^{35}Cl NQR Spectra of Substituted N-(Phenyl)-2,2,2-Trichloroacetamides

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Several substituted acetamides, $X_yC_6H_{5-y}NHCOCCl_3$ (X=CH_3, NO_2, or Br and y=1 or 2) have been synthesized and studied by NQR. The effect of ring substitution on the average $\nu(^{35}Cl)$ NQR of the trichloroacetyl group is not substantial, but it affects the crystal structure of the substituted compounds. The NQR spectra of $X_yC_6H_{5-y}NHCOCCl_3$ (where X_y=4−CH_3, 4−NO_2, and 2,3−$(CH_3)_2$) show six ^{35}Cl NQR frequencies, each indicating the presence of two molecules in their respective asymmetric units. The temperature dependence of $\nu(^{35}Cl)$ NQR of N-(4-methylphenyl)-2,2,2-trichloroacetamide reveals that it undergoes a first order phase transition around 205 K. Its spectrum shows six lines up to 205 K and three lines thereafter. The latter triplet part of the spectrum fades out around 250 K due to librational motions in the crystal lattice, as the torsional motions of the CCl_3 group are easily excited. The ^{35}Cl NQR spectra of all the methylsubstituted amides have been compared with those of the corresponding chlorosubstituted compounds. Generally there is no systematic variation of the mean values of $\nu(^{35}Cl)$ NQR or the trichloroacetyl group with the substituents in the phenyl ring. The ω C-Cl frequencies of the trichloroacetyl group of all the ν-substituted N-(phenyl)-2,2,2-trichloroacetamides have been estimated using NQR substituent parameters (k) and the frequencies of N-(phenyl)-2,2,2-trichloroacetamide. Agreement between these values and the experimental frequencies is quite good. The $\nu(^{35}Cl)$ NQR of these amides has also been correlated with Σk_i of the substituents. Further $\nu(^{35}Cl)$ NQR spectra of mono- and trichloroacetamides have been correlated.

Amides are one of the well known classes of organic compounds in which the hydroxy groups of carboxylic acids are replaced by amino groups. They are represented by the general structure $R^1CO\text{-}NX\text{-}R^2$, where X=H, OH, NR^3_2, COR^3, R^3 and R^1, R^2, R^3=H, alkyl or aryl group. Amides are of fundamental chemical interest as conjugation between nitrogen lone pair electrons and the carbonyl π-bond results in distinct physical and chemical properties [1, 2]. The amide moiety is an important constituent of many biologically significant compounds. Thus an understanding of the formation, properties and reactions of amides is central to future development in such areas as polypeptide and protein chemistry. Many imides, hydroxamic acids and hydrazides exhibit pharmacological activity, which has further stimulated recent interest in their chemistry. Many acetanilides exhibit fungicidal, herbicidal and pharmacological activities [3–8].

NQR studies provide information on the nature of the chemical bonding in molecules and crystals [9–13]. Work on the NQR of amides needs to be done at varied conditions before one can rationalize characteristics such as correlations of frequencies with chemical bond parameters. Pies et al. [14] have studied the ^{35}Cl NQR spectra of a number of N-(chlorophenyl)-2,2,2-trichloroacetamides. But there are no reports on the effects of electron donating or repelling group substitution in the phenyl ring, as chlorine is electron withdrawing. We report here the ^{35}Cl NQR spectra of other substituted phenyl trichloroacetamides and correlate them with the corresponding chlorosubstituted compounds.

Materials and Methods

The title compounds were prepared from aniline, trichloroacetic acid and phosphoryl chloride [15] (Aldrich, Germany). The commercial anilines were purified by either double distillation or zone refining. The respective anilines were treated with a clear mixture of thrichloroacetic acid and phosphoryl chloride under constant stirring. The mixture was slowly warmed to expel HCl. Excess phosphoryl chloride was hydrolysed by adding cold water drop wise under ice cold conditions. The solid was filtered under suction, washed thoroughly with water and dried. The products were recrystallised from ethanol several times. The purity of the compounds was checked by elemental analysis (C, H, and N) and by determining their

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Table 1. Elemental analysis of acetanilides studied, $X_yC_6H_{5-y}$ $NHCOCCl_3$ with X_y.

