)	ν_1	$Cl^{(N)}$	53.774 (30)	53.688 (20)	53.530 (15)	53.297 (15)	53.033 (15)	52.899 (10)	52.733 (5)
	ν_2	$Cl^{(2)}$	36.515 (40)	36.465 (25)	36.382 (15)	36.265 (15)	36.133 (15)	36.066 (10)	35.984 (10)
	ν_3	$Cl^{(5)}$	35.672 (35)	35.625 (25)	35.543 (20)	35.423 (15)	35.289 (10)	35.223 (10)	35.141 (8)
	ν_4	$Cl^{(W)}$	36.625 (35)	36.493 (25)	36.267 (10)	35.933 (5)	35.547 (3)	35.368 (2)	
(13)	ν_1	$Cl^{(N)}$	52.529 (40)	52.444 (20)	52.286 (20)	52.074 (15)	51.841 (15)	51.727 (10)	51.588 (10)
	ν_2	$Cl^{(2,6)}$	35.820 (25)	35.772 (20)	35.688 (20)	35.564 (15)	35.427 (10)	35.353 (10)	35.262 (10)
	ν_3	$Cl^{(2,6)}$	36.389 (35)	36.337 (25)	36.243 (20)	36.106 (20)	35.951 (15)	35.869 (10)	35.765 (10)
	ν_4	$Cl^{(W)}$	36.303 (30)	36.200 (20)	36.011 (15)	35.705 (10)	35.296 (10)	35.055 (10)	34.716 (5)
(14)	ν_1	$Cl^{(N)}$	No ^{35}Cl resonance found						
	ν_2	$Cl^{(3)}$	36.450 (20)						
	ν_3	$Cl^{(4)}$	36.411 (20)						
	ν_4	$Cl^{(W)}$	No ^{35}Cl resonance found						
(15)	ν_1	$Cl^{(N)}$	53.857 (15)	53.767 (10)	53.607 (5)	53.402 (5)			
	ν_2	$Cl^{(W)}$	36.442 (10)	36.338 (5)	36.370 (10)	36.322 (5)			
(16)	ν_1	$Cl^{(N)}$	52.846 (15)	52.756 (15)	52.588 (5)				
	ν_2	$Cl^{(W)}$	36.449 (10)						
(17)	ν_1	$Cl^{(N)}$	No ^{35}Cl resonance found						
	ν_2	$Cl^{(W)}$	No ^{35}Cl resonance found						
(18)	ν_1	$Cl^{(N)}$	No ^{35}Cl resonance found						

rather uncertain. We give the $\nu/c(C=O)$ wave numbers for the compounds as well for R–NH–CO–CH_2Cl as for R–NCl–CO–CH_2Cl of compounds comparable with the title compounds. Belaj and Nachbaur [25] report $\nu/c(C=O) = 1781$ cm^{-1}, $\nu/c(N-Cl) = 673$ cm^{-1} for N,N,N-trichloro-isocyanuric acid (data taken from Dehnicke and Leimeister [26]) and $\nu/c(C=O) = 1776$ cm^{-1}, $\nu/c(N-Cl) = 527$ cm^{-1} for N-chlorosuccinimide (data from Woldbaek et al. [27]). On substituted acetanilides Bennett and Maire [28] observed in the IR spectrum of a number of compounds in $CHCl_3$- and CH_3CN-solution $\nu/c(C=O)$ in the range 1690 to 1709 cm^{-1}. In a study (Raman, IR) of N-chloro-chloroformimidoyl chloride Cl_2CNCl in the gaseous, liquid, and solid phase Burke and Mitchell [29] observed the N–Cl stretching wave number at 746 cm^{-1}. Carter and Devia [30] find in N,N-dichloromethylcarbamate,

