^{35}Cl NQR and Structural Studies of Chloroacetanilides $C_6H_3Cl_2NHCOCH_{3-x}Cl_x$, $1 \leq x \leq 3$ *

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The temperature dependence of ^{35}Cl NQR frequencies and the phase transition behaviour of chloroacetanilides (N-[2,6-dichlorophenyl]-2-chloroacetamide, -2,2-dichloroacetamide, -2,2,2-trichloroacetamide) were investigated. The crystal structure determination of N-[2,6-dichlorophenyl]-2-chloroacetamide leads to the following: $a = 1893.8$ pm, $b = 1110.7$ pm, $c = 472.1$ pm, space group $P2_12_12_1 = D_2^4$ with $Z = 4$ molecules per unit cell. The arrangement of the molecules and their geometry is comparable to the high temperature phase of the acetyl compound N-[2,6-dichlorophenyl]-acetamide. For N-[2,6-diclorophenyl]-2,2,2-trichloroacetamide it was found: $a = 1016.6$ pm, $b = 1194.3$ pm, $c = 1006.7$ pm, $\beta = 101.79°$, space group $P2_1/c = C_{2h}^5$, $Z = 4$. The structure is similar to the low temperature phase of N-[2,6-dichlorophenyl]-acetamide. Parallelism between the temperature dependence of the ^{35}Cl NQR lines of the CCl_3 group and the X-ray diffraction results concerning the different behaviour of the chlorine atoms was observed. The structures of the compounds show intermolecular hydrogen bonding of the $N-H \cdots O-C$ type. The phenyl group and the HNCO function are nearly planar.

A bleaching out of several ^{35}Cl NQR lines at a temperature far below the melting point of the substances was observed. The different types of chlorine atoms (aromatic, chloromethyl) can be distinguished by their temperature coefficients of the ^{35}Cl NQR frequencies. All the resonances found show normal "Bayer" temperature behaviour.

N-[2,6-dichlorophenyl]-2,2-dichloroacetamide shows several solid phases. One stable low temperature phase and an instable high temperature phase (at room temperature) were observed. The different phases were detected by means of ^{35}Cl NQR spectroscopy and thermal analysis.

Introduction

The first ^{35}Cl nuclear quadrupole resonance (NQR) studies on chloroacetanilides were done by Pies et al. [1]. The authors investigated the shift of the NQR frequencies of the aromatic chlorine atoms as function of the substitution of the phenyl ring with chloroacetamide groups. We became interested to study the bleaching out of ^{35}Cl NQR lines in chloroacetamides. Bleaching out (fading out) is often caused by reorientational motions. Well known examples for such reorientational motions are molecules with CCl_3 groups i.e. [2–3a, b]. A bleaching out of CH_2Cl or $CHCl_2$ groups is rarely observed. We want to study the influence of the substitution of the chloromethyl group on the onset of the bleaching out. For the CCl_3 group the reorientation takes place around the pseudo threefold axis of the group. For the two other chloromethyl groups a reorientation seems unlikely because of the missing of the pseudo symmetry. Anomalies of the temperature variation of the ^{35}Cl NQR frequencies in compounds containing the CH_2Cl and $CHCl_2$ group were investigated in the past [4–6].

Experimental

The substances containing the chloromethyl or dichloromethyl group were prepared from zone refined 2,6-dichloroaniline and the corresponding chloroacetylchloride in anhydrous acetic acid [7]. N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide was synthesized from trichloroacetic acid and 2,6-dichloroaniline with phosphorylchloride [8]. The yield was 70–90%. The products were crystallized several times from ethanol-water mixtures by slowly cooling down hot saturated solutions. The purity of the compounds was checked by using the melting points. The compounds will be abbreviated in the following

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manner: N-[2,6-dichlorophenyl]-2-chloroacetamide: DCPH2CL, N-[2,6-dichlorophenyl]-2,2-dichloroacetamide: DCPHCL2, and N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide: DCPCL3.

The NQR measurements were made using a DECCA superregenerative oscillator. The temperature was achieved by means of a heated nitrogen gas ($T = 100-200$ K), a methanol filled cryostat ($T = 200-295$ K), and a heated oil bath ($T > 295$ K). For the measurement at 77 K the sample was immersed in liquid nitrogen. The temperature was measured with a copper-constantan thermocouple with an accuracy of ± 0.2 K. The samples were sealed into glass ampoules. The monochloromethyl and dichloromethyl samples have been melted to get a better filling of the ampoules. The accuracy of the measured NQR frequencies is about ± 5 kHz. The signal to noise ratio (S/N) of the ^{35}Cl NQR lines varied between 30 and 2. The lower value S/N ratio corresponds to the temperature near the bleaching out of the signals. The S/N ratio was measured using lock-in detection with a time constant of 10 sec.

The crystal structures were determined with aid of a 4 circle X-ray diffractometer, Mo Kα (71.069 pm) radiation, graphite monochromator (0 0 2). A list of the experimental parameters for the structure determinations and crystallographic data is given in Table 1. All experiments were carried out at room temperature. The refinements were made by using the programs SHELX76 and SHELX86 [9, 10]. The calculation of the dihedral angles and of the best planes by least squares methods was made with aid of a home made program.

Table 1. Experimental conditions for the X-ray diffraction experiments and crystallographic data of N-[2,6-dichlorophenyl]-2-chloroacetamide and N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide.

Compound	N-[2,6-dichlorophenyl]-2-chloroacetamide	N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide
Formula	$C_8H_6Cl_3NO$	$C_8H_4Cl_5NO$
Mass/g · mole^{-1}	238.5	307.4
Crystal habitus	colourless needle	colourless prism
Size/mm^3	$(0.25 \times 0.28 \times 1.3)$	$(0.2 \times 0.4 \times 1.4)$
Diffractometer	STOE-Stadi 4	
Wavelength Mo Kα/pm	71.069	
Monochromator	Graphite (0 0 2)	
Temperature/K	296	
Absorption coefficient/m^{-1}	880	1190
Scan	$2\theta/\omega$	
$(\sin\theta/\lambda)_{max}$/ $(10^{-2}$ pm$^{-1})$	0.7035	0.5947
Number of measured reflections	4585	3121
Symmetry independent reflections	2900	2096
Reflections considered	2619	1897
Number of free parameters	137	149
$R(F)$/%	4.33	7.45
$R_w(F)$/%	3.57	6.90
Lattice constants		
a/pm	1893.8(8)	1016.6(3)
b/pm	1110.7(5)	1194.3(3)
c/pm	472.1(2)	1006.7(3)
β/°		101.79(1)
Volume of the unit cell V/(10^6 pm^3)	993.0(1.5)	1196.5(1.0)
Space group	$P2_12_12_1$-D_2^4	$P2_1/c$-C_{2h}^5
Formula units per unit cell	$Z = 4$	
ϱ_X/Mg · m^{-3}	1.595(2)	1.707(2)
ϱ_{pyk}/Mg · m^{-3}	1.59	1.67
Point positions:	all atoms in 4a:	all atoms in 4e:
	$x, y, z;\ \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z;$	$x, y, z;\ \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z;$
	$\frac{1}{2}+x, \frac{1}{2}-y, \bar{z};\ \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	$\bar{x}, \bar{y}, \bar{z};\ x, \frac{1}{2}-y, \frac{1}{2}+z$

Results

Crystal Structures of N-[2,6-dichlorophenyl]-2-chloroacetamide (DCPH2CL) and N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide (DCPCL3)

The structure determination of DCPH2CL leads to the noncentrosymmetric space group $P2_12_12_1 = D_2^4$ with 4 molecules per unit cell. The cell constants were determined to $a = 1893.8$ pm, $b = 1110.7$ pm, $c = 472.1$ pm. The structure was refined to a final R value of 4.3% ($R_w = 3.6\%$). The positions of the hydrogen atoms were determined using difference Fourier methods. The thermal parameters of these atoms were fixed. The molecules are connected by intermolecular hydrogen bonds of the type N–H ··· O–C along the crystallographic c axis (Figure 1). A projection of the crystal structure along the c axis is given in Figure 2. The positions of the atoms and their equivalent isotropic thermal parameters are listed in Table 2. The phenyl ring as well as the amide group have a nearly planar geometry. The best planes of the phenyl ring and the amide group are shown in fractional coordinates in Table 3a, b. Some dihedral angles for the amide group have been calculated and are listed in Table 4.