Compd. (X_y)	% Nitrogen		% Carbon		% Hydrogen		m.p. (°C)
	calc.	found	calc.	found	calc.	found	
-H	5.87	5.90	40.25	40.28	2.52	2.50	83
2-CH_3	5.55	5.64	42.77	42.78	3.17	3.03	90
3-CH_3	5.55	5.65	42.77	42.76	3.17	3.04	98
4-CH_3	5.55	5.59	42.77	42.51	3.17	3.15	104
2-NO_2	11.12	9.88	35.90	35.86	2.03	1.80	60
3-NO_2	11.12	9.94	35.90	33.78	2.03	1.62	100
4-NO_2	11.12	9.99	35.90	33.98	2.03	1.68	138
4-Br	4.41	4.09	30.27	28.51	1.59	1.91	130
2,3-$(CH_3)_2$	5.25	5.27	45.00	45.05	3.75	3.78	91
2,4-$(CH_3)_2$	5.25	5.30	45.03	44.86	3.75	3.83	89
2,5-$(CH_3)_2$	5.25	5.27	45.03	44.60	3.75	3.75	72
2,6-$(CH_3)_2$	5.25	5.23	45.03	44.72	3.75	3.76	138

melting points (Table 1). They were further characterised by their infrared spectra. All other reagents employed in the preparations and purification of reagents were of analytical grade.

^{35}Cl Frequency Measurements

Polycrystalline samples of the title compounds were employed. The ^{35}Cl NQR spectra were measured at 77 K or in the range $77 \leq T/K \leq 300$. They were registered by the continuous wave method with a superregenerative spectrometer. Temperature at the sample site was produced by a stream of temperature- and flow-regulated nitrogen gas or with a liquid nitrogen bath at 77 K. The temperatures were measured by copper-constantan thermocouples to ± 1 K. The resonance frequencies were registered to an accuracy of ± 5 kHz, which was determined by the line width of the resonances, which was between 10 and 20 kHz.

The parent compound, N-(phenyl)-2,2,2-trichloroacetamide was also prepared, characterised and ^{35}Cl NQR measured under identical conditions for comparison. In fact, all the corresponding N-(chlorophenyl)-2,2,2-trichloroacetamides were prepared and characterised, and their ^{35}Cl NQR frequencies were checked at 77 K.

Table 2. ^{35}Cl NQR frequencies of substituted N-(phenyl)-2,2,2-trichloroacetamides, $X_yC_6H_{5-y}$ $NHCOCCl_3$ with X_y.

	ν_i (MHz) at 77 K					
X_y	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
-H	39.986 (50)	39.452 (40)	39.428 (40)			
2-CH_3	39.242 (25)					
3-CH_3	40.131 (20)	39.453 (25)	39.243 (25)			
4-CH_3	40.127 (30)	40.095 (25)	39.710 (20)	39.525 (20)	39.142 (15)	39.023 (10)
2-NO_2	40.318 (20)	40.070 (18)	39.723 (15)	39.459 (15)	39.090 (12)	38.863 (10)
3-NO_2	40.229 (10)	39.793 (15)	39.468 (8)			
4-NO_2	40.070 (50)	39.353 (45)	39.357 (40)			
4-Br	39.934 (40)					
2,3-$(CH_3)_2$	40.254 (25)	39.974 (25)	39.340 (15)	39.263 (15)	39.091 (12)	38.968 (10)
2,4-$(CH_3)_2$	No resonance					
2,5-$(CH_3)_2$	39.582 (60)	39.087 (55)				
2,6-$(CH_3)_2$	39.713 (45)	39.523 (40)	39.072 (35)			

Table 3. Coefficients of the power series development $\nu(^{35}\mathrm{Cl}) = f(T)$ of N-(4-methylphenyl)-2,2,2-trichloroacetamide.

