The Bond N–Cl. Crystal Structures and ^{35}Cl NQR of N–Chloro-N-Phenyl-2-chloroacetamide, N-Chloro-N-phenyl-2,2-dichloroacetamide, N-Chloro-N-phenyl-2,2,2-trichloroacetamide, and N-Phenyl-2,2,2-trichloroacetamide

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Dedicated to Professor Ewald Wicke on the occasion of his 80th birthday

The crystal structures of $C_6H_5NClCOCH_2Cl$ (**1**), $C_6H_5NClCOCHCl_2$ (**2**), $C_6H_5NClCOCCl_3$ (**3**), and $C_6H_5NHCOCCl_3$ (**4**) have been determined at room temperature (lattice constants, d in pm). (**1**): $P2_1/c$, $Z=4$, $a=738$, $b=645$, $c=1891$, $\beta=90.41°$, d (N–Cl) = 171, d (C=O) = 121; (**2**): $P2_1/c$, $Z=4$, $a=820$, $b=1495$, $c=905$, $\beta=114.78°$, d (N–Cl) = 171, d (C=O) = 120; (**3**): $P2_1/c$, $Z=4$, $a=819$, $b=1853$, $c=718$, $\beta=103.64°$, d (N–Cl) = 172, d (C=O) = 120; (**4**): $P2_1/c$, $Z=4$, $a=551$, $b=1704$, $c=1035$, $\beta=93.08°$, d (C=O) = 121.

For (**2**), (**3**), and (**4**) the ^{35}Cl NQR frequencies have been determined in the range $77 \leq T/K \leq 300$. At 77 K (ν in MHz): (**2**): $\nu^{(w,1)} = 37.600$, $\nu^{(w,2)} = 38.188$, $\nu^{(N)} = 51.858$; (**3**): $\nu^{(w,1)} = 39.944$, $\nu^{(w,2)} = 40.512$, $\nu^{(w,3)} = 40.739$, $\nu^{(N)} = 52.791$; (**4**): $\nu^{(w,1)} = 39.428$, $\nu^{(w,2)} = 39.452$, $\nu^{(w,3)} = 39.986$. For the compound $C_6H_5NHCOCHCl_2$ (**5**) the ^{35}Cl NQR measured at 77 K is: $\nu^{(w,1)} = 37.195$ MHz, $\nu^{(w,2)} = 37.596$ MHz. The relation, $\nu(^{35}Cl) = d$ (N–Cl) is discussed.

Introduction

N-Chloro compounds are interesting and intensively used chemicals in oxidation reactions. Recently we have reported on ^{35}Cl nuclear quadrupole resonance (NQR) and IR spectroscopy of a series of such compounds of the general configuration $C_6H_{5-z}X_zNYCO(CH_2Cl)$, where X = Cl or NO_2, Y = Cl or H [1]. In N-chloro compounds the ^{35}Cl NQR frequencies, covering the range $44 \leq \nu/MHz \leq 58$, depend strongly on R,R′ of RR′NCl. Particularly the bond lengths N–Cl and C=O are of interest. For compound (**1**), for which we report and discuss the crystal structures here, the ^{35}Cl NQR is already reported in [1], and the title compounds are in close connection with the ^{35}Cl NQR and diffraction work (X, N) on 2,6-dichloro-2 chloroacetamides [2, 3]. Some crystals structure studies on N–Cl compounds are reported in [4], [5] and [6].

In the following we report on the crystal structure of $C_6H_5NClCOCH_2Cl$ (**1**), $C_6H_5NClCOCHCl_2$ (**2**), $C_6H_5NClCOCCl_3$ (**3**), and $C_6H_5NHCOCCl_3$ (**4**). The ^{35}Cl NQR spectra are given for (**2**)–(**4**) and for $C_6H_5NHCOCHCl_2$ (**5**). For (**4**) the ^{35}Cl NQR spectrum at 77 K is reported in [7]. We discuss the results of the crystal structure determinations and ^{35}Cl NQR.

Experimental

N-phenyl chloroacetamides were prepared from aniline and chloroacetylchlorides by the methods given in [8]. 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 [1, 7]. The new acetanilide (**5**) was analyzed by C, H, N elemental analysis, and its ^{35}Cl NQR frequencies were measured. The N-phenyl chloroacetamides were N-chlorinated by the method reported in [1]. But the procedure had to be continued for a longer period with di- and trichloroacetamide, complete chlorination needing 6–8 h, depending on the concentration of the NaOCl solution. N-chlorocompounds were recrystallized from cyclohexane, toluene or mixtures of the two solvents. The purity of the compounds was checked by estimating the active chlorine content by the iodometric method. The analysis gave the following:

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Table 1. Experimental conditions for the crystal structure determination and crystallographic data of $(C_6H_5)NClCOCH_2Cl$ (**1**), $C_6H_5NClCOCHCl_2$ (**2**), $C_6H_5NClCOCCl_3$ (**3**), and $(C_6H_5)NHCOCCl_3$ (**4**). Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm (MoKα); monochromator: Graphite (002); scan $2\vartheta/\omega$. (**1**): $C_8H_7Cl_2NO$, $M = 204.05$ (**2**): $C_8H_6Cl_3NO$, $M = 238.49$; (**3**): $C_8H_5Cl_4NO$, $M = 272.94$; (**4**): $C_8H_6Cl_3NO$, $M = 238.49$.

