The Bond N–Cl. (III): A ^{35}Cl NQR and X-Ray Diffraction Study of N-Chloro-N-(2,6-Dichlorophenyl)-Acetamides *

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The crystal structures at room temperature of the N-chloro-N-(2,6-dichlorophenyl)-chloroacetamides 2,6-$Cl_2C_6H_3$ $NClCOCCl_3$ (**1**) and 2,6-$Cl_2C_6H_3NClCOCH_2Cl$ (**2**) have been determined. (**1**): orthorhombic, Pbca, $Z=8$, $a=2051.7(8)$ pm, $b=1134.8(4)$ pm, $c=1089.0(4)$ pm. (**2**): orthorhombic, Pbca, $Z=8$, $a=2078.7(4)$ pm, $b=1487.9(4)$ pm, $c=694.0(2)$ pm. The ^{35}Cl NQR spectrum of (**1**) was studied in the range $77 \leq T/K \leq 370$. At 77 K, a sextet spectrum is observed (ν in MHz): $\nu_1 = \nu(Cl^{(N)}) = 56.327$; $\nu_2 = 40.636$, $\nu_3 = 40.317$, $\nu_4 = 40.294$; $\nu_5 = 36.532$, $\nu_6 = 36.182$. The lines ν_2, ν_3, and ν_4 are assigned to the CCl_3 group because of their position in the frequency scale. Also, due to librational motions, this triplet part of the spectrum fades out at $T_f \approx 320$ K. There is no problem in assigning in both compounds, on the basis of the known ^{35}Cl NQR frequency scale, the line ν_1 to the Cl atom attached to the nitrogen atom and the lines ν_5 and ν_6 to the ring chlorines ($Cl^{(2)}$ and $Cl^{(6)}$). The crystal structures and NQR spectra of (**1**) and (**2**) are discussed together with literature data for 2,6-$Cl_2C_6H_3NHCOR$, $C_6H_5NClCOR$ (where $R=CCl_3$, $CClH_2$) and other substituted acetamides.

Introduction

Recently we have started studies on the N–Cl bond in solids by ^{35}Cl-NQR and crystal structure determinations [1, 2]. The majority of the compounds considered belong to the group of acetanilides, for many of which C–^{35}Cl NQR data are available [3]. Structure (X-, neutron-diffraction) and ^{35}Cl NQR work in detail was done for some 2,6-dichlorophenyl-acetamides [4, 5]. Here we report studies (crystal structures and ^{35}Cl NQR) on the N-chlorinated 2,6-dichlorophenyl-chloroacetamides 2,6-$Cl_2C_6H_3NClCOCCl_3$ (**1**) and 2,6-$Cl_2C_6H_3NClCOCClH_2$ (**2**) and discuss the results with those for N-chloro-N-phenyl-chloroacetamides, N-(2,6-dichlorophenyl)-chloro-acetamides and other substituted amides.

Experimental

The preparation of acetanilides is described in [3], and that of N-chlorinated compounds in [1]. The X-ray methods to determine the crystal structures have been discussed in [2], and the details of ^{35}Cl NQR measurements are described in [1].

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Results

Crystal Structures

In Table 1 the crystal data and the experimental conditions for the structure determinations of (**1**) and (**2**) are listed. Figures 1 a and b show the molecule of (**1**) and (**2**), respectively with the thermal ellipsoids and the numbering of the atoms used throughout the paper. In Table 2 we have given the atomic coordinates and the thermal parameters of the atoms in the unit cell. A projection of the unit cell of (**1**) along the axis [010] onto the *ac* plane is given in Fig. 2, and the unit cell of (**2**) is projected along [011] onto the (011) plane in Figure 3. In Table 3 we have compiled the intramolecular distances and angles for (**1**) and (**2**). The C–C bond distances within the benzene ring are found in the range $136.2 \leq d(C-C)/pm \leq 139.1$ with the mean value 138.0 pm for (**1**), and $137.2 \leq d(C-C)/pm \leq 139.1$ with the mean value 138.2 pm for (**2**). As regards to the ring angles, they are observed between 118.8° and 122.3° with the mean value of 120.0° (**1**), and 118.8° and 121.6°, with the mean value of 120° (**2**). The C_6 rings are planar, with deviations. The equations for the planes are given in Table 4. Within the

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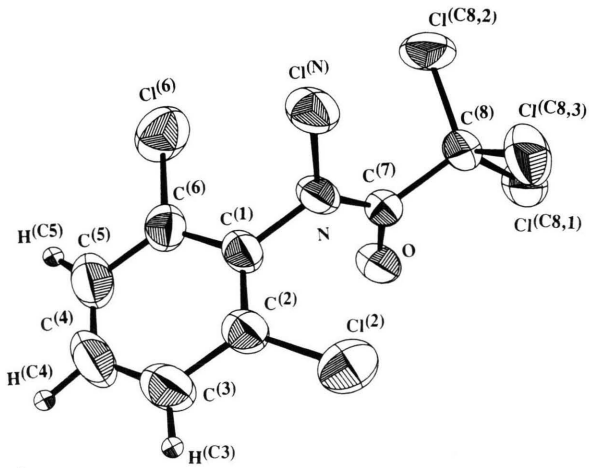
limits of error no influence of changing from the side substituent $NClCOCCl_3$ to $NClCOCH_2Cl$ is seen. Selected torsional angles of (**1**) and (**2**), compared with those of N-chloro-N-phenyl-2,2,2-trichloroacetamide (**1 ph**) and N-chloro-N-phenyl-2-chloroacetamide (**2 ph**) may be found in Table 5.

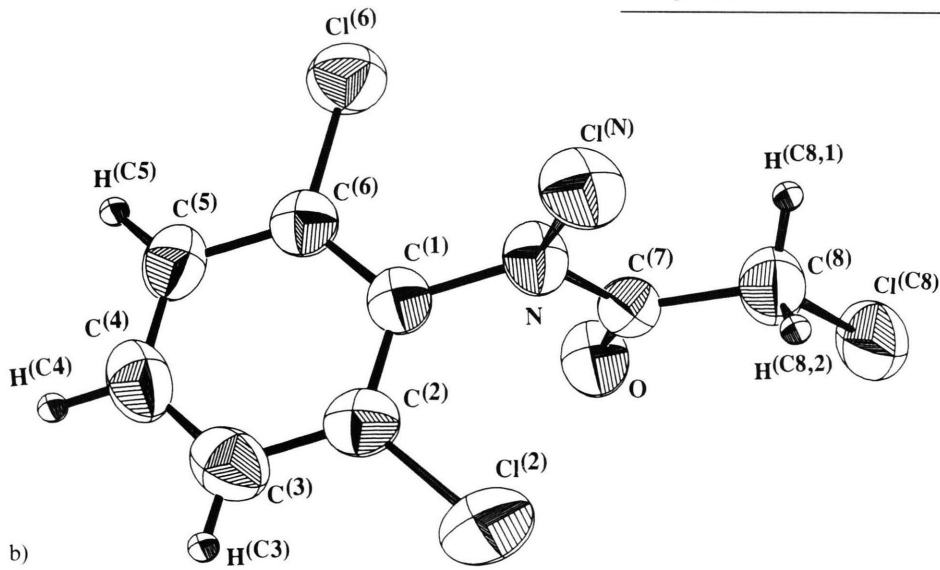
As far as the molecular packing is concerned, the molecules of (**1**) are arranged in planes of 2,6-dichlorophenyl rings in *bc* planes centered at $x=0$ and $x=0.5$, the $NClCOCCl_3$ groups in *bc*-planes centered at $x=0$ and $x=0.5$, the $NClCOCCl_3$ groups in *bc*-planes centered at $x=0.25$ and 0.75 (see Figure 2).