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}
Before phase transition						
ν_1	12	8.9	40.9957	−29.6940	−6.5273	3.6470
ν_2	12	5.2	40.0694	3.6800	0.7055	−12.9624
ν_3	12	5.7	41.9123	−79.6613	−17.2596	27.1287
ν_4	12	6.4	40.4012	−31.2812	−6.4130	4.0139
ν_5	12	1.0	40.0440	−30.4798	−6.8447	3.7291
ν_6	12	1.7	40.8734	−65.4056	−14.5912	20.3908
After phase transition						
ν_2	7	1.9	30.7980	740.9739	38.3428	−61.3857
ν_4	7	2.3	43.4667	−323.7140	−15.7723	10.7271
ν_5	7	4.7	26.3308	1005.2600	53.736	685.6022

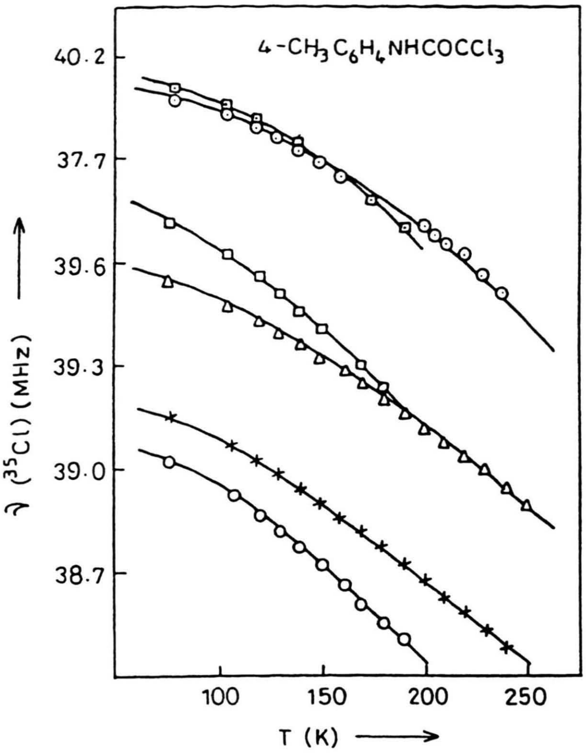

Fig. 1. Plot of ν (^{35}Cl NQR) vs. temperature.

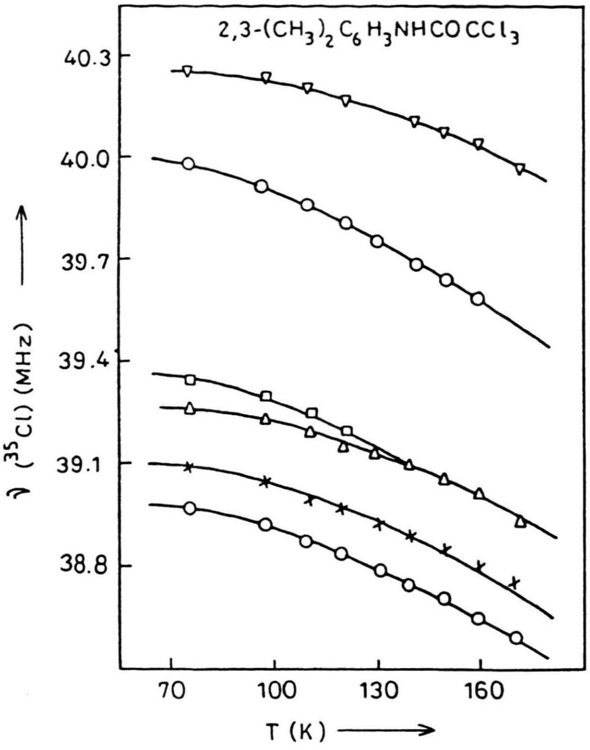

Fig. 2. Plot of ν (^{35}Cl NQR) vs. temperature.

Table 4. Coefficients of the power series development $\nu(^{35}\mathrm{Cl})=f(T)$ for 4-$CH_3C_6H_4NHCOCCl_3$ and 2,3-$(CH_3)_2C_6H_3NHCOCCl_3$[a].

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}
4-$CH_3C_6H_4NHCOCCl_3$						
ν_1	5	4.3	40.4014	−9.5650	−1.1243	−10.7228
ν_2	18	9.9	41.0231	−33.5551	−6.8461	5.4762
ν_3	10	3.5	41.3960	−60.3264	−12.9035	15.4351
ν_4	19	5.5	40.1685	−21.8937	−4.6317	−0.2055
ν_5	18	8.1	39.9626	−27.1676	−6.2347	2.3172
ν_6	10	5.7	40.2780	−41.8745	−9.9460	9.2310
2,3-$(CH_3)_2C_6H_3NHCOCCl_3$						
ν_1	9	6.4	41.6617	−50.8969	−11.1019	18.4602
ν_2	9	4.2	42.5041	−85.7507	−21.6621	42.3956
ν_3	9	5.6	42.2060	−96.9336	−25.3154	57.7740
ν_4	9	8.8	39.6075	−14.6851	−4.0447	−2.0723
ν_5	9	6.9	40.5022	−43.6544	−9.8708	14.9396
ν_6	9	8.2	40.0806	−37.7171	−8.6495	7.4727

[a] please see text.