Compound	(1)	(2)	(3)	(4)
Crystal size $(mm)^3$	$0.50 \times 0.30 \times 0.15$	$0.60 \times 0.50 \times 0.25$	$0.30 \times 0.38 \times 1.3$	$0.90 \times 0.54 \times 0.13$
Temperature/K	297 (2)	298 (2)	298 (2)	297 (2)
Absorpt. Coeff. μ/m^{-1}	669	867	992	821
Θ-range for data coll.	$2.15 \leq \Theta/° \leq 24.95$	$2.72 \leq \Theta/° \leq 25.00$	$2.20 \leq \Theta/° \leq 24.95$	$2.30 \leq \Theta/° \leq 26.97$
Index ranges	$-8 \leq h \leq 8$, $-7 \leq k \leq 0$, $-22 \leq l \leq 22$	$-9 \leq h \leq 3$, $0 \leq k \leq 17$, $-10 \leq l \leq 10$	$-9 \leq h \leq 9$, $0 \leq k \leq 22$, $-8 \leq l \leq 3$	$-7 \leq h \leq 7$, $0 \leq k \leq 21$, $-12 \leq l \leq 12$
Lattice constants/pm	$a =$ 737.6 (3)	820.0 (3)	819.2 (3)	551.3 (2)
	$b =$ 644.9 (3)	1495.4 (5)	1853.2 (7)	1703.9 (7)
	$c =$ 1890.6 (7)	904.8 (3)	718.1 (3)	1034.8 (4)
	$\beta =$ 90.410 (10)°	114.78 (1)°	103.640 (10)	93.080 (10)
$V \cdot 10^{-6}/(pm)^3$	899.3 (6)	1007.3 (6)	1059.4 (7)	970.6 (7)
Space group	$C_{2h}^5-P2_1/c$	$C_{2h}^5-P2_1/c$	$C_{2h}^5-P2_1/c$	$C_{2h}^5-P2_1/c$
Formula units Z	4	4	4	4
$\varrho_{calc}/(Mg \cdot m^{-3})$	1.507 (2)	1.572 (1)	1.711 (2)	1.632 (2)
F (000)	416	480	544	480
Reflections collected	3277	2677	2663	4188
Symmetry independent	1588	1772	1863	2100
$[R_{int}]$	0.0237	0.029	0.0179	0.0249
Data	1587	1767	1863	2100
Restraints/parameters	0/109	0/119	0/127	0/138
Goodness of fit on F^2	1.107	1.049	0.762	1.050
Final R ($I > 2\sigma(I)$)	$R_1 = 0.0409$, $wR_2 = 0.1164$	$R_1 = 0.0444$, $wR_2 = 0.1174$	$R_1 = 0.0296$, $wR_2 = 0.0895$	$R_1 = 0.0320$, $wR_2 = 0.0820$
R (all data)	$R_1 = 0.0460$, $wR_2 = 0.1233$	$R_1 = 0.0528$, $wR_2 = 0.1331$	$R_1 = 0.0336$, $wR_2 = 0.0983$	$R_1 = 0.0365$, $wR_2 = 0.0862$
Largest diff: (peak, hole)/ $(10^{-6}\ e\ (pm)^3)$	0.236, −0.252	0.362, −0.328	0.269, −0.283	0.475, −0.396
Max. and min. transm.	0.999 and 0.883	0.800 and 0.607	0.764 and 0.612	0.836 and 0.668
Extinction coeff.	0.000 (2)	0.012 (3)	0.002 (1)	0.007 (2)
Point positions:	all atoms in 4*e*			

Active Cl(calc/found): (**1**): 17.37/17.12; (**2**): 14.86/14.78; (**3**): 12.99/12.82 (**5**) (calc/found): C (47.09/47.05), H (3.46/3.43), N (6.86/6.86). T_m/°C: (**1**): 75; (**2**): 71; (**3**): 101; (**4**): 91–92 (^{35}Cl NQR at 77 K measured by Semin et al. [7]); (**5**): 116.

Small crystals of (**1**), (**2**), (**3**), (**4**) were selected for X-ray diffraction and studied at room temperature with a 4-circle goniometer. The collected intensity data were corrected for Lorentz-polarisation factor and absorption. By direct methods and least squares refinement [9] the point positions were found, including the positions of the hydrogen atoms. For the determination of the hydrogen positions the distances C–H were fixed to 93 pm for the ring hydrogen atoms, to 97 pm for the CH_2Cl group and to 98 pm for the $CHCl_2$ group. The hydrogen bond to the nitrogen atom in (**4**) was found from Fourier synthesis, $d(N-Cl) = 80$ (2 pm). In Table 1 the experimental conditions for the structure determinations and some crystallographic data are given for (**1**), (**2**), (**3**), (**4**). About the measurements of the ^{35}Cl NQR spectra, see [1]. The line widths of the ^{35}Cl NQR were 10–15 kHz.

Results

X-ray Diffraction (Crystal Structures)

In Table 1 the crystallographic data of the title compounds (lattice constants, space group etc.) are listed. The atomic coordinates and mean thermal parameters are given for (**1**)–(**4**) in Tables 2–5, respectively. For the full matrix of the mean squares displacement of the atoms, see [10]. Table 6 lists the intramolecular distances and angles of the title compounds, and in Table 7 we have collected some intermolecular distances which are within the sum of the concerned van der Waals radii. Table 8 reports the plane equations for the C_6 rings of the compounds considered and the equations for the planes $NC^{(7)}C^{(8)}O$. In Fig. 1 we show

Table 2. Atomic coordinates ($\times 10^4$) and isotropic mean thermal parameters [U_{eq}] of $(C_6H_5)NClCOCH_2Cl$ (**1**). [U_{eq}] is defined as 1/3 of the trace of the orthogonalized tensor U_{ij} and is given in $(pm)^2$.

Atom	x	y	z	[U_{eq}]
$C^{(1)}$	2011 (3)	3303 (3)	1236 (1)	420 (5)
$C^{(2)}$	0475 (4)	2217 (4)	1426 (1)	484 (6)
$H^{(C2)}$	−0591 (4)	2331 (4)	1163 (1)	580
$C^{(3)}$	0559 (4)	0954 (4)	2018 (1)	555 (7)
$H^{(C3)}$	−0460 (4)	0209 (4)	2155 (1)	666
$C^{(4)}$	2135 (4)	0796 (4)	2402 (1)	576 (7)
$H^{(C4)}$	2174 (4)	−0043 (4)	2802 (1)	691
$C^{(5)}$	3663 (4)	1870 (5)	2202 (1)	581 (7)
$H^{(C5)}$	4732 (4)	1741 (5)	2462 (1)	697
$C^{(6)}$	3602 (4)	3140 (4)	1613 (1)	510 (6)
$H^{(C6)}$	4625 (4)	3873 (4)	1474 (1)	612
N	1921 (3)	4674 (3)	0633 (1)	487 (5)
$Cl^{(N)}$	1357 (1)	7172 (1)	0832 (1)	652 (3)
$C^{(7)}$	2706 (3)	4325 (4)	−0007 (1)	459 (6)
O	2913 (3)	5659 (3)	−0448 (1)	643 (6)
$C^{(8)}$	3259 (4)	2077 (4)	−0105 (1)	547 (7)
$Cl^{(C,8)}$	3707 (1)	1498 (1)	−0992 (1)	686 (3)
$H^{(C8,1)}$	2295 (4)	1183 (4)	0062 (1)	656
$H^{(C8,2)}$	4334 (4)	1797 (4)	0178 (1)	656

Table 3. Atomic coordinates ($\times 10^4$) and isotropic mean thermal parameters [U_{eq}] (see Table 2) of $C_6H_5NClCOCHCl_2$ (**2**). [U_{eq}] is given in $(pm)^2$.