Table 1. Experimental conditions for the crystal structure determinations and crystallographic data of (**1**), $C_8H_3Cl_6NO$, $M=341.82$, and (**2**), $C_8H_5Cl_4NO$, $M=272.93$. Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm (MoKα); monochromator: Graphite (002); scan $2\,g/\omega$).

Compound	(**1**)	(**2**)
Crystal size (mm^3)	$0.2\times0.3\times0.7$	$0.80\times0.55\times0.15$
Temperature/K	293(2)	298(2)
Absorption coeff. μ/m^{-1}	1231	1066
Θ-range for data coll.	$1.99\leq\Theta/^\circ\leq24.96$	$1.96\leq\Theta/^\circ\leq24.99$
Index ranges	$0\leq h\leq24$, $0\leq k\leq13$ $-12\leq l\leq7$	$0\leq h\leq24$, $-17\leq k\leq10$, $0\leq l\leq8$
Lattice constants/pm	$a=2051.7(8)$	2078.4(7)
	$b=1134.8(4)$	1487.9(4)
	$c=1089.0(4)$	694.0(2)
	$\alpha=90^\circ$	90°
	$\beta=90^\circ$	90°
	$\gamma=90^\circ$	90°
$V\cdot10^{-6}/(pm)^3$	2536(2)	2146.2(11)
Space group	D_{2h}^{15}–Pbca	D_{2h}^{15}–Pbca
Formula units Z	8	8
$\varrho_{calc}/Mg\cdot m^{-3}$)	1.791(2)	1.689(2)
F (000)	1344	1088
Reflections collec.	4198	3286
Symmetry independent	2231	1894
$[R_{int}]$	0.0702	0.0270
Data	2225	1891
Restraints/Parameters	0/158	0/128
Goodness of fit on F^2	1.204	1.063
Final R ($I>2\sigma(I)$)	$R_1=0.0629$	0.0349
	$wR_2=0.1680$	0.0869
R (all data)	$R_1=0.0753$	0.0457
	$wR_2=0.1868$	0.0981
Max./min.transmission		0.799/0.544
largest diff: (peak, hole)/ $(10^{-6}\,e(pm)^3)$	0.450 and −0.487	0.362 and −0.430
extinct. coeff.	0.0033(10)	0.0007(3)
Point positions:	all atoms in 8c	



a)



b)

Fig. 1. Geometries of the molecules a) 2,6-$Cl_2C_6H_3NClCOCCl_3$ (**1**) and b) 2,6-$Cl_2C_6H_3NClCOCClH_2$ (**2**), with the numbering of the atoms and thermal ellipsoids.

Table 2. Atomic coordinates (· 10^4) and displacement parameters U_{eq} and U_{ij} (in pm^2) for 2,6-$Cl_2C_6H_3NClCOCCl_3$ (**1**) and 2,6-$Cl_2C_6H_3NClCOCH_2Cl$ (**2**). U_{eq} is defined as one third of the trace of the orthogonalized tensor U_{ij}. The temperature factor has the form:

$$T = \exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)].$$

Atom	Compound (**1**)			
	x	y	z	U_{eq}
$C^{(1)}$	5702(2)	6656(4)	3719(4)	458(10)
$C^{(2)}$	5415(2)	5626(4)	3321(4)	496(10)
$Cl^{(2)}$	5885(1)	4557(1)	2629(1)	732(5)
$C^{(3)}$	4749(3)	5440(5)	3506(6)	672(14)
$H^{(3)}$	4571(26)	4687(47)	3114(53)	626(142)
$C^{(4)}$	4393(3)	6287(7)	4085(7)	774(18)
$H^{(4)}$	3948(38)	6088(61)	4104(69)	1042(139)
$C^{(5)}$	4664(3)	7311(6)	4497(6)	690(15)
$H^{(5)}$	4503(45)	7916(79)	4878(92)	1353(345)
$C^{(6)}$	5323(2)	7503(5)	4304(5)	535(11)
$Cl^{(6)}$	5672(1)	8806(1)	4787(2)	819(5)
N	6385(2)	6876(3)	3528(3)	467(9)
$Cl^{(N)}$	6553(1)	7742(1)	2286(1)	596(4)
$C^{(7)}$	6829(2)	6407(4)	4314(4)	392(9)
O	6651(1)	5814(3)	5177(3)	503(8)
$C^{(8)}$	7563(2)	6624(4)	4096(5)	491(11)
$Cl^{(C8,1)}$	8007(1)	5920(1)	5275(2)	698(5)
$Cl^{(C8,2)}$	7738(1)	8140(1)	4172(2)	774(5)
$Cl^{(C8,3)}$	7796(1)	5997(2)	2674(2)	797(5)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$C^{(1)}$	336(20)	535(24)	501(22)	−5(17)	−20(18)	84(20)
$C^{(2)}$	437(22)	530(24)	521(24)	−37(19)	−25(19)	25(21)
$Cl^{(2)}$	856(10)	599(8)	726(8)	17(8)	7(7)	−112(6)
$C^{(3)}$	512(27)	719(32)	784(34)	−163(26)	−109(26)	95(29)
$C^{(4)}$	327(24)	1027(47)	967(44)	−6(28)	39(28)	267(40)
$C^{(5)}$	439(26)	839(41)	791(35)	131(27)	82(26)	161(32)
$C^{(6)}$	459(23)	550(24)	597(25)	82(21)	−53(21)	18(22)
$Cl^{(6)}$	875(11)	623(8)	726(8)	84(7)	−125(9)	−172(8)
N	342(18)	525(20)	535(20)	−64(15)	12(15)	151(17)
$Cl^{(N)}$	521(7)	692(8)	575(7)	−65(5)	2(5)	210(6)
$C^{(7)}$	351(19)	345(20)	440(21)	−9(16)	2(18)	−13(17)
O	430(17)	572(18)	508(17)	−74(14)	1(14)	69(15)
$C^{(8)}$	336(21)	496(24)	641(27)	−8(17)	−26(20)	42(21)
$Cl^{(C8,1)}$	449(7)	738(9)	913(10)	12(6)	−173(6)	178(8)
$Cl^{(C8,2)}$	623(8)	523(8)	1175(12)	−207(6)	−205(8)	128(8)
$Cl^{(C8,3)}$	611(8)	998(11)	781(9)	130(7)	252(7)	−41(8)