Results and Discussion

The ^{35}Cl NQR frequencies of N-(phenyl)-2,2,2-trichloroacetamide, N-(2/3/4-nitrophenyl)-2,2,2-trichloroacetamides, N-(4-bromophenyl)-2,2,2-trichloroacetamide and seven N-(methylphenyl)-2,2,2-trichloroacetamides are shown in Table 2. The temperature dependences of ^{35}Cl NQR frequencies of N-(4-methylphenyl)-

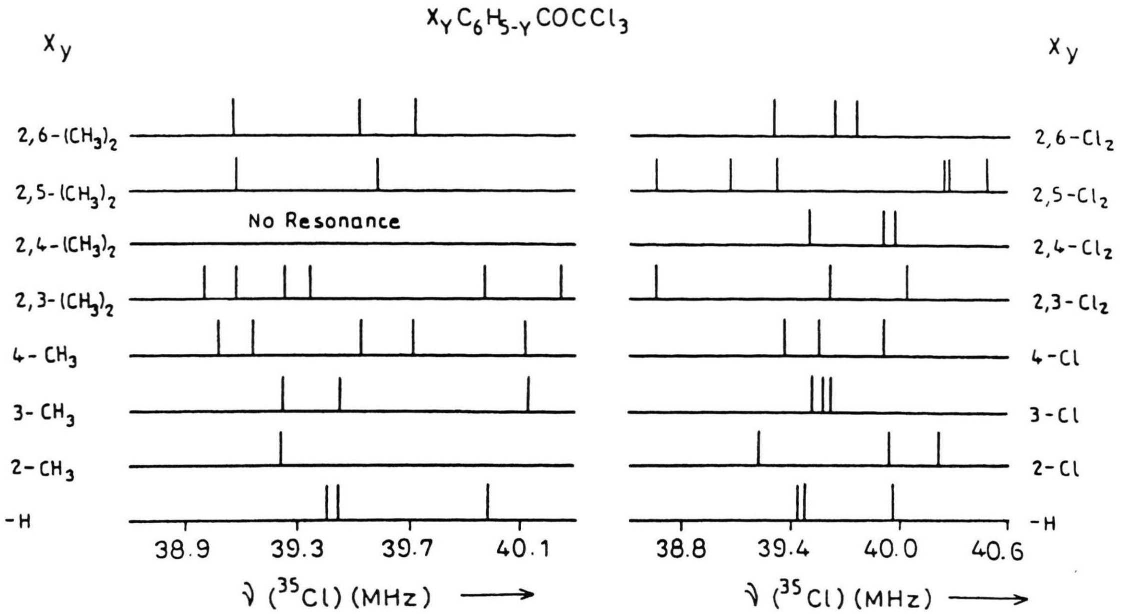

Fig. 3. Variation of ν (^{35}Cl NQR) with substitution.

2,2,2-trichloroacetamide and N-(2,3-dimethylphenyl)-2,2,2-trichloroacetamide were followed up to 250 K and 170 K, respectively, the detection limits of the frequencies. Thereafter the signal to noise ratio was very low. No further measurements were made with the latter compound, while with the former they fade out around 250 K. These frequencies have been plotted as function of temperature (Figs. 1 and 2). The frequencies decrease with increasing temperature according to the theory of Bayer [16]. The coefficients a_i of the power series development of the ^{35}Cl NAR frequencies as $f(T)$ are listed in Tables 3 and 4.