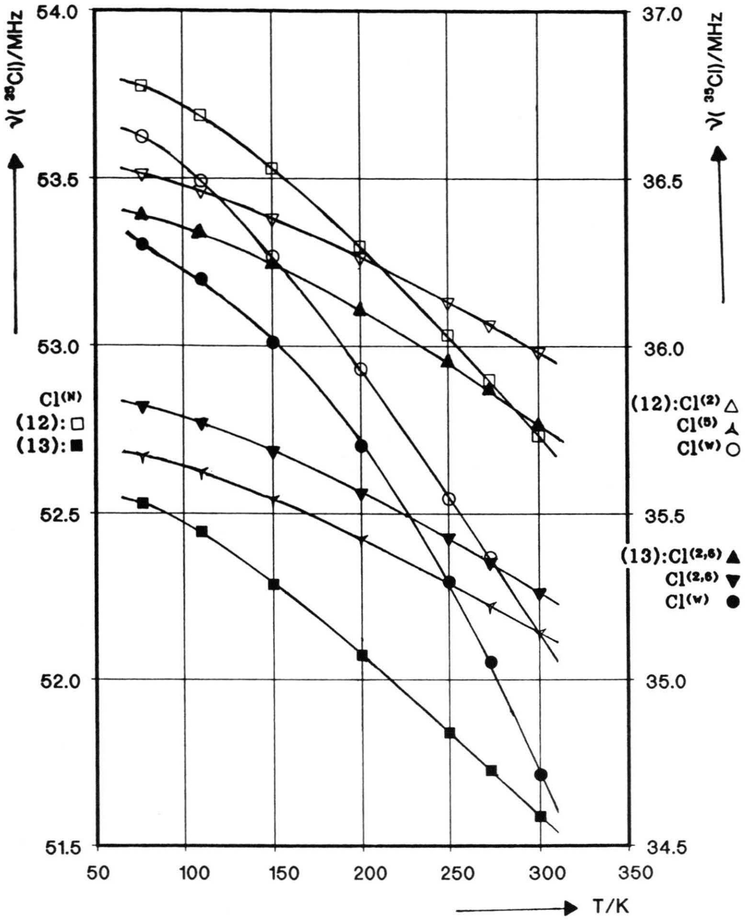

Fig. 3. ^{35}Cl NQR frequencies of N–Cl–N-[2,5-dichlorophenyl]-2-chloroacetamide (**12**) and N–Cl–N-[2,6-dichlorophenyl]-2-chloroacetamide (**13**) as function of temperature.

Table 3. Coefficients a_i of the power series development $\nu(^{35}\mathrm{Cl}) = f(T)$, (1) of title compounds (Table 1). z is the number of experimental data taken for (1), σ is the mean squares deviation (in kHz).

Compound	ν_1	z	σ kHz	a_0 MHz	a_{-1} MHz·K	$a_1 \cdot 10^3$ MHz·K^{-1}	$a_2 \cdot 10^6$ MHz·K^{-2}
(**6**)	ν_1	17	6.3	52.6683	−14.4147	−3.5781	−6.3433
	ν_2	17	7.2	37.2517	−2.8573	−1.7005	−12.3325
(**7**)	ν_1	7	2.5	52.9613	−12.0199	−3.6256	−3.9463
	ν_2	7	1.7	35.8775	−8.8842	−2.5618	−0.8220
	ν_3	7	7.6	36.4758	−13.7378	−3.4975	−9.6186
(**10**)	ν_1	7	10.3	52.8050	−5.1732	−2.9223	−5.0062
	ν_2	7	2.5	37.0951	−5.6987	−2.0420	−1.9208
	ν_3	7	1.8	36.8804	−8.8706	−2.4164	−1.8725
	ν_4	6	5.2	37.7755	−0.6980	−1.1804	−18.0126
(**11**)	ν_1	7	6.7	53.8823	−20.7754	−4.9910	−2.9263
	ν_2	7	2.1	36.4020	−7.1010	−2.0102	−1.7568
	ν_3	7	2.3	35.7656	−9.1021	−2.5059	−2.2199
	ν_4	7	4.7	36.9286	−3.1754	−1.4872	−7.3360
(**12**)	ν_1	7	2.4	54.2465	−13.8730	−3.4099	−4.9213
	ν_2	7	1.3	36.7159	−4.5752	−1.6408	−2.4868
	ν_3	7	0.7	35.9336	−7.5374	−1.9752	−1.9375
	ν_4	6	4.1	37.3824	−22.4909	−5.6378	−5.3045
(**13**)	ν_1	7	3.8	53.0652	−15.4023	−4.2161	−1.7705
	ν_2	7	2.7	36.0067	−4.3862	−1.4172	−3.3720
	ν_3	7	3.0	36.5909	−4.8021	−1.4942	−3.9960
	ν_4	7	14.1	35.8059	24.4046	4.5451	−28.0556