Atom	x	y	z	[U_{eq}]
$C^{(1)}$	2046 (4)	1146 (2)	2032 (3)	480 (6)
$C^{(2)}$	0941 (4)	1734 (2)	0874 (4)	640 (8)
$H^{(C2)}$	0406 (4)	2205 (2)	1181 (4)	768
$C^{(3)}$	0627 (6)	1630 (3)	−0725 (4)	814 (11)
$H^{(C3)}$	−0140 (6)	2019 (3)	−1511 (4)	977
$C^{(4)}$	1441 (7)	0956 (3)	−1155 (5)	900 (14)
$H^{(C4)}$	1262 (7)	0899 (3)	−2237 (5)	1080
$C^{(5)}$	2532 (6)	0350 (3)	−0018 (5)	901 (13)
$H^{(C5)}$	3069 (6)	−0114 (3)	−0335 (5)	1082
$C^{(6)}$	2825 (5)	0439 (2)	1615 (4)	671 (8)
$H^{(C6)}$	3530 (5)	0029 (2)	2394 (4)	805
N	2314 (3)	1270 (2)	3695 (3)	517 (6)
$Cl^{(N)}$	0630 (1)	0876 (1)	4157 (1)	696 (3)
$C^{(7)}$	3769 (4)	1593 (2)	4973 (3)	496 (6)
O	3927 (3)	1594 (2)	6351 (2)	724 (4)
$C^{(8)}$	5213 (4)	1971 (2)	4490 (3)	530 (7)
$Cl^{(1,C8)}$	6218 (1)	2904 (1)	5724 (1)	844 (4)
$Cl^{(2,C8)}$	6822 (1)	1120 (1)	4800 (1)	830 (4)
$H^{(C,8)}$	4670 (4)	2149 (2)	3341 (3)	636

Table 4. Atomic coordinates ($\times 10^4$) and [U_{eq}] of $C_6H_5NClCOCCl_3$ (**3**). For the definition of [U_{eq}] see Table 2. [U_{eq}] is given in $(pm)^2$.

Atom	x	y	z	[U_{eq}]
$C^{(1)}$	−1854 (2)	3793 (1)	2529 (3)	406 (2)
$C^{(2)}$	−2319 (3)	3087 (1)	2151 (3)	490 (5)
$H^{(C2)}$	−1806 (3)	2719 (1)	2964 (3)	590
$C^{(3)}$	−3570 (3)	2932 (2)	0533 (4)	598 (6)
$H^{(C3)}$	−3910 (3)	2457 (2)	0263 (4)	720
$C^{(4)}$	−4306 (3)	3472 (2)	−0669 (3)	606 (7)
$H^{(C4)}$	−5133 (3)	3361 (2)	−1760 (3)	730
$C^{(5)}$	−3837 (3)	4177 (2)	−0281 (3)	568 (6)
$H^{(C5)}$	−4342 (3)	4541 (2)	−1112 (3)	680
$C^{(6)}$	−2613 (3)	4348 (1)	0346 (3)	476 (5)
$H^{(C6)}$	−2308 (3)	4825 (1)	1637 (3)	570
N	−0625 (2)	3971 (1)	4263 (2)	467 (5)
$Cl^{(N)}$	−1508 (1)	4150 (1)	6162 (1)	656 (2)
$C^{(7)}$	1060 (3)	3914 (1)	4757 (3)	406 (5)
O	1874 (2)	4007 (1)	6362 (2)	634 (5)
$C^{(8)}$	1998 (3)	3690 (1)	3189 (3)	458 (5)
$Cl^{(1,C8)}$	1201 (1)	4050 (1)	0886 (1)	634 (2)
$Cl^{(2,C8)}$	1941 (1)	2736 (1)	3071 (1)	671 (2)
$Cl^{(3,C8)}$	4106 (1)	3974 (1)	3953 (1)	715 (2)

Table 5. Atomic coordinates ($\times 10^4$) and thermal parameters [U_{eq}] of $C_6H_5NHCOCCl_3$ (**4**). [U_{eq}] is defined in Table 2 and given in $(pm)^2$.

Atom	x	y	z	[U_{eq}]
$C^{(1)}$	8321 (3)	1557 (1)	3682 (2)	345 (3)
$C^{(2)}$	10256 (3)	1538 (1)	4598 (2)	436 (3)
$H^{(C2)}$	10435 (3)	1931 (1)	5220 (2)	520
$C^{(3)}$	11919 (4)	0928 (1)	4579 (2)	516 (5)
$H^{(C3)}$	13224 (4)	0917 (1)	5187 (2)	620
$C^{(4)}$	11659 (4)	0342 (1)	3673 (2)	521 (5)
$H^{(C4)}$	12783 (4)	−0066 (1)	3668 (2)	630
$C^{(5)}$	9721 (4)	0358 (1)	2769 (2)	513 (5)
$H^{(C5)}$	9536 (4)	−0041 (1)	2159 (2)	620
$C^{(6)}$	8055 (3)	0964 (1)	2767 (2)	434 (4)
$H^{(C6)}$	6758 (3)	0975 (1)	2154 (2)	520
N	6649 (3)	2194 (1)	3596 (1)	371 (3)
$H^{(N)}$	6103 (38)	2301 (12)	2887 (22)	450 (50)
$C^{(7)}$	5902 (3)	2608 (1)	4598 (2)	436 (4)
O	6462 (3)	2492 (1)	5731 (1)	498 (3)
$C^{(8)}$	4253 (3)	3328 (1)	4222 (2)	377 (4)
$Cl^{(1,C8)}$	2318 (1)	3164 (1)	2830 (1)	538 (2)
$Cl^{(2,C8)}$	2445 (1)	3574 (1)	5515 (1)	501 (2)
$Cl^{(3,C8)}$	6217 (1)	4125 (1)	3939 (1)	639 (2)

the molecules of the title compounds as they appear in suitable projection with their thermal ellipsoids and with the numbering of the atoms used throughout the paper. For comparison of the molecular structure of the title compounds we list in Table 6 the intramolecular distances and angles of (**1**–**4**). In Fig. 2 the unit cell of (**1**) is projected along the short axis b (645 pm) onto the ac plane. Projections of the unit cell of (**2**), (**3**), and (**4**) are shown in Figs. 3, 4, and 5, respectively.

Nuclear Quadrupole Resonance, ^{35}Cl

The ^{35}Cl NQR spectrum of (**1**) is reported in [1]. For (**2**), (**3**), and (**4**) the spectra have been measured

Table 6. Intramolecular distances (bond lengths) d/pm and angles (degree) in $C_6H_5NClCOCH_2Cl$ (**1**), $C_6H_5NClCOCHCl_2$ (**2**), $C_6H_5NClCOCCl_3$ (**3**), $C_6H_5NHCOCCl_3$ (**4**).