There is no problem in assigning the frequencies as there are only ω C-Cl frequencies in all the compounds. It is interesting to note that N-(2-methylphenyl)-2,2,2-trichloroacetamide, N-(3-methylphenyl)-2,2,2-trichloroacetamide and N-(4-methylphenyl)-2,2,2-trichloroacetamide show one, three, and six frequencies, respectively, indicating that the first compound has all the three Cl atoms equivalent and the third has two molecules in the asymmetric unit. The sextet ^{35}Cl NQR spectrum of the latter compound changes to triplet around 205 K, indicating that it undergoes a first order phase transition at this temperature. The triplet part of the spectrum fades out around 250 K due to librational motions in the crys-

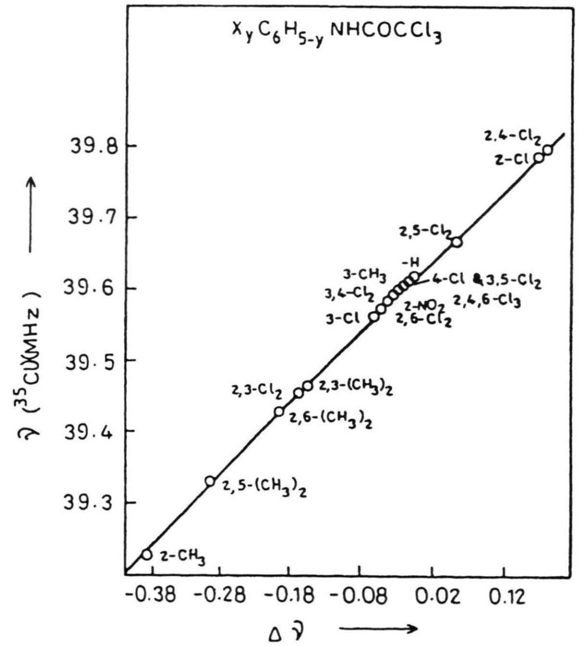

Fig. 4. Plot of ν (^{35}Cl NQR) vs. $\Delta\nu$.

Table 5. Observed and calculated ^{35}Cl NQR frequencies for amides of configuration $X_yC_6H_{5-y}NHCOCCl_3$ with X_y.

X_y	ν (MHz)	
	obsd	calc.
-H	39.986	
	39.452	
	39.428	
	39.622 (av)	
2-CH_3	39.242	39.230
3-CH_3	40.131	39.779
	39.453	39.245
	39.243	39.221
	39.609	39.415 (av)
4-CH_3	40.127	39.990
	40.095	39.456
	39.710	39.432
	39.525	
	39.142	
	39.023	
	39.603	39.626 (av)
2,3-$(CH_3)_2$	40.254	39.387
	39.974	38.853
	39.340	38.829
	39.263	
	39.091	
	38.968	
	39.465	39.023 (av)
2,4-$(CH_3)_2$	No resonance	
2,5-$(CH_3)_2$	39.582	39.387
	39.087	38.853
		38.829
	39.335	39.023 (av)
2,6-$(CH_3)_2$	39.713	39.202
	39.523	38.668
	39.072	38.644
	39.436	38.838 (av)
2-NO_2	40.318	42.682
	40.070	41.548
	39.723	41.524
	39.459	
	39.090	
	38.863	
	39.587	41.718
3-NO_2	40.229	41.055
	39.793	40.521
	39.468	40.497
	39.830	40.691 (av)
4-NO_2	40.070	40.053
	39.353	39.519
	39.257	39.495
	39.560	39.689 (av)
2-Cl	40.239	41.192
	39.908	40.658
	39.225	40.634
	39.791	40.828 (av)
3-Cl	39.604	40.485
	39.586	39.951
	39.521	39.927
	39.570	40.121 (av)
4-Cl	39.902	40.315
	39.562	39.791
	39.392	39.757
	39.619	39.951 (av)
2,3-Cl_2	40.049	41.691
	39.649	41.157
	38.686	41.133
	39.461	41.327 (av)
2,4-Cl_2	39.983	41.521
	39.931	40.987
	39.488	40.963
	39.801	41.160 (av)
2,5-Cl_2	40.470	41.691
	40.290	41.157
	40.279	41.133
	39.328	
	39.091	
	38.680	
	39.690	41.327 (av)
2,6-Cl_2	39.732	42.398
	39.671	41.864
	39.322	41.840
	39.575	42.034 (av)
3,4-Cl_2	39.856	40.814
	39.556	40.280
	39.420	40.256
	39.611	40.450 (av)
3,5-Cl_2	39.817	40.984
	39.550	40.450
	39.479	40.426
	39.615	40.620 (av)
4-Br	39.934	40.298
		39.764
		39.740
		39.934 (av)