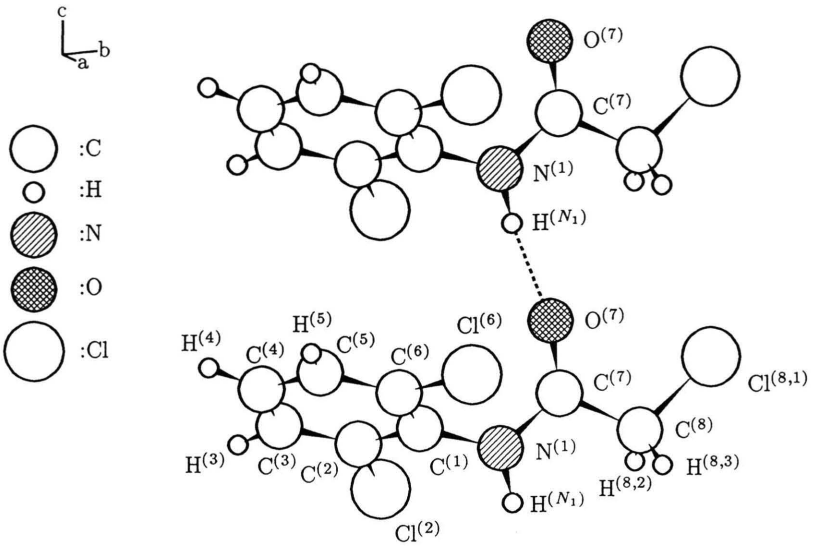

Fig. 1. Intermolecular hydrogen bond in N-[2,6-dichlorophenyl]-2-chloroacetamide. Only one "chain" within the unit cell along the *c* axis is shown.

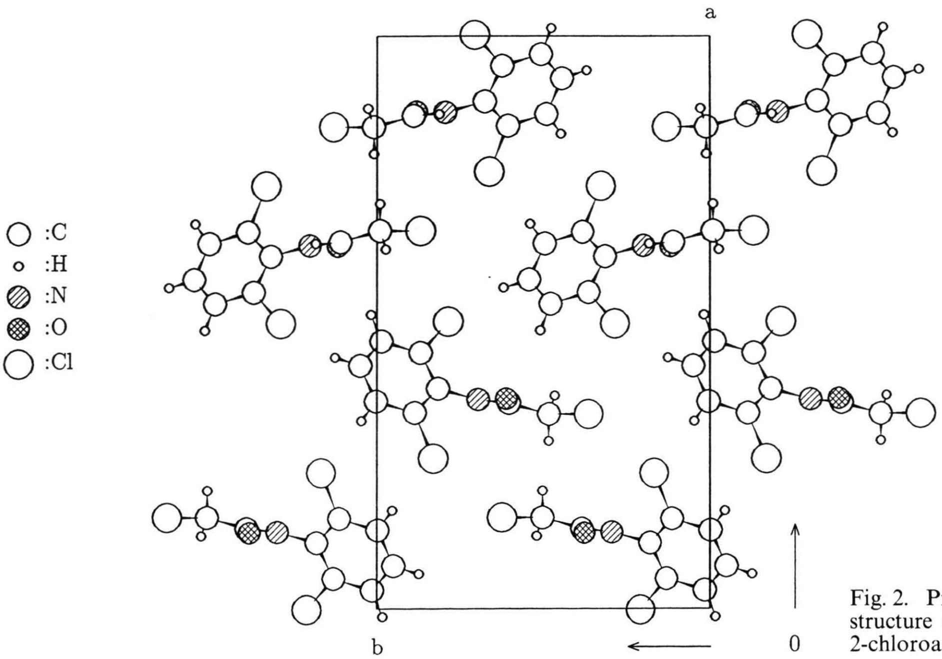

Fig. 2. Projection of the crystal structure of N-[2,6-dichlorophenyl]-2-chloroacetamide along the *c* axis.

The crystal structure of the DCPCL3 was determined and leads to the following cell parameters: $a = 1016.6$ pm, $b = 1194.3$ pm, $c = 1006.7$ pm, $\beta = 101.79°$ (monoclinic). The space group is $P2_1/c = C^5_{2h}$ (centrosymmetric) with 4 molecules per unit cell. The structure was refined to a final R value of 7.6% ($R_w = 6.9$%). Like in the structure of the first compound the different molecules are connected by intermolecular hydrogen bonds (N–H ··· O–C type) along the crystallographic *c* axis (Figure 3). The hydrogen positions were calculated from difference Fourier synthesis. The refined atomic positions with equivalent isotropic thermal parameters are summed up in Table 5. The phenyl ring and the amide group show nearly planar conformation. The calculated best planes and the distances to these planes are referred in Table 6 a, b. The dihedral angles for the amide group are given (Table 4).

Table 2. Atomic positions and equivalent isotropic thermal parameters for N-[2,6-dichlorophenyl]-2-chloroacetamide.

$$B_{equ} = \frac{4}{3} \cdot \{\beta_{11}\, a^2 + \ldots + 2\beta_{12}\, ab \cos\gamma + \ldots\}$$

Atom	x/a	y/b	z/c	B_{equ}/ (10^4 pm^2)
$Cl^{(8,1)}$	0.1597(1)	0.6299(1)	0.2538(2)	5.48(8)
$Cl^{(2)}$	−0.0016(1)	0.2107(1)	−0.2559(2)	4.83(8)
$Cl^{(6)}$	0.2376(1)	0.1676(1)	0.3602(2)	5.65(8)
$C^{(1)}$	0.1152(1)	0.1809(2)	0.0657(5)	3.03(11)
$C^{(2)}$	0.0528(1)	0.1298(2)	−0.0309(5)	3.37(12)
$C^{(3)}$	0.0324(1)	0.0142(2)	0.0449(7)	4.50(13)
$C^{(4)}$	0.0748(2)	−0.0494(2)	0.2262(9)	5.60(14)
$C^{(5)}$	0.1373(2)	−0.0025(2)	0.3265(7)	5.21(14)
$C^{(6)}$	0.1575(1)	0.1125(2)	0.2430(6)	3.88(12)
$C^{(7)}$	0.1404(1)	0.3909(2)	0.1620(5)	2.94(11)
$C^{(8)}$	0.1599(1)	0.5094(2)	0.0185(6)	4.28(12)
$N^{(1)}$	0.1343(1)	0.2988(2)	−0.0185(4)	3.18(10)
$O^{(7)}$	0.1325(1)	0.3828(2)	0.4171(3)	3.97(10)
$H^{(3)}$	−0.0135(11)	−0.0168(20)	−0.0524(58)	4.74 (*)
$H^{(4)}$	0.0608(11)	−0.1251(19)	0.3098(61)	4.74 (*)
$H^{(5)}$	0.1716(10)	−0.0457(20)	0.4328(65)	4.74 (*)
$H^{(8,2)}$	0.1272(10)	0.5269(22)	−0.1224(60)	4.74 (*)
$H^{(8,3)}$	0.2064(10)	0.5093(20)	−0.0677(58)	4.74 (*)
$H^{(N_1)}$	0.1373(11)	0.3160(22)	−0.2153(59)	4.74 (*)

(*) Thermal parameters of hydrogen were fixed (B_{iso}).