Compound connection	(1)	(2)	(3)	(4)
	d/pm			
$C^{(1)}-C^{(6)}$	137.3 (4)	136.7 (4)	138.4 (3)	138.6 (2)
$C^{(1)}-C^{(2)}$	138.3 (4)	137.8 (4)	137.3 (3)	139.0 (2)
$C^{(1)}-N$	144.4 (3)	143.7 (3)	144.3 (3)	142.4 (2)
$C^{(2)}-C^{(3)}$	138.5 (4)	136.7 (5)	138.6 (3)	138.6 (3)
$C^{(3)}-C^{(4)}$	137.0 (4)	135.3 (6)	136.5 (4)	137.3 (3)
$C^{(4)}-C^{(5)}$	137.9 (4)	138.1 (6)	137.1 (4)	138.2 (3)
$C^{(5)}-C^{(6)}$	138.3 (4)	139.9 (5)	138.5 (3)	138.2 (3)
$N-C^{(7)}$	136.3 (3)	135.5 (4)	134.6 (3)	133.7 (2)
$N-Cl^{(N)}$	170.6 (2)	170.7 (2)	172.0 (2)	
$C^{(7)}-O$	120.9 (3)	119.7 (3)	120.0 (3)	121.1 (2)
$C^{(7)}-C^{(8)}$	151.8 (4)	153.1 (4)	156.2 (3)	156.4 (2)
$C^{(8)}-Cl^{(1,C8)}$	175.1 (3)	176.0 (3)	175.9 (2)	176.8 (2)
$C^{(8)}-Cl^{(2,C8)}$		177.0 (3)	177.0 (3)	176.2 (2)
$C^{(8)}-Cl^{(3,C8)}$			176.4 (2)	177.2 (2)
	angle/°			
$C^{(6)}-C^{(1)}-C^{(2)}$	121.7 (2)	121.2 (3)	121.5 (2)	119.9 (2)
$C^{(6)}-C^{(1)}-N$	119.5 (2)	120.3 (3)	118.8 (2)	117.9 (2)
$C^{(2)}-C^{(1)}-N$	118.9 (2)	118.4 (3)	119.6 (2)	122.1 (2)
$C^{(1)}-C^{(2)}-C^{(3)}$	118.5 (2)	120.2 (4)	118.6 (2)	119.5 (2)
$C^{(4)}-C^{(3)}-C^{(2)}$	120.3 (2)	119.5 (4)	120.5 (2)	120.7 (2)
$C^{(3)}-C^{(4)}-C^{(5)}$	120.6 (3)	121.2 (3)	120.6 (2)	119.7 (2)
$C^{(4)}-C^{(5)}-C^{(6)}$	119.8 (3)	119.7 (4)	120.1 (2)	120.4 (2)
$C^{(1)}-C^{(6)}-C^{(5)}$	119.1 (3)	118.1 (3)	118.6 (2)	119.8 (2)
$C^{(7)}-N-C^{(1)}$	125.6 (2)	129.2 (2)	132.3 (2)	125.4 (1)
$C^{(7)}-N-Cl^{(N)}$	117.3 (2)	115.3 (2)	113.8 (1)	
$C^{(1)}-N-Cl^{(N)}$	114.4 (2)	115.2 (2)	113.0 (1)	
$O-C^{(7)}-N$	123.5 (2)	124.1 (3)	123.0 (2)	126.3 (2)
$O-C^{(7)}-C^{(8)}$	124.0 (2)	122.5 (3)	118.3 (2)	118.9 (1)
$N-C^{(7)}-C^{(8)}$	112.5 (2)	113.4 (2)	118.6 (2)	114.8 (1)
$C^{(7)}-C^{(8)}-Cl^{(1,C8)}$	112.0 (2)	108.9 (2)	116.1 (2)	113.4 (1)
$C^{(7)}-C^{(8)}-Cl^{(2,C8)}$		107.7 (2)	106.8 (2)	110.0 (1)
$C^{(7)}-C^{(8)}-Cl^{(3,C8)}$			107.9 (2)	106.9 (1)
$Cl^{(1,C8)}-C^{(8)}-Cl^{(2,C8)}$		110.5 (2)	109.5 (1)	108.4 (1)
$Cl^{(1,C8)}-C^{(8)}-Cl^{(3,C8)}$			107.4 (1)	109.5 (1)
$Cl^{(2,C8)}-C^{(8)}-Cl^{(3,C8)}$			109.0 (1)	108.6 (1)

Table 7. Intermolecular distances d (in pm). Taking the van der Waals radii [13, 14] (in pm): $r(Cl^{(N)}) = r(Cl^{(C)}) = r(NH) = r(CH) = 180$, $r(O) = 150$, we consider distances $Cl \cdots Cl \leq 370$, $Cl \cdots O \leq 340$, $Cl \cdots CH = 370$, $O \cdots O \leq 310$ pm, $(CH \cdots O) = \leq 340$, $CH \cdots CH \leq 370$.

Compound connection	(1)	(2)	(3)	(4)
$Cl \cdots Cl$	385[1]	354[13]	370[17]	
		343[14]		
$Cl \cdots O$				342[22]
$Cl \cdots CH$	371[2]		374[18]	351[23]
	357[3]		369[19]	354[24]
	368[4]			337[25]
	350[5]			360[26]
	337[6]			365[27]
	369[7]			
$Cl^{(N)} \cdots C^{(7)}$	350[8]			
$O \cdots CH$	348[9]	340[15]	345[20]	
	334[10]	336[16]		
	340[11]			
	339[12]			
$CH \cdots CH$			342[21]	350[28]

(**4**): Hydrogen bond $N-H \cdots O$: $d(N \cdots O) = 301$, $d(O \cdots H) = 228$, angle $(N-H \cdots O) = 152.5°$; N, H in x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

(**1**) [1] $Cl^{(N)} \cdots Cl^{(C8)}$ $(-x, 1-y, -z)$; [2] $Cl^{(C8)} \cdots CH^{(5)}$ $(1-x, -y, -z)$; [3] $Cl^{(C8)} \cdots CH^{(5)}$ $(x, \frac{1}{2}-y, z-\frac{1}{2})$; [4] $Cl^{(8)} \cdots CH^{(4)}$ $(x, \frac{1}{2}-y, z-\frac{1}{2})$; [5] $Cl^{(N)} \cdots CH^{(2)}$ $(x, 1+y, z)$; [6] $Cl^{(N)} \cdots CH^{(3)}$ $(x, 1+y, z)$; [7] $Cl^{(N)} \cdots CH^{(8)}$ $(-x, 1-y, -z)$; [8] $Cl^{(N)} \cdots C^{(7)}$ $(-x, 1-y, -z)$; [9] $O \cdots CH^{(6)}$ $(1-x, 1-y, -z)$; [10] $O \cdots C^{(7)}$ $(1-x, 1-y, -z)$; [11] $O \cdots CH^{(8)}$ $(1-x, 1-y, -z)$; [12] $O \cdots CH^{(2)}$ $(-x, 1-y, -z)$; (**2**) [13] $Cl^{(N)} \cdots Cl^{(2,8)}$ $(1-x, -y, 1-z)$; [14] $Cl^{(2,8)} \cdots Cl^{(N)}$ $(1+x, y, z)$; [15] $O \cdots CH^{(2)}$ $(x, \frac{1}{2}-y, \frac{1}{2}+z)$; [16] $O \cdots CH^{(8)}$ $(x, \frac{1}{2}-y, \frac{1}{2}+z)$; (**3**) [17] $Cl^{(2,8)} \cdots Cl^{(2,8)}$ $(x, \frac{1}{2}-y, \frac{1}{2}+z)$; [18] $Cl^{(2,8)} \cdots CH^{(4)}$ $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$; [19] $Cl^{(1,8)} \cdots CH^{(6)}$ $(-x, 1-y, -z)$; [20] $O \cdots CH^{(6)}$ $(-x, 1-y, 1-z)$; [21] $CH^{(3)} \cdots CH^{(2)}$ $(x, \frac{1}{2}-y, z-\frac{1}{2})$; (**4**) [22] $(Cl^{(1,8)} \cdots O$ $(x, \frac{1}{2}-y, z-\frac{1}{2})$; [23] $Cl^{(1,8)} \cdots CH^{(2)}$ $(x-1, \frac{1}{2}-y, z-\frac{1}{2})$; [24] $Cl^{(2,8)} \cdots CH^{(6)}$ $(x-1, \frac{1}{2}-y, \frac{1}{2}+z)$; [25] $Cl^{(2,8)} \cdots CH^{(5)}$ $(x-1, \frac{1}{2}-y, \frac{1}{2}+z)$; [26] $Cl^{(3,8)} \cdots CH^{(5)}$ $(2-x, \frac{1}{2}+y, \frac{1}{2}-z)$; [27] $Cl^{(3,8)} \cdots CH^{(4)}$ $(2-x, \frac{1}{2}+y, \frac{1}{2}-z)$; [28] $CH^{(3)} \cdots CH^{(4)}$ $(2-x, -y, 1-z)$.