Atom	Compound (**2**)			
	x	y	z	U_{eq}
$C^{(1)}$	1614(1)	4363(2)	3783(3)	448(6)
$C^{(2)}$	2011(1)	3612(2)	3712(4)	515(7)
$Cl^{(2)}$	1663(1)	2564(1)	3520(1)	734(3)
$C^{(3)}$	2670(1)	3698(2)	3812(4)	634(8)
$H^{(3)}$	2933(1)	3193(2)	3757(4)	760
$C^{(4)}$	2933(1)	4539(3)	3994(4)	654(8)
$H^{(4)}$	3378(1)	4598(3)	4067(4)	785
$C^{(5)}$	2555(1)	5299(2)	4070(4)	573(7)
$H^{(5)}$	2741(1)	5864(2)	4194(4)	687
$C^{(6)}$	1890(1)	5204(2)	3958(4)	487(6)
$Cl^{(6)}$	1411(1)	6152(1)	4082(1)	684(3)
N	0931(1)	4264(2)	3722(3)	507(6)
$Cl^{(N)}$	0588(1)	4045(1)	5929(1)	633(2)
$C^{(7)}$	0624(1)	4030(2)	2037(4)	460(6)
O	0894(1)	4118(2)	0516(3)	591(5)
$C^{(8)}$	−0053(1)	3682(2)	2262(5)	650(8)
$Cl^{(C8)}$	−0418(1)	3481(1)	0020(1)	832(3)
$H^{(C8,1)}$	−0306(1)	4118(2)	2973(5)	780
$H^{(C8,2)}$	−0045(1)	3129(2)	3001(5)	780

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$C^{(1)}$	446(13)	585(15)	313(12)	−24(11)	−3(10)	−2(11)
$C^{(2)}$	609(16)	566(15)	370(14)	28(12)	−8(12)	−14(12)
$Cl^{(2)}$	975(6)	550(4)	676(5)	−20(4)	−45(5)	−4(4)
$C^{(3)}$	588(17)	799(21)	514(17)	146(16)	−39(14)	−29(16)
$C^{(4)}$	459(15)	1003(24)	501(17)	9(16)	−43(13)	−59(17)
$C^{(5)}$	551(15)	705(18)	463(15)	−148(14)	−15(13)	−37(15)
$C^{(6)}$	530(14)	568(15)	362(13)	−21(12)	7(11)	0(12)
$Cl^{(6)}$	721(5)	597(4)	733(5)	56(4)	−30(4)	−5(4)
N	449(11)	710(14)	366(11)	−82(119)	48(9)	19(11)
$Cl^{(N)}$	651(4)	820(5)	427(4)	−23(4)	145(3)	35(4)
$C^{(7)}$	443(13)	471(13)	467(15)	−1(11)	−4(12)	−30(12)
O	546(10)	832(14)	394(10)	−65(11)	4(9)	−4(10)
$C^{(8)}$	508(15)	830(22)	611(19)	−102(15)	1(14)	−106(17)
$Cl^{(C8)}$	560(4)	1071(7)	866(7)	24(4)	−196(4)	−287(6)

This leads to a maximum compensation of the molecular dipole moments in the direction [100]. A similar dipole compensating molecular arrangement is found in (**2**), as shown in Figure 3. Here the molecular dipoles are also compensating in the [100] direction, the molecules forming layers of dichlorophenyl rings in the *bc* plane at $x = 0.25$ and $x = 0.75$, and the $NClCOCClH_2$ groups are centered in the *bc* planes at $x = 0$ and $x = 0.5$.

The intermolecular distances within the van der Waals distances < 380 pm for (**1**) and (**2**) are given in Table 6. The van der Waals interactions are of three types: a) C···C (ring benzene·· benzene), b) Cl···Cl, and c) carbonyl oxygen ··Cl. For r_{vdW}(Cl) we take 180 pm for the ring attached chlorines and 177 pm for the aliphatic Cl atoms [6, 7]. $r_{vdW}(Cl^{(N)})$ is probably smaller than the aliphatic r_{vdW}, and we assume 170 pm for it.

^{35}Cl NQR

The ^{35}Cl spectrum of (**1**) was studied in the temperature range $77 \leq T/K \leq 370$. For (**2**) the NQR frequen-

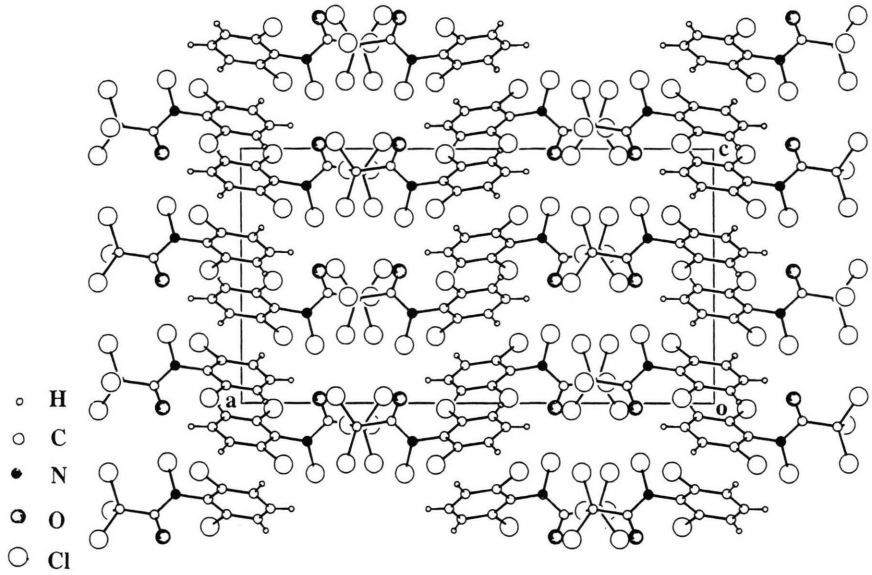


Fig. 2. Projection of the unit cell of (**1**) along [010] onto the *ac* plane.

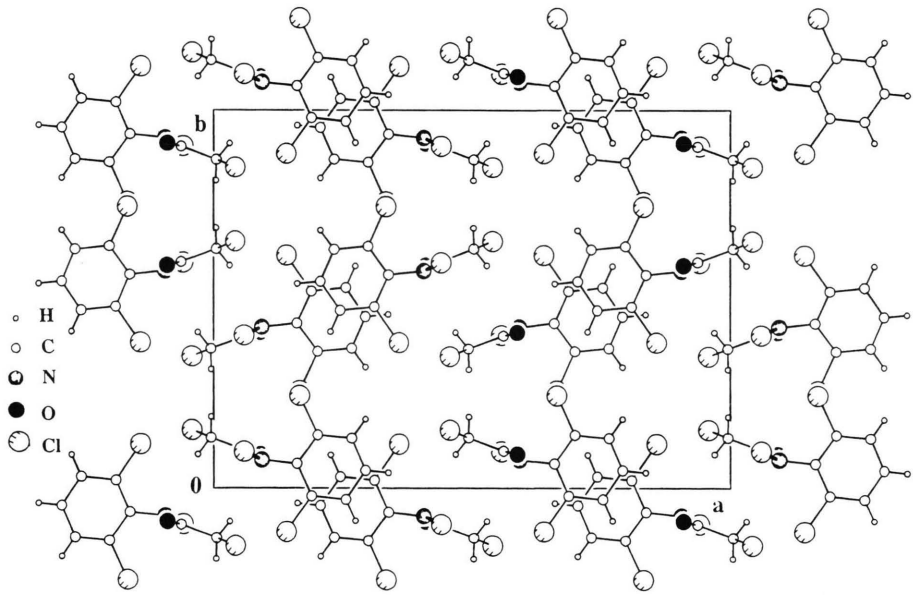


Fig. 3. Projection of the unit cell of (**2**) onto the (011) plane.

cies have been given in [1]. There is a printing error in [1] in the formula of (**13**), here (**2**). It should read $C_8H_5Cl_4NO$, not $C_6H_5Cl_4NO$. In Figs. 4 and 5 the ^{35}Cl NQR frequencies of (**1**) and (**2**) are plotted as functions of temperature. The frequencies decrease smoothly with increasing temperature as expected for molecular crystals, obeying predictions of the theory of Bayer [8]. The coefficients a_i of the power series development of the ^{35}Cl NQR frequencies as $f(T)$ according to

$$\nu = \sum a_i T^i \qquad -1 \leq i \leq 2\,.$$

Table 3. Intramolecular distances (bond lengths) *d*/pm and angles/° of (**1**) and (**2**).