Table 4. Infrared stretching frequencies ν(N–H), ν(C=O) and ν(N–Cl) (probable stretching and deformation frequencies) of the title compounds R–NHCO–R′ and R–NClCO–R′ (see Table 1). The wave numbers ν/c are given in cm^{-1}. Measurements of solid compounds in Nujol. Abbreviations: b: broad; d: doublet; m: medium; s: strong; sh: shoulder; w: weak.

Compound	R–NHCO–CH$_2$Cl		R–NClCO–CH$_2$Cl	
	ν/c(N–H)	ν/c(C=O)	ν/c(N–Cl)	ν/c(C=O)
(**1**), (**6**)	3290 s	1700 s	648 s, 892 s	1717 s
(**7a**), (**7**)	3260 s	1673 m 1707 s	462 s, 488 s, 642 s 705 s, 892 m	1670 sh 1710 s
(**2**), (**8**)	3270 s	1685 s 1702 s	468 s, 483 m, 642 w 878 m	1680 s 1706 s
(**10a**), (**10**)	3270 s	1680 s 1713 s	485 s, 753 m, 800 s 920 m	1683 s 1717 s
(**11a**), (**11**)	3250 s	1675 s, d	480 s, 650 s, 880 s	1695 s, b
(**12a**), (**12**)	3350 s	1685 s 1710 s	480 m, 665 s, 893 m	1705 s
(**13a**), (**13**)	3210 s	1654 sh 1684 s	457 s, 710 s, 890 m	1684 s 1710 s
(**3**), (**15**)	3310 s	1685 s	463 s, 595 s, 656 s 690 s, 900 m	1692 s
(**4**), (**16**)	3290 s	1685 s, d	456 m, 646 m, 783 s 856 s, 930 s	1705 s
(**18a**), (**18**)[1]	3300 s	1670 s	456 s, 672 s, 878 s	1690 s

[1] R′ = CH$_3$

$H_3COCONCl_2$, $\nu/c(C=O) = 1755\ cm^{-1}$, $\nu/c(N-Cl) = 423\ cm^{-1}$. Extensive studies of the IR spectra of N-halogenated secondary amides in solvents have been reported by de Klein and Plesman [31] and de Klein [32]. The N–Cl stretching frequencies of a number of compounds related to isocyanuric acid were studied by Petterson et al. [33]. The valence frequencies of a number of N-alkyl-N-chloroalkanes and their $SbCl_6$-salts have been observed by Thiel et al. [34]; they found considerable shifts to higher wave numbers by going from the molecules to the salts.

Discussion

The first point we raise is the assignment of the ^{35}Cl NQR lines to the positions of the Cl atoms in the molecule. There is no problem to do so. In the N-chloroacetanilides the ^{35}Cl NQR frequencies of $Cl^{(N)}$ are found at much higher values than of $Cl^{(C)}$, somewhere between 51 and 54 MHz, and therefore the assignment is unique. The w-Cl atoms have, as shown before [17, 24], much higher temperature coefficients as the ring chlorines have, and no difficulty in assignment arises. Also the intensities, respectively S/N is helpful in this respect (see Table 2), and in some compounds the signals of the w-Cl even bleach out below room temperature due to the onset of strong librational motions of the CH_2Cl group.