Table 3 a. Best plane for the phenyl group of N-[2,6-dichlorophenyl]-2-chloroacetamide.

Atom	d/pm	Atom	d/pm
$Cl^{(8,1)}$	−223.5	$Cl^{(2)}$	−0.2 *
$Cl^{(6)}$	3.7 *	$C^{(1)}$	−2.3 *
$C^{(2)}$	−0.8 *	$C^{(3)}$	1.7 *
$C^{(4)}$	−0.7 *	$C^{(5)}$	−1.8 *
$C^{(6)}$	−1.3 *	$C^{(7)}$	−104.9
$C^{(8)}$	−84.2	$N^{(1)}$	−3.8 *
$O^{(7)}$	−203.9	$H^{(8,2)}$	−68.4
$H^{(8,3)}$	−10.0	$H^{(3)}$	9.9 *
$H^{(4)}$	−12.4 *	$H^{(5)}$	7.8 *
$H^{(N_1)}$	65.1		

Equation for the best plane in triclinic fractional coordinates:

$$d = 9.0199\,x - 4.2556\,y - 3.7363\,z - 0.0468\,.$$

d: distance to plane in [Å], * atoms used for the calculation of the plane.

Table 3 b. Best plane for the amide group of N-[2,6-dichlorophenyl]-2-chloroacetamide.

Atom	d/pm	Atom	d/pm
$Cl^{(8,1)}$	18.4	$Cl^{(2)}$	235.3
$Cl^{(6)}$	−241.4	$C^{(1)}$	−0.5 *
$C^{(2)}$	106.1	$C^{(3)}$	112.5
$C^{(4)}$	11.4	$C^{(5)}$	−96.6
$C^{(6)}$	−102.4	$C^{(7)}$	0.1 *
$C^{(8)}$	−1.2 *	$N^{(1)}$	−3.5 *
$O^{(7)}$	1.8 *	$H^{(8,2)}$	69.2
$H^{(8,3)}$	−83.2	$H^{(3)}$	193.5
$H^{(4)}$	15.3	$H^{(5)}$	−174.6
$H^{(N_1)}$	3.5 *		

Equation for the best plane in triclinic fractional coordinates:

$$d = -18.4047\,x + 2.4214\,y - 0.4222\,z + 1.7054\,.$$

d: distance to plane in [Å], * atoms used for the calculation of the plane.

Table 4. Dihedral angles in N-[2,6-dichlorophenyl]-2-chloroacetamide, DCPH2CL and N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide, DCPCL3.

Atom 1–2–3–4	DCPCL3 angle/°	DCPH2CL angle/°
$H^{(N_1)}$–$N^{(1)}$–$C^{(7)}$–$O^{(7)}$	168.6	174.5
$H^{(N_1)}$–$N^{(1)}$–$C^{(1)}$–$C^{(2)}$	−66.0	−55.7
$H^{(N_1)}$–$N^{(1)}$–$C^{(1)}$–$C^{(6)}$	113.5	123.7
$C^{(1)}$–$N^{(1)}$–$H^{(N_1)}$–$C^{(7)}$	170.6	172.4
$N^{(1)}$–$C^{(7)}$–$O^{(7)}$–$C^{(8)}$	179.4	178.8

^{35}Cl NQR

The temperature variation of the ^{35}Cl NQR lines for DCPH2CL is shown in Figure 4. The substance shows three ^{35}Cl resonances. The different temperature variation of the side chain chlorine atom (ν_3) can easily be seen. The line ν_3 bleaches out at a temperature (T_b) of 362 K ($T_m = 449$ K) whereas the resonances of the aromatic atoms can be detected up to the melting point of the substance. The ^{35}Cl NQR frequencies were fitted using a polynomial corresponding to the Bayer theory. The coefficients are listed in Table 7.

The second compound investigated is DCPHCL2. Four ^{35}Cl NQR frequencies were observed at room temperature for the material which was melted into the ampoule. After two days a new measurement shows new relative broad lines at different frequencies. Temperature dependent ^{35}Cl NQR studies of the instable high temperature phase were made (Figure 5). The resulting points were fitted with the same polynomial as for the first compound (Table 7). The experiments show a discontinuity of the four frequencies at 281.7 K. The discontinuity is accompanied with a small hysteresis (≈3 K). The two higher frequencies ν_3 and ν_4 were assigned to the dichloromethyl group. Comparable frequencies of dichloroacetamide at 77 K are reported in the literature [11]. At a temperature above the phase transition the two lower frequencies corresponding to the dichloroacetyl group are relatively broad. No temperature dependent measurements were made for these lines. The mean temperature coefficients of the frequencies below the phase

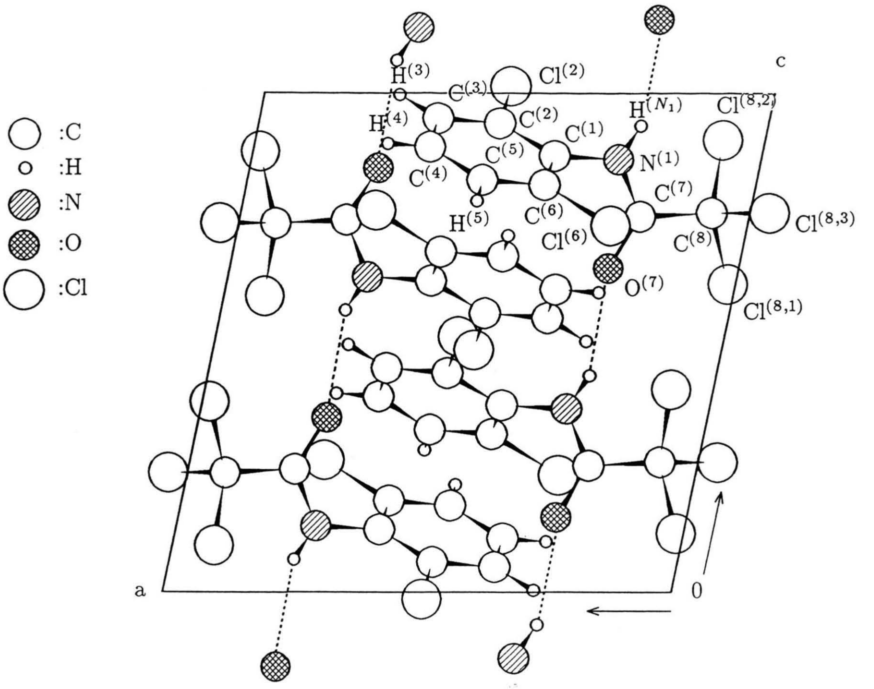

Fig. 3. Projection of the crystal structure of N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide along the *b* axis. The hydrogen bonds are marked by dashed lines.