Table 8. Equations of planes, mean deviations of atomic positions from the plane, angle between the planes.

Plane	Compound	Equation
$C^{(1 \cdots 6)}$	(**1**)	$-2.109\,(8)\,x + 4.953\,(5)\,y + 10.873\,(18)\,z = 2.551\,(4)$
	(**2**)	$6.561\,(8)\,x + 8.665\,(20)\,y - 1.757\,(13)\,z = 1.965\,(2)$
	(**3**)	$-6.913\,(5)\,x - 1.755\,(18)\,y - 5.114\,(5)\,z = 3.247\,(6)$
	(**4**)	$3.232\,(4)\,x - 8.930\,(12)\,y + 6.709\,(7)\,z = 1.607\,(5)$
$NC^{(7)}C^{(8)}O$	(**1**)	$6.611\,(6)\,x + 1.334\,(10)\,y + 7.293\,(24)\,z = 2.356\,(4)$
	(**2**)	$-3.370\,(12)\,x + 13.471\,(12)\,y + 0.405\,(15)\,z = 1.080\,(8)$
	(**3**)	$1.206\,(10)\,x + 17.897\,(10)\,y - 1.741\,(9)\,z = 6.293\,(7)$
	(**4**)	$4.461\,(4)\,x + 9.970\,(13)\,y - 0.996\,(10)\,z = 4.791\,(5)$

Mean deviation $\langle\delta\rangle$ (in pm) of the C-atoms from the plane $C^{(1 \cdots 6)}$; mean deviation $\langle d\rangle$ (in pm) of the atoms from the plane $NC^{(7)}C^{(8)}O$; angle ε between the benzene ring plane and the plane $NC^{(7)}C^{(8)}O$.

Compound	$\langle\delta\rangle$/pm	$\langle d\rangle$ pm	ε/°
(**1**)	0.3	0.3	82.6 (1)
(**2**)	1.1	0.1	80.1 (1)
(**3**)	0.6	0.7	81.5 (1)
(**4**)	0.3	0.9	35.4 (1)

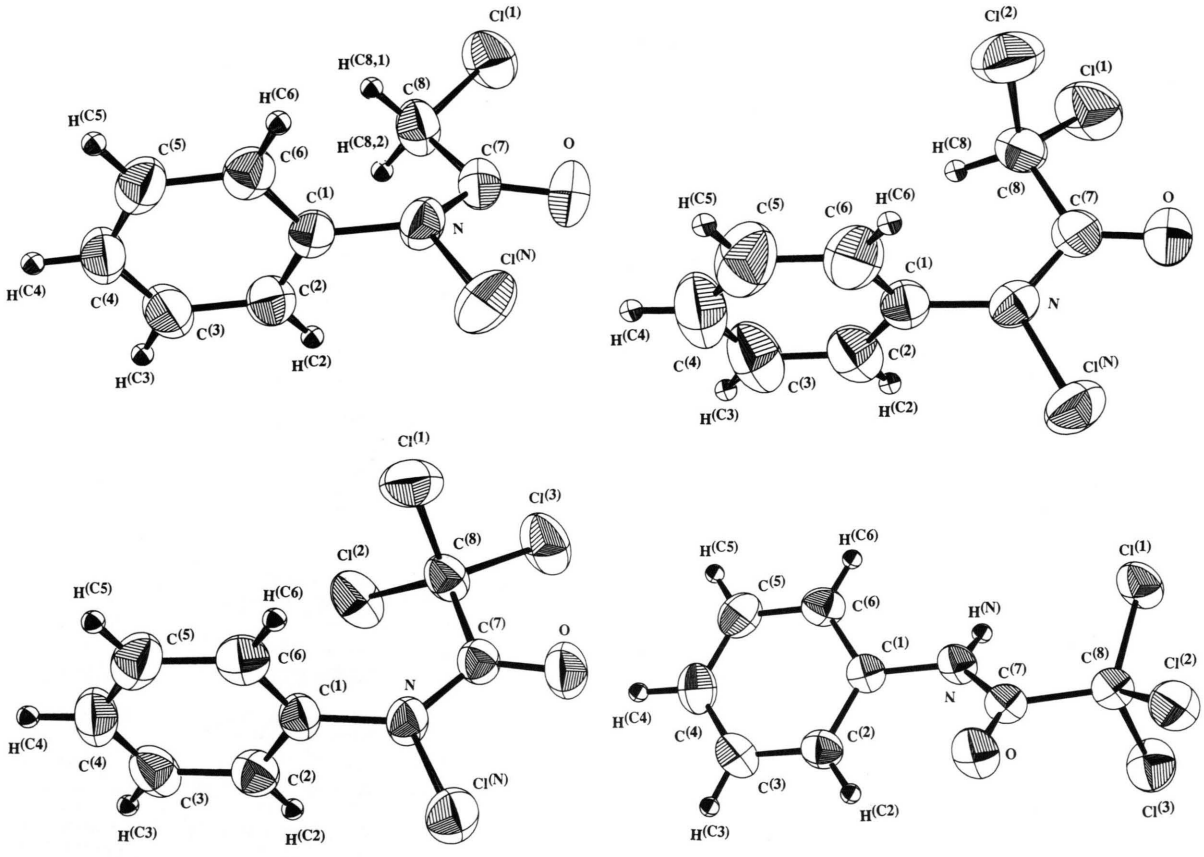

Fig. 1. Geometry of the molecules of the title compounds. Given are projections of the molecules in suitable orientation including the thermal ellipsoids. a) $C_6H_5NClCOCH_2Cl$ (**1**); b) $C_6H_5NClCOCHCl_2$ (**2**); c) $C_6H_5NClCOCCl_3$ (**3**); $C_6H_5NHCOCCl_3$ (**4**).