Several of the compounds with the general configuration: $C_6H_{5-y}X_y-NCl-CO-CH_3$ (I) do not show $^{35}Cl^{(N)}$ NQR, while many of the compounds with the configuration: $C_6H_{5-y}X_y-NCl-CO-CH_2Cl$ (X = H, Cl, NO_2) (II) show $^{35}Cl^{(N)}$ NQR (Table 2). Only $^{35}Cl^{(N)}$ NQR's of 2-chloro, 2,5-dichloro and 2,6-dichloro phenyl substituted compounds of configuration I are known. The values are 52.560 MHz, 53.079 MHz and 53.396 MHz, compared to the respective values of 52.502 MHz, 53.774 MHz and 52.529 MHz of the corresponding compounds of configuration II.

An interesting point is the correlation of NQR and other bond dependent physical properties (e.g. $\nu(Cl^{(N)})$ with the bond distances N–Cl). Such relations are discussed at length by Weiss and Wigand [35], and a typical example is the correlation between $\nu(^{35}Cl)$ and the bond distances Hg–Cl and the stretching frequencies $\nu(Hg-Cl)$ in mercury chloride complexes, where an increase of $\nu/c(Hg-Cl)$ from $250\ cm^{-1}$ to $400\ cm^{-1}$ is linearly connected with a change of $\nu(^{35}Cl)$ from 13 MHz to 23 MHz and $\nu(^{35}Cl)$ decreases strongly with increasig bond distance Hg–Cl (Scaife [36]. $\nu(^{35}Cl) = f(d(Sn-Cl))$ is reported by Storck and Weiss [37].

We consider first a possible correlation between the ring substitution and $\nu(C=O)$; the data are given in Table 4. Comparing the compounds R–NHCO–R′ with R–NClCO–R′, there is an upward shift of $\nu/c(C=O)$ by the exchange $N-H \rightarrow N-Cl$. The shift is between 0 and $20\ cm^{-1}$, and it is not correlated with the ring substitution pattern.

The IR wave numbers assigned to the group N–Cl (Table 4) are found at $527\ cm^{-1}$ for N-chlorosuccinimide [25] and $673\ cm^{-1}$ for N-trichloroisocyanuric acid. We observe wave numbers in the range 450–930 cm^{-1}. The assignment and the finding out of correlations between $\nu(^{35}Cl^{(N)})$ and $\nu(N-Cl)$ is not straightforward.

As much as the relation $\nu(^{35}Cl^{(N)}) = f(d(N-Cl))$ is concerned, the experimental material is small. For N-chlorosuccinimide the crystal structure was reported by Brown [38], and he found d(N–Cl) = 169 pm. We report for (**6**) d(N–Cl) = 170.6(2) pm [39]. Thiel et al. [34] in their study of hexachloroantimonates(V) with N-chloroalkane-ammonium cations determined the crystal structure of N-ethyl-N-chloroethylammonium hexachloroantimonate(V) and found bond distances d(N–Cl) of 175.6(13) and 178.4(14) pm. The crystal structure of trichloroisocyanuric acid, $(ClCNO)_3 \cdot \frac{1}{2}(C_2H_4Cl_2)$ was reported by Belaj and Nachbaur [25]; they found for the three crystallographically inequivalent Cl atoms in the molecule within the limits of error $\langle d(N-Cl)\rangle = 169$ pm. The conclusion is: (d(N–Cl)) is only weakly increasing with decreasing $\nu(^{35}Cl^{(N)})$. Combined studies of $^{35}Cl^{(N)}$ in bonds N–Cl and crystal structure studies are necessary, particularly of compounds with $\nu(^{35}Cl^{(N)})$ in the 45 MHz region and in the 58 MHz range.

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