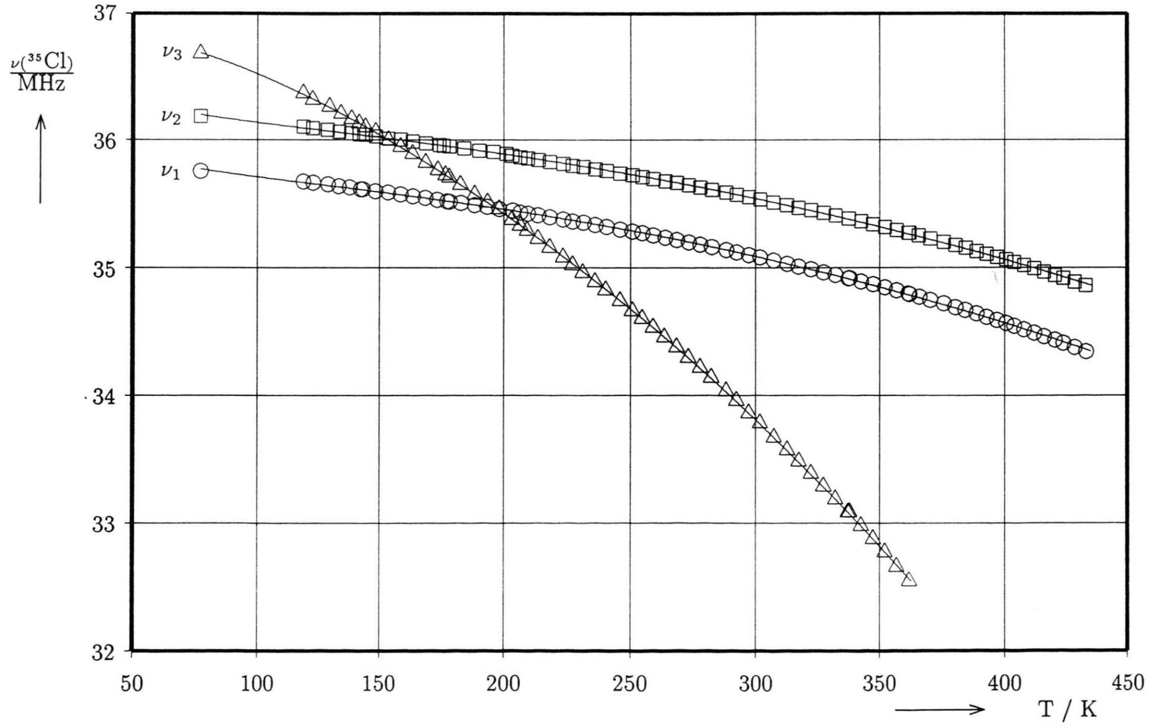

Fig. 4. Temperature dependence of the ^{35}Cl NQR frequencies of N-[2,6-dichlorophenyl]-2-chloroacetamide.

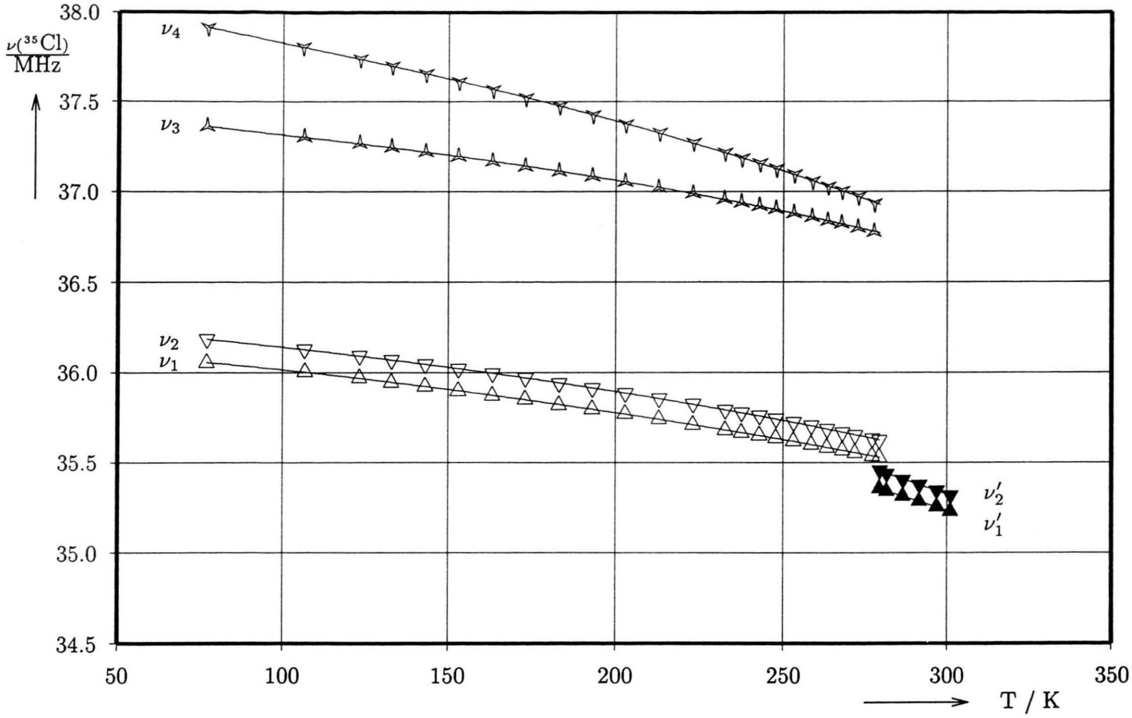

Fig. 5. Temperature dependence of the ^{35}Cl NQR frequencies of N-[2,6-dichlorophenyl]-2,2-dichloroacetamide (high temperature phases).

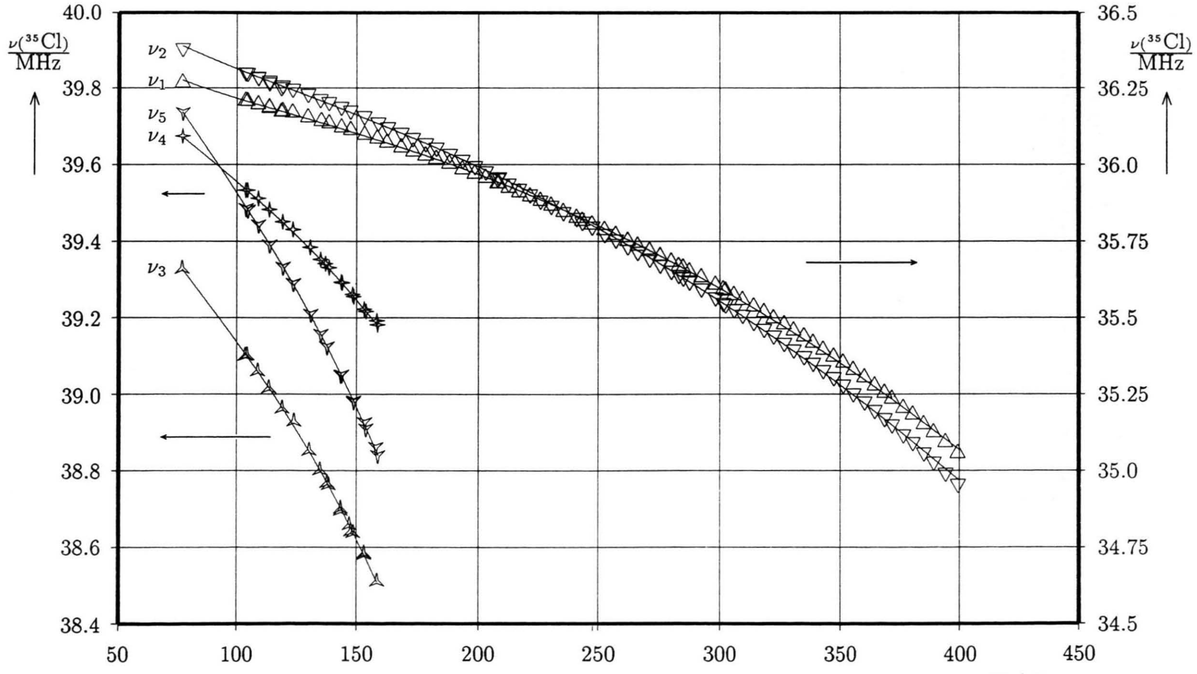

Fig. 6. Temperature dependence of the ^{35}Cl NQR frequencies of N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide.