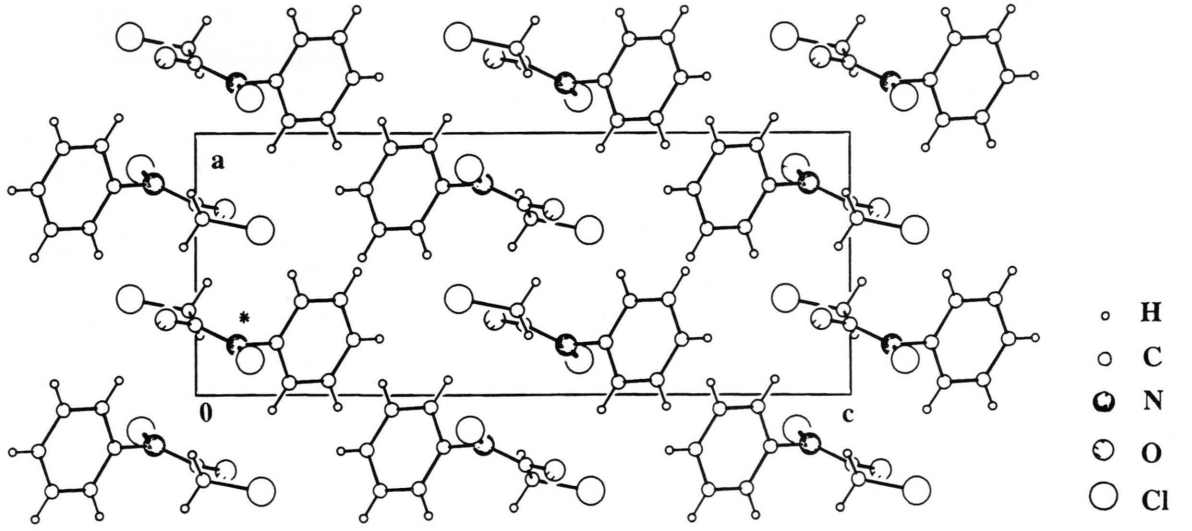

Fig. 2. Projection of the unit cell of (**1**) along the axis [010] onto the *a c* plane. The molecule for which the position coordinates are listed in Table 2 is marked by (*).

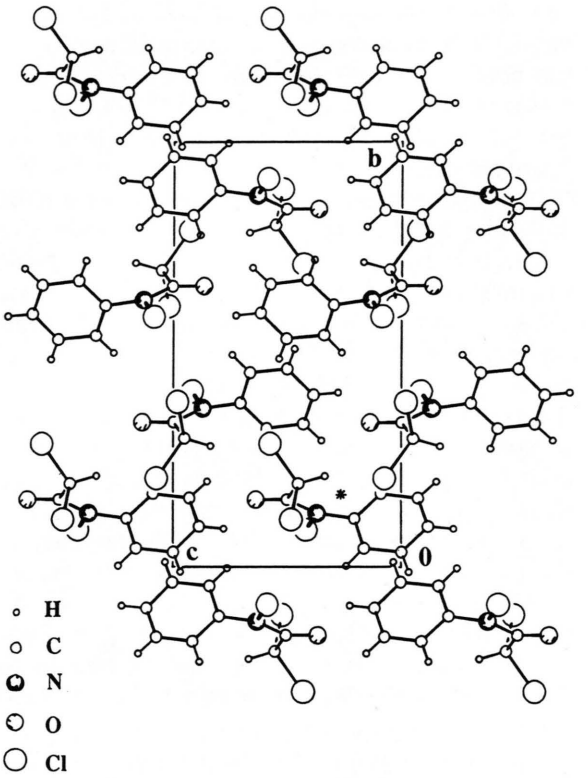

Fig. 3. Projection of the unit cell of (**2**) along [100] onto the *b c* plane. The molecule for which the position coordinates are listed in Table 3 is marked by (*).

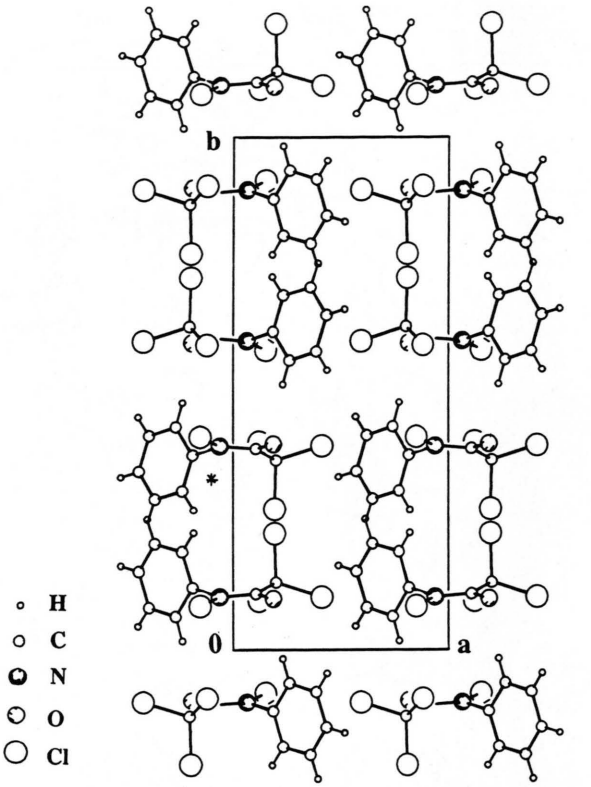

Fig. 4. Projection of the unit cell of (**3**) along [001] onto the *a b* plane. The molecule for which the positional coordinates are listed in Table 4 is marked by (*).

from 77 K on up to 300 K or up to the temperature T_f at which the NQR signals fade out. The temperature dependence of ^{35}Cl NQR is rationalized by a power series development

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

In Table 9 one finds the coefficients a_i and the frequency values at two temperatures (77 K and 273 K) and in case there was no fade out, also at 300 K. Individual frequencies including the signal to noise ratio can be found in [10]. $\nu = f(T)$ is shown in Figs. 6 and 7.

Discussion

First we shall discuss the intramolecular geometry of the four title compounds in comparison. The individual data are given in Table 6. Comparing the $C^{(i)}-C^{(j)}$ bond distances within the C_6-rings of the four title compounds we find a mean distance $\langle d(C-C)\rangle$ of 137.8 pm, the minimum at 135.3 pm, the maximum at 138.9 pm. This spread shows no significant change of the ring distances by the monosubstitution; the intra-ring distances are hard bond parameters. Also the bond angles are soft bond parameters we find a mean angle for the four title compounds between 118.9° and 121.1°, again no significant deviation from 120° by the monosubstitution of the ring. The distances $C^{(1)}-N$ are for the compounds (**1**)–(**4**): 142.3 $\leq d/\text{pm} \leq$ 144.3. The smallest value belongs to (**4**) with the group NH. For the bond $N-Cl^{(7)}$ we find $\langle d(N-C^{(7)})\rangle = 135.0$ pm; a small shortening of this bond with increasing number of Cl on the group CCl_xH_{3-x} seems to be present. The mean of $d(C^{(7)}-C^{(8)})$ is 154.4 pm; there one observes an increase with the number of chlorines at $C^{(8)}$ of $d(C^{(7)}-C^{(8)})$ which may be significant. The distances C=O are with $\langle d\rangle$