Compound	(**1**)	(**2**)
Connection	*d*/pm	*d*/pm
$C^{(1)}-C^{(2)}$	138.0(6)	139.0(4)
$C^{(2)}-C^{(3)}$	139.7(7)	137.6(4)
$C^{(3)}-C^{(4)}$	136.2(9)	137.2(4)
$C^{(4)}-C^{(5)}$	136.4(10)	137.8(4)
$C^{(5)}-C^{(6)}$	138.5(7)	139.1(4)
$C^{(6)}-C^{(1)}$	139.1(7)	138.3(4)
$C^{(7)}-C^{(8)}$	154.5(6)	150.7(4)
$C^{(1)}-N$	143.8(5)	142.7(3)
$C^{(7)}-N$	136.0(6)	137.7(3)
$C^{(7)}-O$	121.3(5)	120.3(3)
$C^{(2)}-Cl^{(2)}$	172.2(5)	172.6(3)
$C^{(6)}-Cl^{(6)}$	172.6(5)	172.7(3)
$C^{(8)}-Cl^{(C8,1)}$	176.5(5)	175.8(3)
$C^{(8)}-Cl^{(C8,2)}$	175.9(5)	
$C^{(8)}-Cl^{(C8,3)}$	176.9(5)	
$N-Cl^{(N)}$	170.7(4)	172.1(2)
Connection	Angle/°	Angle/°
$C^{(1)}-C^{(2)}-C^{(3)}$	120.0(5)	121.0(3)
$C^{(2)}-C^{(3)}-C^{(4)}$	119.0(5)	119.0(3)
$C^{(3)}-C^{(4)}-C^{(5)}$	122.3(5)	121.6(3)
$C^{(4)}-C^{(5)}-C^{(6)}$	118.8(6)	118.8(3)
$C^{(5)}-C^{(6)}-C^{(1)}$	120.5(5)	120.6(3)
$C^{(6)}-C^{(1)}-C^{(2)}$	119.4(4)	118.9(2)
$C^{(2)}-C^{(3)}-H^{(3)}$	115(3)	120.5(2)
$C^{(4)}-C^{(3)}-H^{(3)}$	126(3)	120.5(2)
$C^{(3)}-C^{(4)}-H^{(4)}$	111(5)	119.2(2)
$C^{(5)}-C^{(4)}-H^{(4)}$	126(5)	119.2(2)
$C^{(4)}-C^{(5)}-H^{(5)}$	133(6)	120.6(2)
$C^{(6)}-C^{(5)}-H^{(5)}$	109(6)	120.6(2)
$N-C^{(1)}-C^{(2)}$	121.2(4)	120.5(2)
$N-C^{(1)}-C^{(6)}$	119.5(4)	120.6(2)
$Cl^{(2)}-C^{(2)}-C^{(1)}$	119.7(3)	118.6(2)
$Cl^{(2)}-C^{(2)}-C^{(3)}$	120.3(4)	120.3(2)
$Cl^{(6)}-C^{(6)}-C^{(1)}$	119.9(4)	120.3(2)
$Cl^{(6)}-C^{(6)}-C^{(5)}$	119.6(4)	119.1(2)
$C^{(1)}-N-C^{(7)}$	119.6(3)	120.8(2)
$Cl^{(N)}-N-C^{(1)}$	114.3(3)	113.9(2)
$Cl^{(N)}-N-C^{(7)}$	126.1(3)	121.0(2)
$N-C^{(7)}-C^{(8)}$	119.6(4)	115.5(2)
$O-C^{(7)}-N$	120.2(4)	120.1(2)
$O-C^{(7)}-C^{(8)}$	120.2(4)	124.3(2)
$C^{(7)}-C^{(8)}-Cl^{(C8,1)}$	108.6(3)	111.7(2)
$C^{(7)}-C^{(8)}-Cl^{(C8,2)}$	110.3(3)	–
$C^{(7)}-C^{(8)}-Cl^{(C8,3)}$	109.5(3)	–
$Cl^{(C8,1)}-C^{(8)}-Cl^{(C8,2)}$	107.7(3)	–
$Cl^{(C8,1)}-C^{(8)}-Cl^{(C8,3)}$	108.4(2)	–
$Cl^{(C8,2)}-C^{(8)}-Cl^{(C8,3)}$	112.3(3)	–
$C^{(7)}-C^{(8)}-H^{(C8,1)}$	–	109.3(2)
$C^{(7)}-C^{(8)}-H^{(C8,2)}$	–	109.3(2)
$Cl^{(C8)}-C^{(8)}-H^{(C8,1)}$	–	109.3(11)
$Cl^{(C8)}-C^{(8)}-H^{(C8,2)}$	–	109.3(11)
$H^{(C8,1)}-C^{(8)}-H^{(C8,2)}$	–	107.9

Table 4. Plane equations for (**1**) and (**2**).

Assignment	Plane equation
	Compound (**1**)
a) $(C^{(1)}\cdot\cdot C^{(6)})$	$4.077(46)\,x-4.863(23)\,y+9.598(12)\,z=2.657(30)$ *Deviation* in pm $C^{(1)}$: 1(2); $C^{(2)}$: 2(3); $C^{(3)}$: −1(4); $C^{(4)}$: −3(5); $C^{(5)}$: 5(42); $C^{(6)}$: −4(4); N: −12(7); $Cl^{(2)}$: 49(7); $Cl^{(6)}$: −32(7)
b) $(Cl^{(N)}, N, C^{(7)}, O)$	$-1.230(137)\,x+9.280(10)\,y+6.233(8)\,z=7.800(94)$ *Deviation* in pm: $Cl^{(N)}$: 4(1); N: −5(2); $C^{(7)}$: −5(2); O: 5(2)
c)	Angle between the benzene ring and the plane $(Cl^{(N)}, N, C^{(7)}, O)$: 81.83(14)°
	Compound (**2**)
a) $C^{(1)}\cdot\cdot C^{(6)}$	$-0.948(23)\,x-1.161(17)\,y+6.912(2)\,z=1.954(9)$
b) $Cl^{(N)}, N, O, C^{(7)}$	$8.904(74)\,x+13.429(26)\,y-0.301(6)\,z=4.757(17)$
c)	84.60(8)

Table 5. Selected torsional angles of N-chloro compounds, 2,6-$Cl_2C_6H_3NClCOCCl_3$ (**1**), 2,6-$Cl_2C_6H_3NClCOCClH_2$ (**2**), $C_6H_5NClCOCCl_3$ (**1 ph**), and $C_6H_5NClCOCClH_2$ (**2 ph**).