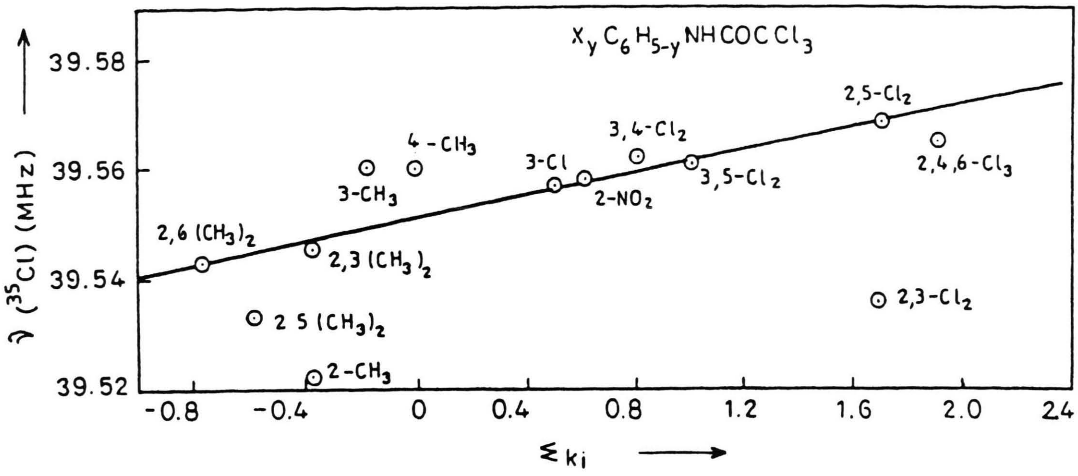

Fig. 5. Plot of ν (^{35}Cl NQR) vs. $\Sigma\, k_i$.