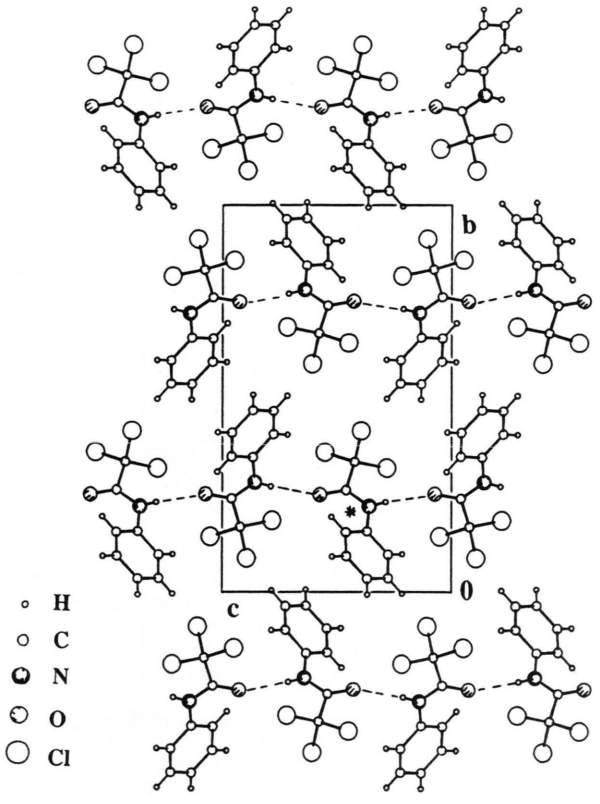

Fig. 5. Projection of the unit cell of (**4**) along [100] onto the *b*c plane. The molecule for which the positional coordinates are listed in Table 5 is marked by (*). The hydrogen bonds N–H ··· O are marked by dashed lines.

= 120.4 pm in the expected range, little shortened by the presence of the Cl atom at the nitrogen of (**4**). All angles C–C–Cl and Cl–C–Cl are found in the range grouped around the tetrahedral angle with deviations up to 116° and down to 107°, the angles Cl–C–Cl being 109.0° ± 1°.

Our main interest was in the determination of the distance N–Cl, which is found to be 170.6 pm for (**1**), 170.7 pm for (**2**), and 172.0 pm for (**3**).

The C_6 ring in the four title compounds is planar within the limits of error. Also the sp^2 carbon $C^{(7)}$ keeps the plane $NC^{(7)}OC^{(8)}$ planar. The maximum deviation of a carbon atom from the ring plane is 0.3 pm for (**1**), 1.5 pm for (**2**), 1.0 pm for (**3**), and 0.4 pm for (**4**). Planarity is also quite rigid for the plane $NC^{(7)}OC^{(8)}$ with maximum deviation of the atoms of 0.5 pm, 0.2 pm, 1.2 pm, and 1.6 pm for (**1**), (**2**), (**3**), and (**4**), respectively. The angle ε between the ring plane and the plane $NC^{(7)}OC^{(8)}$ is for (**1**)–(**3**) between 80° and 82°. For (**4**) we find $\varepsilon = 35°$ (Table 8). This is understandable if one considers the intermolecular hydrogen bond N–H ··· O, (**4**) forms. The intermolecular interactions Cl ··· Cl, Cl ··· CH and O ··· CH are of the van der Waals type. (**4**) is an exception, forming a hydrogen bond N–H ··· O (Table 7). Figure 5 shows that the hydrogen bonds N–H ··· O in (**4**) connect the molecules in the direction [001] to chains.

The temperature dependence of the ^{35}Cl NQR spectra shows (see Figs. 6 and 7) that there is no phase transition within the range $77 \leq T/K \leq 300$. The temperature coefficient $d\nu/dT$ is negative in (**2**), (**3**) and (**4**), changing smoothly. This originates in the spectrum of the librational molecular motions in the lattice. The torsional motions of the CCl_3 groups are easely excited, which results in the fade out of the ^{35}Cl signals at lower temperatures T_f than the $Cl^{(N)}$ signal. It has been shown that the ^{35}Cl NQR frequency of the Cl atom bonded to the nitrogen atom in the N–Cl–N-phenyl-acetamides is in the range from 52 to 53 MHz ($T = 77$ K), and the changes of the resonance frequency of $Cl^{(N)}$ are due to the group $R' = COCH_{3-x}Cl_x$. We are interested in the relation between NQR frequencies and bond distances [11, 12]. Theory shows that the main principal axis Φ_{ZZ} of the electric field gradient tensor, EFGT, depends on the distance d of a charge e from the nucleus in question by

$$\Phi_{ZZ} = a \cdot d^{-3}. \tag{2}$$

The axes Φ_{XX} and Φ_{YY} describe, together with Φ_{ZZ}, the symmetry (asymmetry parameter η) of the EFGT through the relations

$$|\Phi_{XX}| \leq |\Phi_{YY}| \leq |\Phi_{ZZ}|; \quad |\Phi_{XX} - \Phi_{YY}| \leq |\Phi_{ZZ}| = \eta. \tag{3}$$

In the case of nuclear spin $I = 3/2$, which applies to $^{35,37}Cl$, and under the assumption of $\eta(^{35}Cl) \leq 0.18$ we can safely assume that the frequency measured is 1/2 of the nuclear quadrupole coupling constant $eQ\Phi_{ZZ}h^{-1}$, where e is the unit charge, Q the nuclear electric quadrupole moment and h Plancks constant. So we can draw conclusions about (1) from the frequency measurements. The three distances d(N–Cl) measured here, compared with $\nu(^{35}Cl^{(N)})$ at 77 K, (**1**): 170.6 pm, 52.166 MHz; (**2**): 170.7, 51.858 MHz; (**3**): 172.0 pm, 52.791 MHz is not confirming (2). The experimental data we have up to now are not sufficient to argue further. NQR and structure work is necessary on compounds with a) "weak" bond and b) with "strong" bond N–Cl.