Compound	(**1**)	(**2**)	(**1 ph**)	(**2 ph**)
Connection	Angle/°	Angle/°	Angle/°	Angle/°
$C^{(1)}-N-C^{(7)}-O$	−0.6(6)	−18.2(4)	−170.4(2)	−164.7(3)
$C^{(1)}-N-C^{(7)}-C^{(8)}$	178.9(4)	162.6(3)	7.2(4)	16.2(4)
$N-C^{(1)}-C^{(2)}-C^{(3)}$	−179.3(4)	−178.6(4)	−177.7(2)	−178.1(2)
$N-C^{(1)}-C^{(2)}-Cl^{(2)}$	2.3(6)	0.8(3)	–	–
$N-C^{(1)}-C^{(6)}-C^{(5)}$	179.9(5)	178.3(2)	176.4(2)	178.1(2)
$N-C^{(1)}-C^{(6)}-Cl^{(6)}$	0.3(6)	−0.6(3)	–	–
$N-C^{(7)}-C^{(8)}-Cl^{(C8,1)}$	179.3(3)	175.8(2)	38.3(3)	164.5(2)
$N-C^{(7)}-C^{(8)}-Cl^{(C8,2)}$	61.6(5)	–	−84.1(3)	–
$N-C^{(7)}-C^{(8)}-Cl^{(C8,3)}$	−62.6(5)	–	158.9(2)	–
$Cl^{(N)}-N-C^{(1)}-C^{(2)}$	98.2(4)	84.2(3)	86.0(2)	91.5(2)
$Cl^{(N)}-N-C^{(1)}-C^{(6)}$	−81.0(5)	−94.3(3)	−90.0(2)	−87.3(3)
$Cl^{(N)}-N-C^{(7)}-O$	179.1(3)	−173.7(2)	−2.6(3)	−4.7(3)
$Cl^{(N)}-N-C^{(7)}-C^{(8)}$	−1.4(6)	7.1(4)	175.1(2)	176.2(2)
$C^{(7)}-N-C^{(1)}-C^{(2)}$	−82.0(5)	−72.9(3)	−106.1(3)	−108.1(3)
$C^{(7)}-N-C^{(1)}-C^{(6)}$	98.7(5)	108.5(3)	77.9(3)	73.2(3)
$O-C^{(7)}-C^{(8)}-Cl^{(C8,1)}$	−1.3(5)	−3.4(4)	−143.9(2)	−14.7(4)
$O-C^{(7)}-C^{(8)}-Cl^{(C8,2)}$	−119.0(4)	–	93.7(2)	–
$O-C^{(7)}-C^{(8)}-Cl^{(C8,3)}$	116.9(4)	–	−23.4(3)	–
$C^{(2)}-C^{(1)}-C^{(6)}-Cl^{(6)}$	−179.0(4)	−179.2(2)	–	–
$C^{(6)}-C^{(1)}-C^{(2)}-Cl^{(2)}$	−178.4(4)	179.3(2)	–	–
$C^{(4)}-C^{(5)}-C^{(6)}-Cl^{(6)}$	178.6(5)	179.2(2)	–	–
$C^{(4)}-C^{(3)}-C^{(2)}-Cl^{(2)}$	178.3(5)	−179.0(2)	–	–

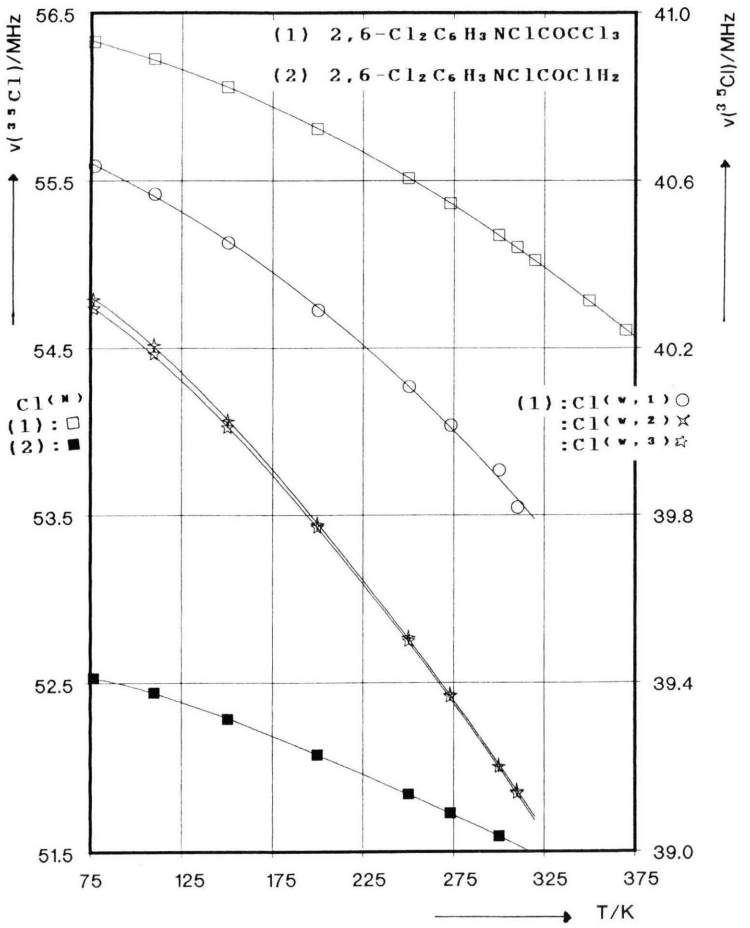


Fig. 4. ^{35}Cl NQR frequencies of (**1**) and (**2**) as functions of temperature.

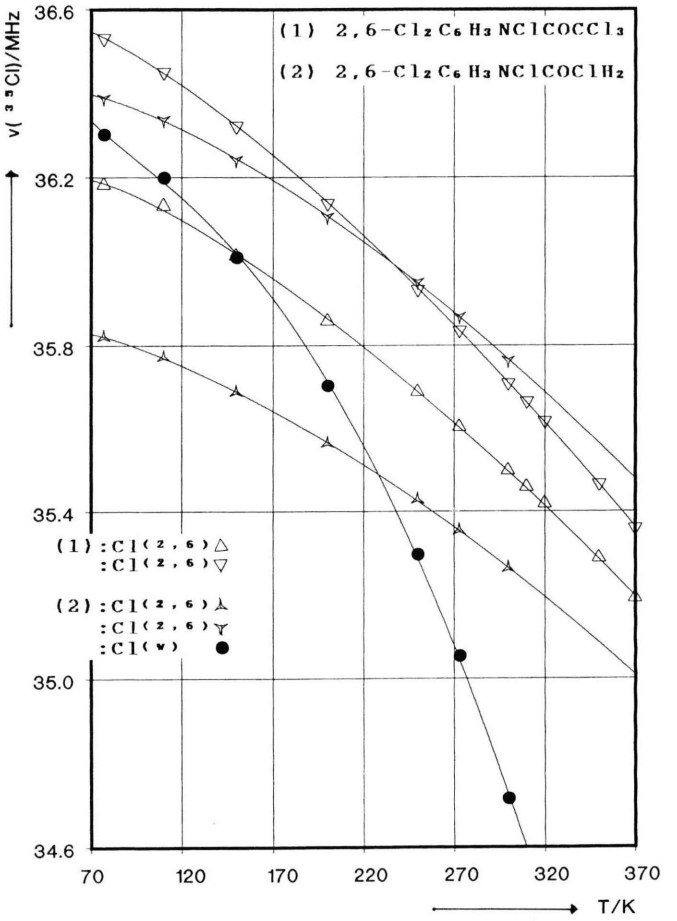


Fig. 5. ^{35}Cl NQR frequencies of (**1**) and (**2**) as functions of temperature.