Table 5. Atomic positions and equivalent isotropic thermal parameters for N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide.

$$B_{\text{equ}} = \tfrac{4}{3} \cdot \{\beta_{11}\, a^2 + \ldots + 2\beta_{12}\, ab \cos\gamma + \ldots\}$$

Atom	x/a	y/b	z/c	$B_{\text{equ}}/(10^4\ \text{pm}^2)$
$Cl^{(8,1)}$	0.0150(1)	0.4054(1)	0.1181(2)	5.10(9)
$Cl^{(8,2)}$	0.0828(2)	0.4029(2)	0.4068(2)	10.59(13)
$Cl^{(8,3)}$	−0.0376(2)	0.2118(2)	0.2608(3)	8.90(12)
$Cl^{(2)}$	0.5178(2)	0.3516(1)	0.5137(2)	5.59(8)
$Cl^{(6)}$	0.2688(1)	0.0002(1)	0.2347(2)	4.98(9)
$C^{(1)}$	0.4062(4)	0.1710(4)	0.3745(5)	3.07(19)
$C^{(2)}$	0.5239(5)	0.2222(4)	0.4400(5)	3.64(23)
$C^{(3)}$	0.6457(5)	0.1692(6)	0.4500(6)	3.48(30)
$C^{(4)}$	0.6498(6)	0.0652(6)	0.3926(7)	5.11(29)
$C^{(5)}$	0.5354(6)	0.0123(5)	0.3262(6)	4.31(25)
$C^{(6)}$	0.4134(5)	0.0659(5)	0.3167(5)	3.40(17)
$C^{(7)}$	0.2143(4)	0.2734(4)	0.2535(5)	2.15(16)
$C^{(8)}$	0.0752(5)	0.3231(5)	0.2613(5)	2.87(22)
$N^{(1)}$	0.2794(4)	0.2247(4)	0.3673(4)	3.26(16)
$O^{(7)}$	0.2564(3)	0.2794(3)	0.1496(3)	3.80(17)
$H^{(3)}$	0.7307(44)	0.2108(41)	0.4968(51)	4.74 (*)
$H^{(4)}$	0.7346(47)	0.0233(42)	0.3992(52)	4.74 (*)
$H^{(5)}$	0.5371(46)	−0.0686(43)	0.2847(53)	4.74 (*)
$H^{(N_1)}$	0.2492(47)	0.2358(49)	0.4344(55)	4.74 (*)

(*) Thermal parameters of the hydrogen atoms were fixed (B_{iso}).

transition are ν_1: −2.6 kHz/K, ν_2: −2.75 kHz/K, ν_3: −2.91 kHz/K, and ν_4: −4.86 kHz/K. These values are small in comparison with the values obtained for the other two title compounds. Above a temperature of 302 K the measurement of the high temperature phase is getting difficult, because of the transition of the compound to the stable low temperature phase. The lines become very broad.

The phase stable at room temperature shows two groups of lines. The frequencies were determined at 77 K to 35.96–36.22 MHz (aromatic chlorine) and 37.39–37.91 MHz (dichloromethyl group). At room temperature the signals were found at 35.43–35.67 MHz and 36.66–36.80 MHz. It was not possible to separate the relative broad lines using the superregenerative oscillator. Sideband suppression cannot be applied because of the low intensities of the lines.

Several trials to determine the crystal structure of the compound were made but did not lead to suitable results. The problems might be caused by the phase transitions of the material. The grown crystals seem to be twinned or bunched.

Table 6a. Best plane for the phenyl group N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide.

Atom	d/pm	Atom	d/pm
$Cl^{(8,1)}$	−239.6	$Cl^{(8,2)}$	−3.8
$Cl^{(8,3)}$	−2.9	$Cl^{(2)}$	−2.0 *
$Cl^{(6)}$	1.3 *	$C^{(1)}$	0.6 *
$C^{(2)}$	0.9 *	$C^{(3)}$	−0.1 *
$C^{(4)}$	0.3 *	$C^{(5)}$	0.9 *
$C^{(6)}$	1.7 *	$C^{(7)}$	107.1
$C^{(8)}$	85.4	$N^{(1)}$	−2.0 *
$O^{(7)}$	216.4	$H^{(3)}$	3.0 *
$H^{(4)}$	−2.6 *	$H^{(5)}$	−2.1 *
$H^{(N_1)}$	−65.8		

Equation for the best plane in triclinic fractional coordinates:

$$d = 2.8653\,x + 5.0708\,y - 9.0587\,z + 1.3674\,.$$

d: distance to plane [Å], * atoms used for the calculation of the plane.

Table 6b. Best plane for the amide group N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide.

Atom	d/pm	Atom	d/pm
$Cl^{(8,1)}$	−29.5	$Cl^{(8,2)}$	−107.7
$Cl^{(8,3)}$	167.9	$Cl^{(2)}$	−255.0
$Cl^{(6)}$	265.2	$C^{(1)}$	4.8 *
$C^{(2)}$	−109.5	$C^{(3)}$	−106.9
$C^{(4)}$	10.1	$C^{(5)}$	124.9
$C^{(6)}$	121.7	$C^{(7)}$	0.2 *
$C^{(8)}$	5.0 *	$N^{(1)}$	3.0 *
$O^{(7)}$	−4.7 *	$H^{(3)}$	−194.1
$H^{(4)}$	17.2	$H^{(5)}$	215.9
$H^{(N_1)}$	−8.2 *		

Equation for the best plane in triclinic fractional coordinates:

$$d = -4.1648\,x - 10.4054\,y - 1.8213\,z + 4.2007\,.$$

d: distance to plane in [Å], * atoms used for the calculation of the plane.

The third compound which was investigated is DCPCL3. The ^{35}Cl NQR spectrum of this compound is a quintet, which can be separated into lines belonging to the side chain and to the aromatic atoms, respectively, on the basis of the frequencies and the temperature coefficient of the lines (Figure 6). The lines of the CCl_3 group (ν_{3-5}) show a strong temperature variation of −6.8 to −10.2 kHz/K (averaged over the whole observable temperature range). They bleach out at $T_b = 159$ K. The aromatic chlorine resonances show a mean temperature coefficient of −4.1 kHz/K. The points of the temperature dependent measurements were fitted by using the same polynomial as used for the other two compounds (Table 7). One of the trichloromethyl resonances has a smaller slope than the other two lines. The resonances of the aromatic chlorine atoms show no discontinuities or anomalies. They can be observed up to the melting point of the substance.

The frequencies for all three compounds at 77 K and at room temperature (295 K) are listed in Table 8.