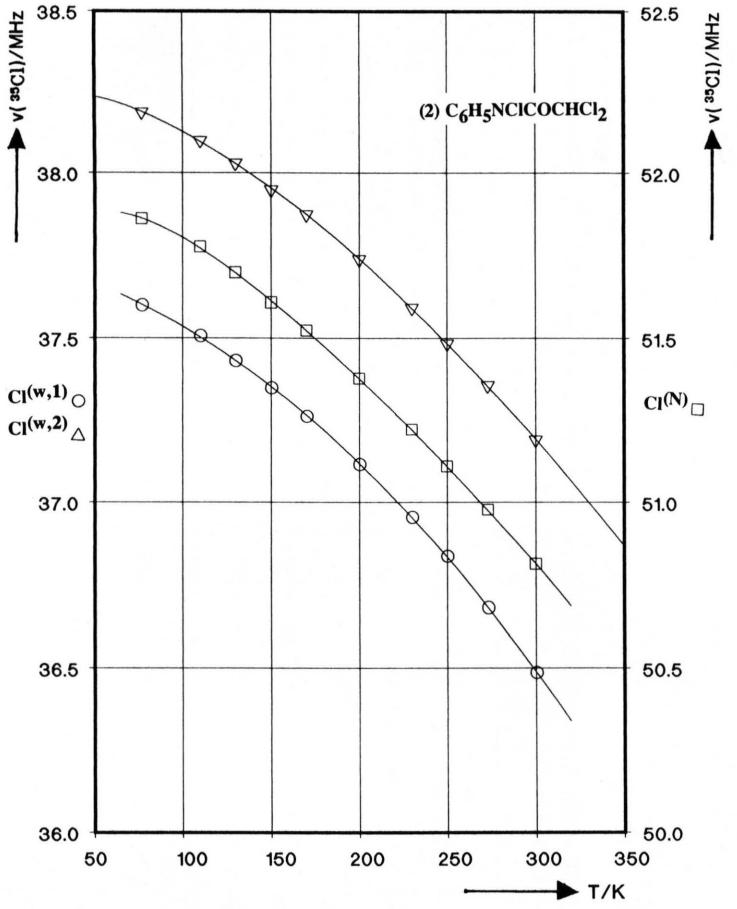

Fig. 6. ^{35}Cl NQR frequencies of (**2**) as functions of temperature.

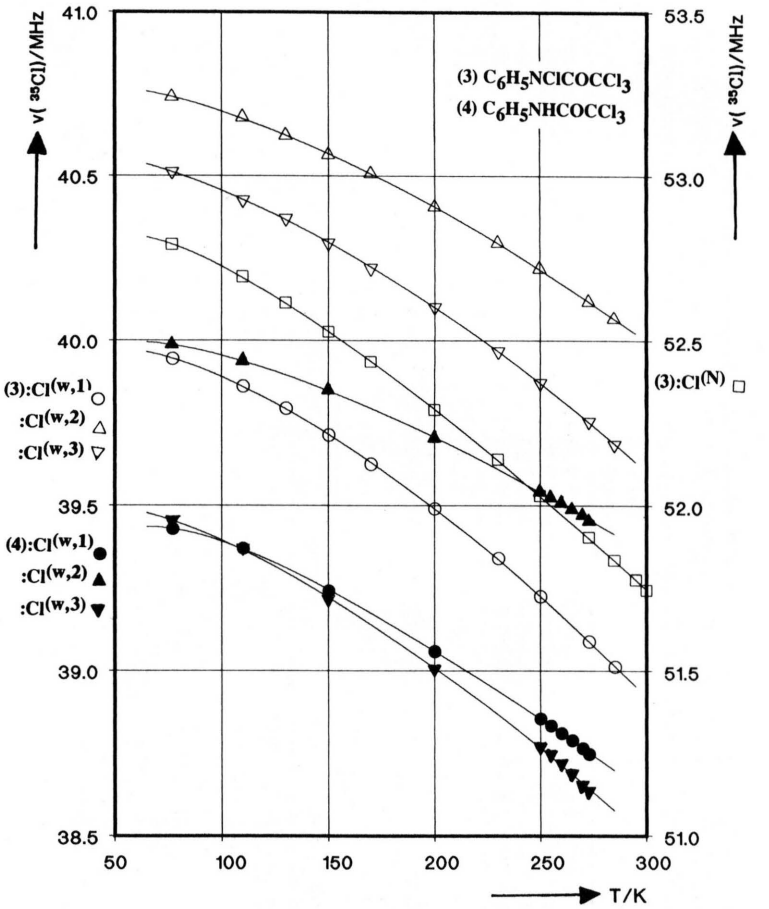

Fig. 7. ^{35}Cl NQR frequencies of (**3**) and (**4**) as functions of temperature.

Table 9. $^{(35)}$Cl NQR frequencies ν at selected temperatures and coefficients a_i of the power series development $\nu = \Sigma\, a_i\, T^i$, $-1 \leq i \leq 2$. z is the number of measurements, σ is the standard deviation. For the a_i of (**1**) see [1]. S/N is the signal to noise ratio (lockin) recorder, time constant 10 s).

Comp.	ν_i	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}
(**2**)	$\nu^{(w,1)}$	10	3.5	37.7411	0.0081	−1.0023	−10.5578
	$\nu^{(w,2)}$	10	3.3	38.4401	−4.3051	−1.9877	−7.0774
	$\nu^{(N)}$	10	3.1	52.3452	−14.2731	−3.5419	−4.7146
(**3**)	$\nu^{(w,1)}$	10	2.8	40.2618	−8.0321	−2.2049	−7.2589
	$\nu^{(w,2)}$	10	2.6	40.7191	−3.0955	−1.6420	−6.8243
	$\nu^{(w,3)}$	10	2.3	40.9560	−4.7233	−1.6230	−5.0395
	$\nu^{(N)}$	12	2.3	53.3089	−13.9706	−4.1122	−3.1583
(**4**)	$\nu^{(w,1)}$	10	2.8	39.9193	−16.4395	−3.4157	−2.3438
	$\nu^{(w,2)}$	10	6.2	39.7743	−7.0226	−2.5579	−5.4685
	$\nu^{(w,3)}$	10	3.1	40.2520	−8.2170	−1.7850	−3.7208

Comp.	$\nu^{(i)}$	ν/MHz (S/N)	T/K	Ref.	Comp.	$\nu^{(i)}$	ν/MHz (S/N)	T/K	Ref.
(**1**)	$\nu^{(w)}$	37.004 (50)	77	[1]	(**3**)	$\nu^{(w,1)}$	39.944 (30)	77	This paper
		35.863 (20)	273				39.090 (10)	273	
		35.611 (15)	300			$\nu^{(w,2)}$	40.512 (30)	77	
	$\nu^{(N)}$	52.166 (60)	77				39.753 (10)	273	
		51.168 (30)	273			$\nu^{(w,3)}$	40.739 (30)	77	
		50.973 (30)	300				40.119 (10)	273	
(**2**)	$\nu^{(w,1)}$	37.600 (40)	77	This paper		$\nu^{(N)}$	52.791 (50)	77	
		36.681 (20)	273				51.902 (20)	273	
		36.488 (15)	300				51.742 (15)	300	
	$\nu^{(w,2)}$	38.188 (40)	77		(**4**)	$\nu^{(w,1)}$	39.428 (40)	77	This paper
		37.357 (20)	273				38.636 (5)	273	
		37.190 (15)	300			$\nu^{(w,2)}$	39.452 (40)	77	
	$\nu^{(N)}$	51.858 (50)	77				38.748 (5)	273	
		50.976 (15)	273			$\nu^{(w,3)}$	39.986 (50)	77	
		50.809 (15)	300				39.452 (5)	273	
					(**5**)	$\nu^{(w,1)}$	37.195 (30)	77	This paper
						$\nu^{(w,2)}$	37.596 (25)	77	

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