Table 6. Intermolecular distances in (**1**) and (**2**) within the van der Waals distances ≤380 pm [6, 7].

Compound Connection	(**1**) d/pm	(**2**) d/pm
$C^{(1)}..C^{(5')}$	–	373
$C^{(2)}..C^{(3')}$	368	–
$C^{(2)}..C^{(4')}$	355	–
$C^{(2)}..C^{(5')}$	341	372
$C^{(3)}..C^{(3')}$	356	–
$C^{(3)}..C^{(4')}$	372	–
$C^{(3)}..C^{(5')}$	–	364
$C^{(4)}..C^{(5')}$	–	357
$C^{(4)}..C^{(5'')}$	–	367
$C^{(4)}..C^{(6')}$	–	353
$C^{(4)}..C^{(6'')}$	–	349
$C^{(5)}..C^{(5')}$	–	359
$C^{(5)}..C^{(6')}$	–	366
$Cl^{(2)}..Cl^{(2')}$	–	348
$Cl^{(2)}..Cl^{(6')}$	364	–
$Cl^{(C8,1)}..Cl^{(C8,2')}$	371	–
$Cl^{(C8,1)}..Cl^{(C8,3')}$	378	–
$Cl^{(C8,2)}..Cl^{(C8,3')}$	379	–
$Cl^{(C8,1)}..Cl^{(2')}$	366	–
$Cl^{(C8,1)}..Cl^{(6')}$	347	–
$Cl^{(C8,2)}..Cl^{(6')}$	366	–
$Cl^{(N)}..Cl^{(2')}$	371	374
$Cl^{(C8,2)}..O$	346	373
$Cl^{(C8,3)}..O'$	359	–
$Cl^{(N)}..O'$	283	325

Table 7. Coefficients a_i of the polynomial $\nu = \sum a_i T^i$, $-1 \le i \le 2$, and ^{35}Cl NQR frequencies at selected temperatures for (**1**) and (**2**). z is the number of measurements, σ the mean squares deviation (in kHz). S/N is the signal to noise ratio, measured by lock in technique, time constant 10 s. For (**2**), see also [1].

Position	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}
	Compound (**1**)						
$Cl^{(N)}$	ν_1	11	4.5	56.493	0.482	−1.452	−9.849
$Cl^{(CCl_3)}$	ν_2	8	2.8	40.695	−7.941	−3.498	−4.660
$Cl^{(CCl_3)}$	ν_3	8	3.7	40.778	−10.169	−3.954	−3.895
$Cl^{(CCl_3)}$	ν_4	8	15.1	40.714	2.036	−0.831	−6.496
$Cl^{(2,6)}$	ν_5	11	2.7	36.823	−5.692	−2.518	−3.757
$Cl^{(2,6)}$	ν_6	11	5.8	36.470	−7.405	−2.205	−3.208
	Compound (**2**)						
$Cl^{(N)}$	ν_1	7	3.8	53.065	−15.402	−4.216	−1.771
$Cl^{(CClH_2)}$	ν_2	7	14.1	35.806	24.405	4.545	28.056
$Cl^{(2,6)}$	ν_3	7	2.7	36.007	−4.386	−1.417	−3.372
$Cl^{(2,6)}$	ν_4	7	3.0	36.591	−4.802	−1.494	−3.996

Assignment	ν_i	MHz (S/N) T=77 K	MHz (S/N) T=273 K	MHz (S/N) T=300 K	MHz (S/N) T=370 K
	Compound (**1**)				
$Cl^{(N)}$	ν_1	56.327(40)	55.364(20)	55.176(20)	54.604(15)
$Cl^{(CCl_3)}$	ν_2	40.636(60)	40.016(25)	39.907(10)	–
$Cl^{(CCl_3)}$	ν_3	40.317(45)	39.373(25)	39.204(10)	–
$Cl^{(CCl_3)}$	ν_4	40.294(50)	39.366(30)	39.199(10)	–
$Cl^{(2,6)}$	ν_5	36.532(50)	35.836(30)	35.710(30)	35.359(15)
$Cl^{(2,6)}$	ν_6	36.182(60)	35.604(30)	35.497(30)	35.190(20)
	Compound (**2**)				
$Cl^{(N)}$	ν_1	52.529(40)	51.727(10)	51.588(10)	
$Cl^{(CClH_2)}$	ν_2	36.303(30)	35.055(10)	34.716(5)	
$Cl^{(2,6)}$	ν_3	36.389(35)	35.869(10)	35.765(10)	
$Cl^{(2,6)}$	ν_4	35.820(25)	35.353(10)	35.262(10)	

are listed in Table 7 together with frequencies at selected temperatures for both the compounds. Among the resonances of the three chemically different kinds of chlorine atoms, as assigned in the discussion section, those from the chlorine bound to nitrogen atoms and to the ring are observed up to 370 K, whereas those from chlorine atoms in the $CClH_2$- and CCl_3-groups fade out above 310 K. This is in contrast to the observation that quite often for the trichloromethyl group fade out above room temperature. Since there is no change in the multiplicity of the spectrum from 77 K up to 370 K (except for dynamical fade out of $\nu(Cl^{CCl_3 \text{ or } CClH_2})$, one can say that, in the present conditions, there is no phase transition of first order in these compounds.

Discussion

It is worthwhile to compare the ^{35}Cl NQR and crystal structure data of (**1**) and (**2**) with the literature data [2, 4] of 2,6-dichlorophenyl-2,2,2-trichloroacetamide (**1nh**), 2,6-dichlorophenyl-2-chloroacetamide (**2nh**), N-chloro-N-phenyl-2,2,2-trichloroacetamide (**1ph**) and N-chloro-N-phenyl-2-chloroacetamide (**2ph**) and other substituted acetamides and chloroacetamides.

The first point we consider is the intramolecular geometry of the title compounds. The individual data are given in Table 3. Comparison of the $C^{(i)}$–$C^{(j)}$ bond distances within the C_6-rings of the two compounds shows that there is no significant change in the ring distances by the side substitution. Similar trends were observed with the corresponding unsubstituted N-Cl-N-phenyl-chloroacetamides $C_6H_5NClCOCCl_3$ (**1ph**) and $C_6H_5NClOCClH_2$ (**2ph**) [2]. The $C^{(2,6)}$–Cl bond lengths are almost the same and are also not different from the respectively N–H compounds, $2,6\text{-}Cl_2C_6H_3NHCOCCl_3$ (**1nh**) and $2,6\text{-}Cl_2C_6H_3\text{-}NHCOCClH_2$ (**2nh**) [4]. The $C^{(1)}$–N bond distances

for compounds (**1**) and (**2**) are 143.8 pm and 142.7 pm, compared to the values of 142.9 pm and 141.6 pm for the N–H compounds (**1 nh**) and (**2 nh**) [4]. For the bond $N-C^{(7)}$, the distances are 136.0 pm and 137.7 pm for (**1**) and (**2**), respectively, and 133.6 pm and 133.6 pm for (**1 nh**) and (**2 nh**). The elongation of this bond is greater with compound (**2**) on N-chlorination. The effect of the latter on the $C^{(7)}-O$ bond length of (**1**) is negligible, while it shortened this bond length of (**2**) by 1.4 pm. On N-chlorination the $C^{(8)}-Cl^{(8.1,8.2,8.3)}$ bond distances in the side chain lengthen by about 2 pm in both the compounds.