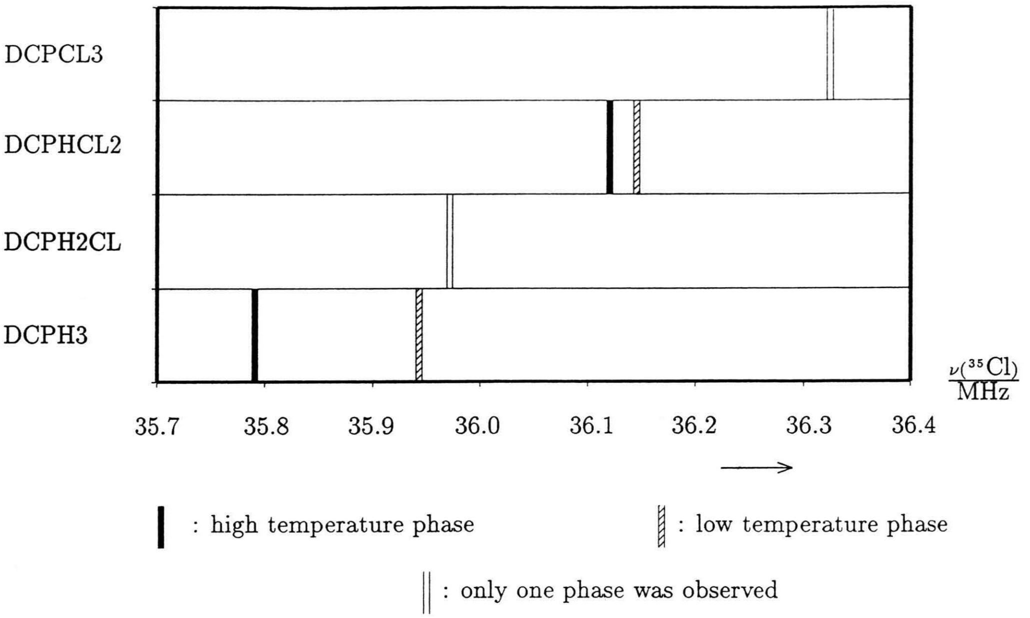

Fig. 7. Variation of the mean aromatic ^{35}Cl NQR frequencies at $T = 77$ K as function of the substitution of the acetyl group with chlorine atoms. DCPH3 = N-[2,6-dichlorophenyl]-acetamide, DCPH2CL = N-[2,6-dichlorophenyl]-2-chloroacetamide, DCPHCL2 = N-[2,6-dichlorophenyl]-2,2-dichloroacetamide, DCPCL3 = N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide.

Table 7. Power series expansion of $\nu(^{35}\mathrm{Cl}) = f(T)$ for N-[2,6-dichlorophenyl]-2-chloroacetamide, DCPH2CL, N-[2,6-dichlorophenyl]-2,2-dichloroacetamide, DCPHCL2, and N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide, DCPCL3.

$f(T) = \sum_{i=-1}^{2} a_i \cdot T^i$, n = number of measurements, $\sigma = \sqrt{\frac{(\nu_{\mathrm{exp}} - \nu_{\mathrm{obs}})^2}{n-4}}$, ΔT = temperature range for which the parameters are valid.

Compound	a_{-1} / MHz · K	a_0 / MHz	a_1 / 10^{-3} MHz · K^{-1}	a_2 / 10^{-6} MHz · K^{-2}	σ / MHz	n	ΔT / K
DCPH2CL							
ν_1	14.9462	35.5738	0.7065	−8.2878	0.006	74	77 ... 433
ν_2	13.2362	36.0430	0.3405	−7.1800	0.006	74	77 ... 433
ν_3 *	−11.2226	37.3086	−4.3762	−23.8778	0.006	56	77 ... 362
DCPHCL2 (high temperature phase I)							
ν_1	−0.3732	36.1763	−1.1826	−4.0365	0.001	19	77 ... 278
ν_2	3.1192	36.2235	−0.5912	−5.6693	0.001	19	77 ... 278
ν_3 *	8.5642	37.2728	0.3647	−8.0836	0.002	19	77 ... 278
ν_4 *	11.5919	37.8724	−0.6050	−10.4302	0.002	19	77 ... 278
DCPHCL2 (high temperature phase II) **							
ν'_1	–	36.9500	−5.7143	–	0.001	5	278 ... 302
ν'_2	–	37.1802	−6.1855	–	0.001	5	278 ... 302
DCPCL3							
ν_1	14.1894	36.0836	0.7563	−8.4579	0.005	74	77 ... 400
ν_2	13.1590	36.2772	−0.1505	−8.0109	0.006	74	77 ... 400
ν_3 *	40.3995	38.5399	8.3111	−63.7709	0.005	19	77 ... 159
ν_4 *	19.9172	39.3583	3.1988	−32.1852	0.003	19	77 ... 159
ν_5 *	38.12332	39.0923	6.6547	−61.2365	0.004	19	77 ... 159

* Chloromethyl chlorine atom. – ** $\nu(T) = a_0 + a_1 \cdot T$, $\sigma = \sqrt{(\nu_{\mathrm{exp}} - \nu_{\mathrm{obs}})^2/(n-2)}$.

Table 8. ^{35}Cl NQR frequencies of N-[2,6-dichlorophenyl]-2-chloroacetamide, DCPH2CL, N-[2,6-dichlorophenyl]-2,2-dichloroacetamide, DCPHCL2, and N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide, DCPCL3.

Compound	$\nu(^{35}Cl)/MHz$ $T=77$ K	S/N	$\nu(^{35}Cl)/MHz$ $T=295$ K	S/N
DCPH2CL				
ν_1	35.758	>30	35.101	15
ν_2	36.186	>30	35.554	15
ν_3 *	36.679	>30	33.859	10
DCPHCL2 (high temperature phase I)				
ν_1	36.056	>30	–	–
ν_2	36.184	>30	–	–
ν_3 *	37.362	>30	–	–
ν_4 *	37.913	>30	–	–
DCPHCL2 (high temperature phase II)				
ν'_1	–	–	35.242	10
ν'_2	–	–	35.332	10
DCPHCL2 (low temperature phase III)				
ν' **	35.96 – 36.22	20	35.43 – 35.67	10
ν'' **	37.39 – 37.91	20	36.66 – 36.80	10
DCPCL3				
ν_1	36.267	>30	35.609	10
ν_2	36.381	>30	35.567	10
ν_3 *	39.327	>30	–	–
ν_4 *	39.673	>30	–	–
ν_5 *	39.737	>30	–	–

* Chloromethyl chlorine atom. – ** Groups of lines.

Table 9. Intramolecular distances in N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide, DCPCL3, N-[2,6-dichlorophenyl]-2-chloroacetamide, DCPH2CL, and N-[2,6-dichlorophenyl]-acetamide (high temperature phase I, DCPH3 I, low temperature phase II, DCPH3 II).

Atom 1	Atom 2	DCPCL 3 d/pm	DCPH3 II d/pm	DCPH2CL d/pm	DCPH3 I d/pm
$C^{(1)}$	$C^{(2)}$	138.5(6)	138.8(4)	138.9(3)	138.9(5)
$C^{(1)}$	$C^{(6)}$	139.2(7)	138.9(4)	138.6(3)	137.5(6)
$C^{(1)}$	$N^{(1)}$	142.9(5)	141.4(3)	141.6(3)	141.9(4)
$C^{(2)}$	$C^{(3)}$	137.6(7)	138.4(4)	138.7(3)	137.7(6)
$C^{(2)}$	$Cl^{(2)}$	172.2(5)	173.2(3)	173.2(2)	173.0(4)
$C^{(3)}$	$C^{(4)}$	137.4(8)	136.7(5)	137.0(4)	136.9(8)
$C^{(3)}$	$H^{(3)}$	102.4(45)	–	104.1(22)	–
$C^{(4)}$	$C^{(5)}$	137.2(8)	137.5(5)	137.8(4)	137.0(8)
$C^{(4)}$	$H^{(4)}$	98.7(47)	–	96.6(22)	–
$C^{(5)}$	$C^{(6)}$	138.1(7)	137.8(4)	139.0(3)	138.3(6)
$C^{(5)}$	$H^{(5)}$	105.4(50)	–	95.1(23)	–
$C^{(6)}$	$Cl^{(6)}$	172.1(5)	172.8(3)	172.5(2)	173.5(4)
$C^{(7)}$	$N^{(1)}$	133.6(6)	134.6(3)	133.6(3)	134.4(5)
$C^{(7)}$	$O^{(7)}$	121.0(5)	122.8(3)	121.7(3)	121.0(5)
$C^{(7)}$	$C^{(8)}$	155.0(6)	149.8(3)	152.5(4)	151.1(5)
$C^{(8)}$	$Cl^{(8,1)}$	174.9(5)	–	173.9(3)	–
$C^{(8)}$	$Cl^{(8,2)}$	173.6(6)	–	–	–
$C^{(8)}$	$Cl^{(8,3)}$	175.4(6)	–	–	–
$C^{(8)}$	$H^{(8,2)}$	–	–	93.0(24)	–
$C^{(8)}$	$H^{(8,3)}$	–	–	96.9(21)	–
$N^{(1)}$	$H^{(N_1)}$	80.5(51)	–	95.0(27)	–
$O^{(7)}$	$H^{(N_1)}$	216.1(50)	186	189.0(27)	191