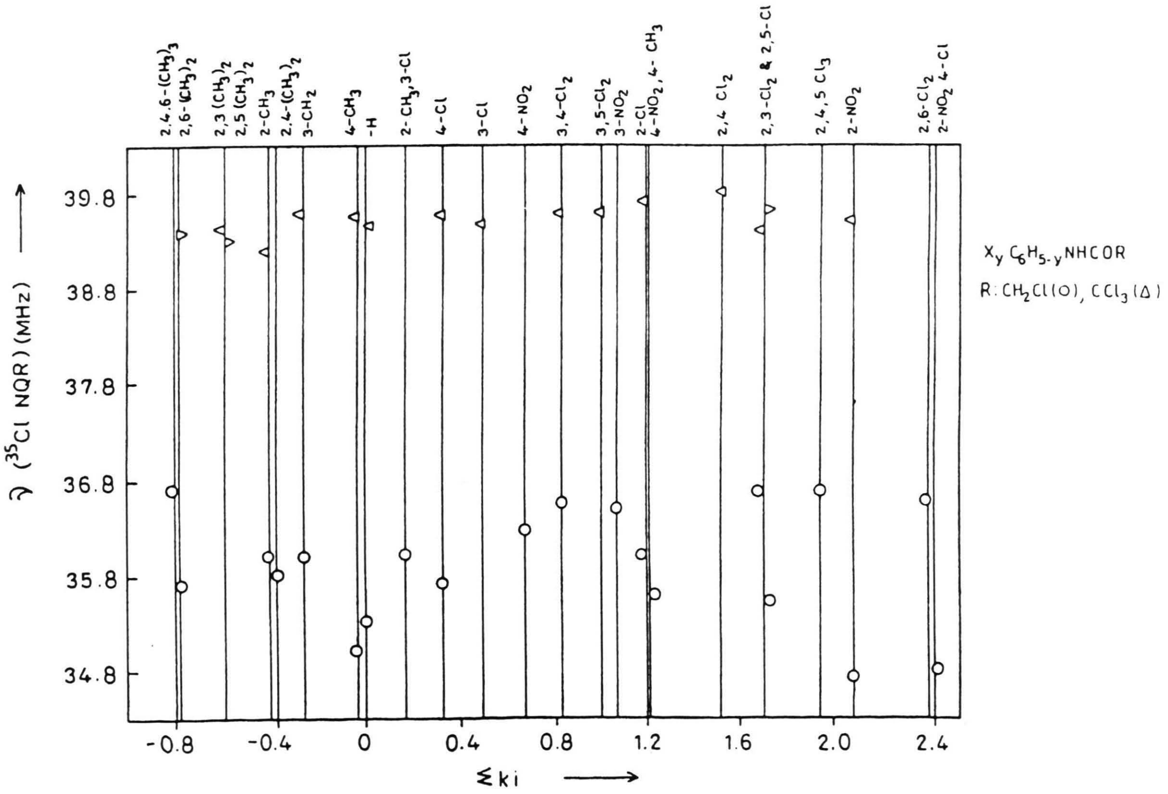

Fig. 6. Variation of ν (^{35}Cl NQR) with $\Sigma\, k_i$.

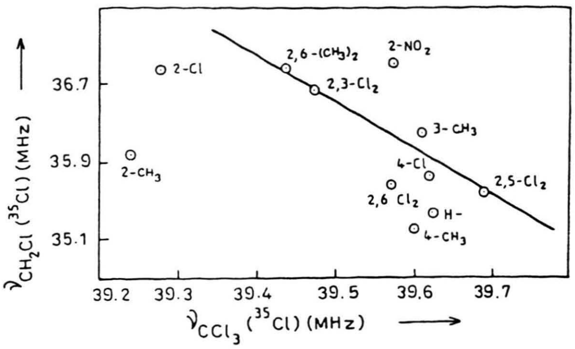

Fig. 7. Plot of ν (^{35}Cl NQR)$_{CN_2Cl}$ vs. ν (^{35}Cl NQR)$_{CCl_3}$.

tal lattice, as the torsional motions of the CCl_3 group are easily excited. N-(2,3-dimethylphenyl)-2,2,2-trichloroacetamide and N-(2-nitrophenyl)-2,2,2-trichloroacetamide also showed the presence of two molecules each in their respective asymmetric units, exhibiting polymorphism. N-(2,4-dimethylphenyl)-2,2,2-trichloroacetamide did not show resonance, while the two frequencies of different intensities observed with N-(2,5-dimethylphenyl)-2,2,2-trichloroacetamide indicated that two of the three ω-Cl atoms are equivalent. N-(2,6-dimethylphenyl)-2,2,2-trichloroacetamide showed three resonance frequencies, indicating that all the Cl atoms in the trichloroacetyl group are crystallographically inequivalent.

^{35}Cl NQR spectra of all the substituted methyl phenyl trichloroacetamides have been compared with the corresponding substituted chloro phenyl trichloroacetamides. The comparisons are schematically represented in Figure 3. Variation of the mean values of ν (^{35}Cl NQR) of the trichloroacetyl group with the substituents in the phenyl ring are shown in Figure 4. Generally there is no systematic variation of the frequencies with the substituents in the phenyl ring, while the substitution at the para position shows a regular trend. With the latter substitution, electron donating or repelling groups decreased ν(^{35}Cl NQR) of mono(ω)-chloroacetamides, while electron withdrawing groups increased the frequencies. With the substituted phenyl-trichloroacetamides the change in frequency is small with either electron donating or withdrawing groups at para position.

The ω C-Cl frequencies of the trichloroacetyl group in (substituted N-(phenyl)-trichloroacetamides were estimated using the k values [17] and the frequencies of N-(phenyl)-trichloroacetamide (Table 5).

Comparison of these values with the observed frequencies showed that the agreement is quite good, considering the approximations involved in deducing the κ values. Further ν (^{35}Cl) of these amides has also been correlated with the $\Sigma\, k_i$ of the compounds (Fig. 5). Variation of ν (^{35}Cl NQR) of mono- and trichloroacetamides with their $\Sigma\, k_i$ is shown in Figure 6. Correlation of ν (^{35}Cl NQR) of mono- and trichloroacetamides is shown in Figure 7.

Although a close examination of ν (^{35}Cl NQR) of the trichloroacetyl group in substituted trichloroacetamides revealed that the effect of ring substitution on the average frequencies is not substantial, substitution affects the crystal structure of the substituted compounds, as is evident from the variation in the number of frequencies observed with different amides.

Acknowledgement

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