As to ring angles, the mean values are 120° for both compounds, as they are for the respective N–H compounds [4]. There are no substantial differences in the bond angles $N-C^{(1)}-C^{(2,6)}$ and $Cl^{(2,6)}-C^{(2,6)}-C^{(1,3,5)}$ of the title compounds. The $C^{(1)}-N-C^{(7)}$ bond angles for the compounds (**1**), (**2**), (**1 nh**), (**2 nh**), (**1 ph**) and (**2 ph**) are 119.6°, 120.8°, 121.4°, 123.4°, 132.3° and 125.6°, respectively [2, 4]. That is, the bond angles narrow down by 1.8–2.6° on N-chlorination of N-(2,6-dichlorophenyl)-chloroacetamides, while the effect of 2,6-dichlorosubstitution into the ring of N-chloro-N-phenyl-chloroacetamides is marked. It shortens the bond angle by 12.7° with trichloroacetamide side chain and by 4.8° with monochloroacetamide. But the dichloro substitution in the benzene ring has no substantial effect on the $Cl^{(N)}-N-C^{(1)}$ bond angle, while the effect is significant on the $Cl^{(N)}-N-C^{(7)}$ bond angle. The values for (**1**) and (**2**) are 126.1° and 121.0°, compared to the values of 113.8° and 117.3° for (**1 ph**) and (**2 ph**) [2]. N-chlorination of N–H compounds also widens these angles. The $H^{(N)}-N-C^{(7)}$ angles are 116.1° and 117.8° for (**1 nh**) and (**2 nh**). Similarly the ($N-C^{(7)}-C^{(8)}$, $N-C^{(7)}-O$ and $O-C^{(7)}-C^{(8)}$ bond angles change to some extent. The changes in bond angles with regard to the side chain are minor in the respective categories.

^{35}Cl NQR

There is no problem in the assignment of the ^{35}Cl NQR frequencies. The six lines observed for (**1**) at 77 K (Table 7) may be assigned as follows: In N-chloroacetanilides, the $^{35}Cl^{(N)}$ frequencies are much higher than those of $^{35}Cl^{(C)}$, generally > 51 MHz [1], and therefore the assignment is unique. Hence $\nu_1 = 56.327$ MHz is assigned to $Cl^{(N)}$. The side chain Cl atoms have much higher temperature coefficients than the ring chlorines [3, 9]. Therefore the frequencies $\nu_2 = 40.636$ MHz, $\nu_3 = 40.317$ MHz, and $\nu_4 = 40.294$ MHz have been assigned to the CCl_3 group. The position of the latter in the frequency scale of $Cl^{(C)}$ is much higher than for the ring chlorines. Also, due to librational motions in the lattice, this triplet part of the spectrum fades out at $T_f = 320$ K, as the torsional motions of the CCl_3 group are easily excited. The remaining two lines, $\nu_5 = 36.532$ MHz and $\nu_6 = 36.182$ MHz are assigned to the ring chlorines ($Cl^{(2)}$ and $Cl^{(6)}$).

Pies et al. [3] have synthesised a large number of N-(chlorophenyl) acetamides and measured their ^{35}Cl NQR. They have observed several phase transitions, besides the fade out of the ^{35}Cl signals, which may, however, often be a property of the vibrational excitations of the considered group in the molecule. Quite an interesting relation was found later by Groke et al. [4], who observed that in the series, 2,6-$Cl_2C_6H_3NHCOCH_{3-x}Cl_x$ $x = 0$, 2 there is a phase transition of first order, whereas there is no phase transition up to the melting point for $x = 1$, 3. We find that the N-chlorination does not influence this pattern for $x = 1$, 3. Substitution within a molecule changes the ^{35}Cl NQR frequencies by the Hammett substituent effect, namely the χ-effect [3].

The present ^{35}Cl NQR frequencies have also been compared with our previous [1, 2] and on-going work [10] and with other results in the literature [11]. The comparisons are schematically represented in Figures 6–8. Figure 6 shows the variation of the mean value of the $C-^{35}Cl^{(2,6)}$ NQR frequencies with Cl substitution in the side chain $CH_{3-x}Cl_x$ in N-(2,6-dichlorophenyl) and N-chloro-N-(2,6-dichlorophenyl) acetamides and chloroacetamides. It generally increases with increase in the number of Cl atoms in the side chain from the level of the mean value 34.704 MHz of the two frequencies 34.398 MHz and 35.010 MHz for 2,6-dichloroaniline [11]. The variation of the $CClH_2$ and CCl_3 frequencies in chloroacetamides, N-phenyl and N-(2,6-dichlorophenyl) chloroacetamides, and N-chloro-N-phenyl and N-chloro-N-(2,6-dichlorophenyl) chloroacetamides is shown in Figure 7. Variations of the $^{35}Cl^{(N)}$ NQR frequencies in $X_yC_6H_{5-y}NClCOCClH_2$ (where X = Cl or NO_2 and $y = 1$ or 2) [1] and 2,6-$Cl_2C_6H_3NClCOR$ (where R = H, CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, C_6H_5, CH_2Cl, and CCl_3) [10], with the changes in ring substitution at constant side chain, and vice versa, are shown in Figure 8.

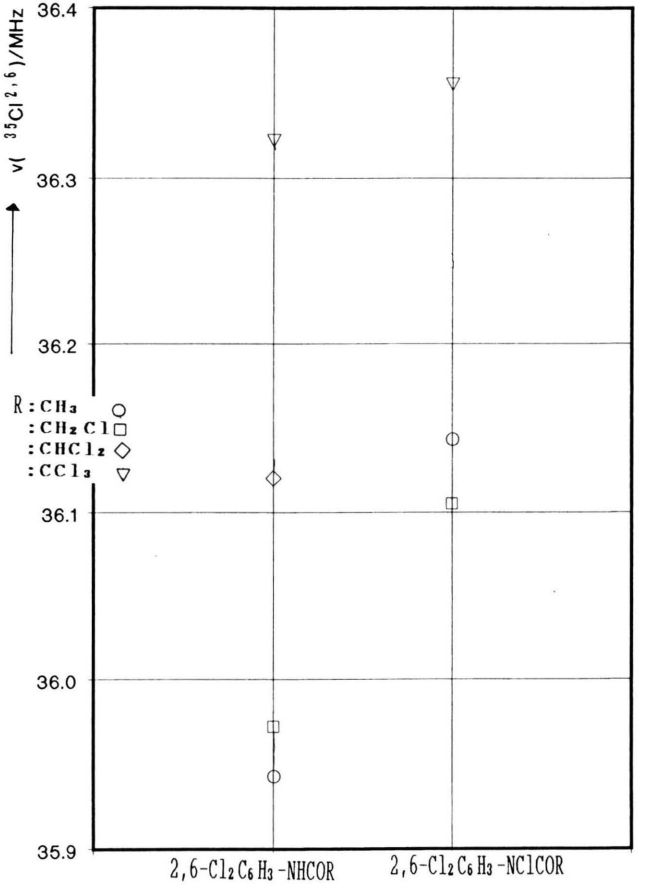


Fig. 6. Variation of the mean value of the C–^{35}Cl$^{(2,6)}$ NQR frequencies with Cl substitution in the side chain $CH_{3-x}Cl_x$ in 2,6-dichlorophenyl acetamides and their N-chlorinated compounds.