$O^{(7)}-H^{(N_1)}$: intermolecular hydrogen bond.

Discussion

X-Ray Structures

The geometry of DCPH2CL and DCPCL3 can be compared with N-[2,6-dichlorophenyl]-acetamide (DCPH3) [12]. The chloroacetyl compound shows cell parameters similar to those of the high temperature phase (I) of the acetyl compound. Both compounds crystallize in the space group $P2_12_12_1$ with $Z=4$. The volumes of the unit cells differ little: $957.3 \cdot 10^6$ pm^3 (acetyl compound) and $993.0 \cdot 10^6$ pm^3 (chloroacetyl compound). The c axes of both compounds are nearly identical: 474.9 pm (acetyl), 472.1 pm (chloroacetyl). The lengths of these axes are caused by the intermolecular hydrogen bonds forming chains of molecules along ***c***. The arrangement of the molecules within the unit cells is comparable, too. The different a and b axes of DCPH2CL, 1893.8 pm and 1110.7 pm, respectively, compared with DCPH3 (high temperature phase I), 1726.8 pm and 1167.4 pm, respectively, can be explained by repulsive interactions between the chlorine atoms of the phenyl group and the chloromethyl chlorine atom. The bond lengths and bond angles of both compounds are referred in Table 9 and 10. All bond lengths are equivalent within the sum of the e.s.d.'s (Table 9). The difference of the endocyclic angles are smaller than the sum of the e.s.d.'s (Table 10). The angles observed for the side chain differ. This can be explained with the substitution of this group. The chlorine atom $Cl^{(8,1)}$ leads to a distortion of the amide function.

The bond lengths and bond angles found in DCPCL3 are comparable to the values found for the chloroacetyl and acetyl compound (Table 9, 10). The arrangement of the molecules within the unit cells of DCPCL3 and the low temperature phase of DCPH3 is similar. The different cell parameters result from the different volumes of the acetyl and trichloroacetyl group. Both structures contain zig-zag chains of molecules formed by the intermolecular hydrogen bond along the crystallographic c axis. The higher molecular volume of DCPCL3, in relation to DCPH3 (II) and the resulting repulsive interactions change the monoclinic angle (β).

Table 10. Angles in N-[2,6-dichlorophenyl]-2,2,2-trichloroacetamide, DCPCL3, N-[2,6-dichlorophenyl]-2-chloroacetamide, DCPH2CL1, and N-[2,6-dichlorophenyl]-acetamide (high temperature phase I, DCPH3 I, low temperature phase II, DCPH3 II).

Atom 1–2–3	DCPCL3 angle/°	DCPH3 II angle/°	DCPH2CL angle/°	DCPH3 I angle/°
$C^{(1)}-C^{(2)}-C^{(3)}$	120.6(5)	121.7(3)	122.1(2)	121.3(5)
$C^{(2)}-C^{(3)}-C^{(4)}$	119.3(5)	119.2(4)	118.4(3)	119.4(5)
$C^{(3)}-C^{(4)}-C^{(5)}$	121.7(5)	121.1(4)	121.6(3)	120.9(6)
$C^{(4)}-C^{(5)}-C^{(6)}$	118.7(7)	119.0(3)	119.1(3)	118.9(5)
$C^{(5)}-C^{(6)}-C^{(1)}$	120.8(5)	121.9(3)	121.1(2)	121.7(5)
$C^{(6)}-C^{(1)}-C^{(2)}$	118.8(4)	117.2(3)	117.8(2)	117.6(5)
$Cl^{(2)}-C^{(2)}-C^{(1)}$	119.8(4)	118.9(2)	119.7(2)	118.8(3)
$Cl^{(2)}-C^{(2)}-C^{(3)}$	119.5(4)	119.4(3)	118.2(2)	119.8(4)
$Cl^{(6)}-C^{(6)}-C^{(1)}$	119.9(4)	119.7(2)	120.5(2)	119.6(3)
$Cl^{(6)}-C^{(6)}-C^{(5)}$	119.2(4)	118.3(2)	118.5(2)	118.6(4)
$N^{(1)}-C^{(1)}-C^{(2)}$	120.6(3)	121.0(3)	120.3(2)	120.5(4)
$N^{(1)}-C^{(1)}-C^{(6)}$	120.6(4)	121.8(3)	121.9(2)	121.8(4)
$C^{(1)}-N^{(1)}-C^{(7)}$	121.4(4)	123.1(3)	123.4(2)	122.4(5)
$N^{(1)}-C^{(7)}-O^{(7)}$	124.6(4)	123.0(2)	124.3(3)	122.7(4)
$N^{(1)}-C^{(7)}-C^{(8)}$	114.8(4)	114.8(2)	113.5(2)	116.1(3)
$O^{(7)}-C^{(7)}-C^{(8)}$	120.6(4)	122.2(3)	122.2(3)	121.2(4)
$Cl^{(8,1)}-C^{(8)}-Cl^{(8,2)}$	109.5(3)	–	–	–
$Cl^{(8,1)}-C^{(8)}-Cl^{(8,3)}$	107.8(3)	–	–	–
$Cl^{(8,2)}-C^{(8)}-Cl^{(8,3)}$	109.5(3)	–	–	–
$Cl^{(8,1)}-C^{(8)}-H^{(8,2)}$	–	–	107.1(16)	–
$Cl^{(8,1)}-C^{(8)}-H^{(8,3)}$	–	–	105.8(15)	–
$H^{(8,2)}-C^{(8)}-H^{(8,3)}$	–	–	107.7(22)	–
$C^{(7)}-C^{(8)}-Cl^{(8,1)}$	110.0(3)	–	112.3(2)	–
$C^{(7)}-C^{(8)}-Cl^{(8,2)}$	1116.(3)	–	–	–
$C^{(7)}-C^{(8)}-Cl^{(8,3)}$	108.2(4)	–	–	–
$C^{(7)}-C^{(8)}-H^{(8,2)}$	–	–	109.7(16)	–
$C^{(7)}-C^{(8)}-H^{(8,3)}$	–	–	113.9(14)	–
$H^{(3)}-C^{(3)}-C^{(2)}$	118.2(28)	–	115.2(14)	–
$H^{(3)}-C^{(3)}-C^{(4)}$	122.5(28)	–	126.4(14)	–
$H^{(4)}-C^{(4)}-C^{(3)}$	122.0(30)	–	122.9(15)	–
$H^{(4)}-C^{(4)}-C^{(5)}$	116.2(30)	–	115.1(15)	–
$H^{(5)}-C^{(5)}-C^{(4)}$	122.3(27)	–	125.3(14)	–
$H^{(5)}-C^{(5)}-C^{(6)}$	119.0(27)	–	115.2(14)	–
$H^{(N_1)}-N^{(1)}-C^{(7)}$	116.1(38)	–	117.8(16)	–
$H^{(N_1)}-N^{(1)}-C^{(1)}$	121.8(37)	–	118.3(16)	–