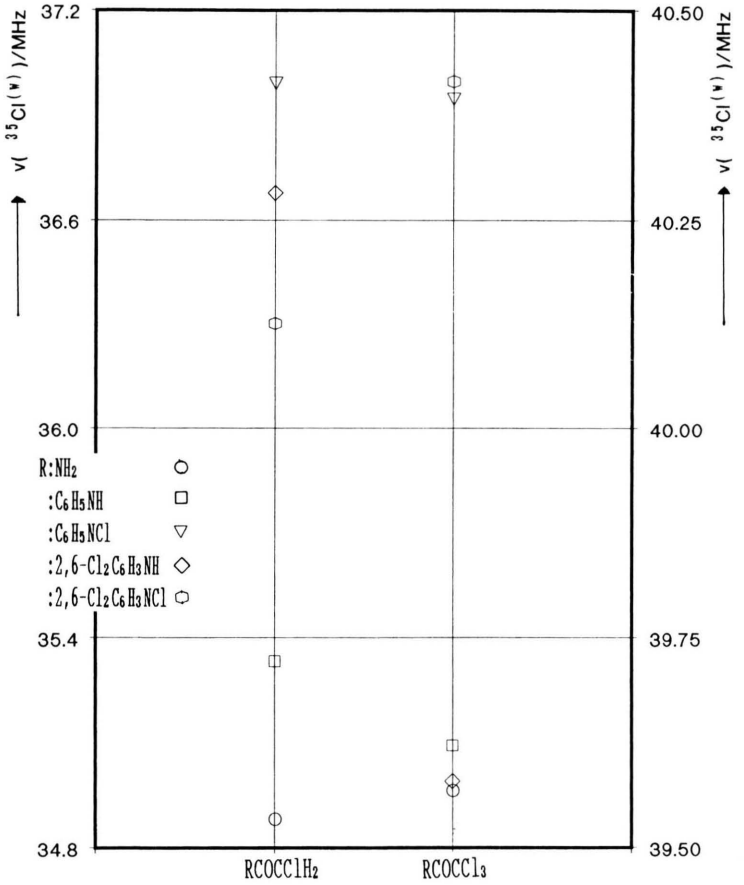


Fig. 7. Variation of the ^{35}Cl NQR frequency in $RCOCClH_2$ and the mean frequency in $RCOCCl_3$ (where $R = NH_2$, C_6H_5NH, C_6H_5NCl, 2,6-$Cl_2C_6H_3NH$ and 2,6-$Cl_2C_6H_3NCl$).

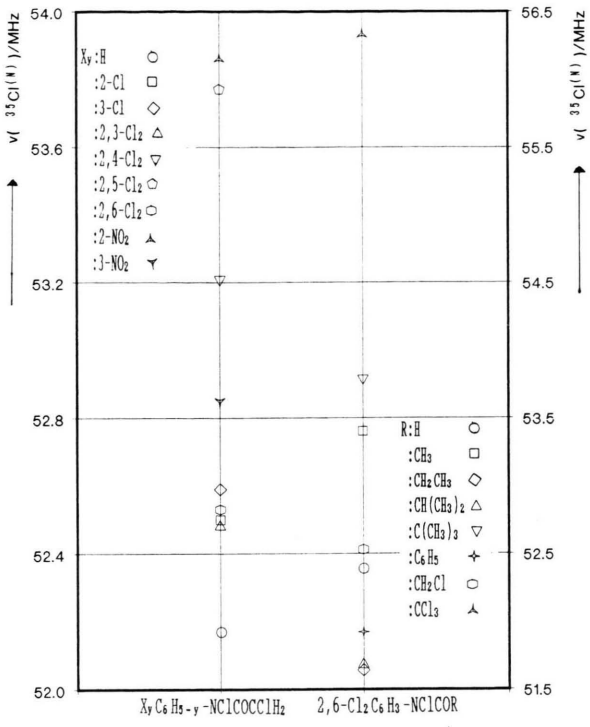


Fig. 8. Variation of the $^{35}Cl^{(N)}$ NQR frequencies with the ring and side chain substitutions, in $X_yC_6H_{5-y}NClCOCClH_2$ (X = Cl, NO_2; $y = 1$, 2) and 2,6-$Cl_2C_6H_3NClCOR$ (where R = H, CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, C_6H_5, CH_2Cl, CCl_3).

The main principal axis Φ_{zz} of the electric field gradient tensor, EFGT, depends on the distance d of a charge e from the quadrupolar nucleus by

$$\Phi_{zz} = a\,d^{-3}.$$

In the case of ^{35}Cl with $I = 3/2$, under the assumption that the asymmetry parameter $n(^{35}\text{Cl}) < 0.18$ it can be assumed 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), from which Φ_{zz} can be calculated with the known values of other constants. Thus the theory allows for a correlation of the NQR frequencies with the bond distances [12, 13]. Hence our main interest is in the correlation of N–Cl bond lengths and the $^{35}Cl^{(N)}$ NQR frequencies.

The N–Cl bond lengths of (**1**), (**2**), (**1ph**) and (**2ph**) are 170.7 pm, 172.1 pm, 172.0 pm and 170.6 pm, respectively. The $^{35}Cl^{(N)}$ NQR frequencies of the above compounds are 56.33 MHz, 52.53 MHz, 52.79 MHz and 52.17 MHz, respectively. The experimental data obtained up to now are not sufficient to correlate between the N–Cl bond lengths and $^{35}Cl^{(N)}$ NQR frequencies. Further NQR and structure work on a series of compounds with weak and strong N–Cl bonds is necessary for the purpose of correlation. Our work in this direction is in progress [14].

Acknowledgement

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[1] B. T. Gowda and Al. Weiss, Z. Naturforsch. **49a,** 695 (1994).
[2] S. Dou, B. T. Gowda, H. Paulus, and Al. Weiss, Z. Naturforsch. **49a,** 1136 (1994).
[3] W. Pies, H. Rager, and Al. Weiss, Org. Magn. Reson. **3,** 147 (1971).
[4] D. Groke, S. Dou, and Al. Weiss, Z. Naturforsch. **47a,** 160 (1992).
[5] D. Groke, G. Heger, P. Schweiss, and Al. Weiss, Z. Kristallogr. **209,** 448 (1994).
[6] A. Bondi, Physical properties of molecular crystals, liquids, and glasses, J. Wiley & Sons, New York 1968.
[7] A. Bondi, J. Phys. Chem. **68,** 441 (1964).
[8] H. Bayer, Z. Physik **130,** 227 (1951).
[9] D. Biedenkapp and Al. Weiss, J. Chem. Phys. **49,** 3933 (1968).
[10] B. T. Gowda and Al. Weiss, under publication.
[11] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, Nuclear quadrupole resonance in chemistry (Engl. Transl.), J. Wiley & Sons, New York 1975, p. 357.
[12] Al. Weiss and S. Wigand, Z. Naturforsch. **45a,** 195 (1990).
[13] P. Storck and Al. Weiss, Ber. Bunsenges. Phys. Chem. **94,** 179 (1990).
[14] B. T. Gowda, S. Dou, and Al. Weiss, to be published.