The thermal parameters of the trichloromethyl chlorine atoms show some interesting details. The parameters of $Cl^{(8,2)}$ and $Cl^{(8,3)}$ are large in comparison to the aromatic chlorine atoms $Cl^{(2)}$ and $Cl^{(6)}$ (Table 5). The higher thermal motion of these chlorine atoms is caused by the reorientation of the CCl_3 group at room temperature. The behaviour of the chlorine atom $Cl^{(8,1)}$ differs from that of $Cl^{(8,2)}$ and $Cl^{(8,3)}$. The temperature factor of $Cl^{(8,1)}$ is comparable to the values of the aromatic chlorine atoms. This result is in agreement with the different slopes of the temperature variation in the NQR experiments. On this basis the NQR line with the smallest slope (ν_4, Fig. 6) can be assigned to $Cl^{(8,1)}$.

The dihedral angle $O^{(7)}-C^{(7)}-C^{(8)}-Cl^{(8,1)}$ has been calculated to $-11.2°$. A comparable value of the angle was found for the DCPH2CL ($O^{(7)}-C^{(7)}-C^{(8)}-Cl^{(8,1)}$: $-6.4°$). The orientation of the CCl_3 group – relative to the carbonyl group – might be the reason of the different behaviour of the $Cl^{(8,1)}$ NQR frequency.

The geometry of the phenyl ring of the trichloro-, chloro-, and acetyl compound shows some common aspects (Table 9, 10). The angles $C^{(5)}-C^{(6)}-C^{(1)}$, $C^{(1)}-C^{(2)}-C^{(3)}$, and $C^{(3)}-C^{(4)}-C^{(5)}$ are larger than the ideal value of 120°. The angles $C^{(6)}-C^{(1)}-C^{(2)}$, $C^{(2)}-C^{(3)}-C^{(4)}$, and $C^{(4)}-C^{(5)}-C^{(6)}$ show smaller values than 120° (Table 10). The distortion of the angle $C^{(6)}-C^{(1)}-C^{(2)}$ can be explained by the repulsive interaction between the chlorine atoms $Cl^{(2)}$, $Cl^{(6)}$ and the nitrogen atom $N^{(1)}$. The geometries of the amide groups of DCPH2CL and DCPCL3 are comparable. The values within this group are quite similar. Different values of the angle $C^{(7)}-C^{(8)}-Cl^{(8,1(2,3))}$ were found. The differences are due to the substitution of the chloromethyl group. For the compound containing the monochloromethyl group, an angle of 112.3° was found compared to 109.9° (averaged) for the trichloromethyl compound. The angles $H^{(N_1)}-N^{(1)}-C^{(1)}-C^{(2)}$ vary between $-55.7°$ for the chloroacetyl and $-66.0°$ for the trichloroacetyl compound. The distances $C^{(8)}-C^{(4)}$ for the trichloro-, chloro-, and acetyl show small differences (648.7 pm (chloroacetyl), 649.6 pm (trichloroacetyl), 648.9 pm (acetyl low temp. phase), 648.5 pm (acetyl high temp. phase)). Nearly equivalent values of the $Cl^{(2)}-Cl^{(6)}$ distances were found in all compounds.

The relatively high R value of 7.5% for the refinement can be understood by the strong thermal motion of the CCl_3 group. Resting intensities were found in the difference fourier synthesis near the positions of the atom $Cl^{(8,2)}$ and $Cl^{(8,3)}$. Most probably these electron densities are caused by anharmonic thermal motions of the chlorine atoms of the CCl_3 group. It was not possible to describe the rest densities by introducing additional atomic positions with a free occupancy factor.

^{35}Cl NQR and Differential Thermal Analysis

The ^{35}Cl NQR lines of DCPH2CL show different temperature variations. The frequency with a temperature coefficient of -14.5 kHz/K was assigned to the CH_2Cl chlorine atom. This assignment is in agreement with the higher frequency of this line at 77 K.

The variation of the aromatic chlorine frequencies is -3.9 kHz/K, which is within the range normally observed for aromatic chlorine atoms. The frequencies at 77 K are similar to the values measured for the DCPH3 (acetyl compound: $35.866 \leq \nu/\mathrm{MHz} \leq 36.019$, $T = 77$ K [12].

The appearance of a new ^{35}Cl NQR spectrum for DCPHCL2 after a period of some days is due to a phase transition. Pies et al. [1] did not observe any ^{35}Cl NQR signals, probably due to the phase transition and the relative broad lines for the stable room temperature phase. A further reason might be the fact that the authors used oscilloscope observation of the ^{35}Cl NQR spectra. The two higher frequencies of the spectrum (ν_3, ν_4, Fig. 5) can be assigned to the $CHCl_2$ chlorine atoms by comparison with the frequencies of dichloroacetamide (ν_1: 37.750 MHz, ν_2: 37.238 MHz, $T = 77$ K) [11]). The lines show a very strong decrease of their frequencies of 1.9 MHz during the phase transition between the two high temperature phases. The aromatic chlorine atoms show smaller changes (≈ 0.1 MHz). The phase transition should be coupled with a strong change in the thermal motion of the dichloromethyl group. The changes of the side chain frequencies cannot be explained by using only the crystal field effect, which is the magnitude of about ± 500 kHz for this kind of compounds [1].

The existence of a phase transition was verified by differential thermal analysis (DTA). A sample of the substance was sealed into a glass ampoule and melted. After cooling down to room temperature within some minutes, the sample was examined. During the heating up of the substance an exothermic signal was detected at about 373 K. Enthalpy and transition temperature vary with the history of the sample. The variation of the transition is probably caused by partly decomposition of the compound. Transition points between 359 K and 380 K were observed. The transition enthalpies vary between -2.6 kJ/mole and -4.6 kJ/mole. While slowly cooling the sample from the melt down to room temperature, no phase transition was detected by DTA. The instable high temperature phase is obtained only by cooling the sample relatively fast to room temperature.

The trichloroacetyl compound DCPCL3 shows a bleaching out for three of the five resonances. These resonances (ν_{3-5}, Fig. 6) are assigned to the CCl_3 group. The bleaching out of the lines is due to a reorientation of the CCl_3 group around the pseudo threefold axis $C^{(7)}-C^{(8)}$.

By comparing DCPH2CL and DCPCL3 the temperature of the bleaching out seems to correlated with the mass distribution within the chloromethyl groups. The bleaching out is observed at lower temperatures for a more symmetric mass distribution of the side chain.

From the increase of the mean ^{35}Cl NQR frequencies of the ring chlorine atoms with increasing x ($0 \leq x \leq 3$) one can extract $\varkappa$ values for the chlorosubstituted acetyl groups. The increase of $\varkappa$ (ortho) with increasing x is in agreement with Hammett theory of NQR frequency shift [13] (Figure 7).

The mean aromatic ^{35}Cl NQR frequencies of the high and low temperature phases of DCPH3 on the one and DCPHCL2 on the other hand show another interesting result. The mean frequencies of the low temperature phases are higher than those of the corresponding high temperature phases. The fact can be explained by taking into account the higher thermal motion of the molecules in the high temperature phases, leading to lower frequencies for the high temperature phases.

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