^{35}Cl NQR Spectra of Arylsulphonamides, N-Chloro and N,N-Dichloro Arylsulphonamides

B. Thimme Gowda, J. D. D'souza and Hartmut Fuess[a]

Department of Studies in Chemistry, Mangalore University,
Mangalagangotri-574 199, Mangalore, India
[a] Institute of Materials Science, Darmstadt University of Technology,
Petersenstr. 23, D-64287 Darmstadt

Reprint requests to Prof. B. T. Gowda; Fax: +91 824 287 367; e-mail: gowdabt@yahoo.com
or Prof. H. Fuess; Fax: +49 6151 16 60 23; e-mail: hfuess@tu-darmstadt.de

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The effect of substitution in the phenyl ring on the γ (^{35}Cl NQR) of N-Cl bonds of the N-chloro- and N,N-dichloro-arylsulphonamides has been studied and correlated. The correlation of ^{35}Cl NQR spectra of both the N-chloro and N,N-dichloro-arylsulphonamides is exceedingly good, although there was no systematic variation in the frequencies with substituents in the phenyl ring. The effect of substitution on the C-^{35}Cl NQR of the phenyl ring has also been correlated. The deviation here is also not systematic due to the fact that the chemically equivalent chlorine atoms may exhibit different NQR frequencies due to crystal field effect. Finally, γ (C – ^{35}Cl NQR) of all the 4-chloro-1-substitutedbenzenes have been correlated through the line diagram.

Key words: ^{35}Cl NQR; N-chloro- and N,N-dichloro-arylsulphonamides.

1. Introduction

Sulphonamides are of fundamental chemical interest as they show distinct physical, chemical and biological properties. Many sulphonamides and their N-chloro compounds exhibit pharmacological activity, which has further stimulated recent interest in their chemistry. Further, many N-chlorosulphonamides exhibit fungicidal and herbicidal activities, because of their oxidising action in aqueous, partial aqueous and non-aqueous media. Therefore an understanding of the formation, properties and reactions of sulphonamides and their N-chloro compounds is of importance in such areas as medicinal and redox chemistry. A great deal of work on the spectroscopic aspects of amides needs to be done for correlating frequencies with the chemical bond parameters. Thus we are interested in the spectroscopic studies of amides in their crystalline state [1 – 11].

We report herein the effect of substitution in the phenyl ring on the γ (^{35}Cl NQR) of N-Cl bonds of the N-chloroaryl sulphonamides ($ArSO_2NaNCl \cdot xH_2O$) and N,N-dichloroaryl-sulphonamides ($ArSO_2NCl_2$). The N-chloro and N,N-dichloroarylsulphonamides studied and correlated are sodium salts of N-chlorobenzenesulphonamide, N-chloro-4-methylbenzenesulphonamide, N-chloro-4-ethyl-benzenesulphonamide, N-chloro-4-chlorobenzenesulphonamide, N-chloro-4-bromobenzenesulphonamide and N-chloro-2,4-dimethylbenzenesulphonamide, potassium salt of N-chloro-benzenesulphonamide, N,N-dichloro-benzenesulphonamide, N,N-dichloro-4-methylbenzensulphonamide, N,N-dichloro-4-chlorobenzenesulphonamide, N,N-dichloro-4-bromobenzensulphonamide. The compounds earlier reported [12 – 20] are also included.

Further, the effect of substitution on the C-^{35}Cl NQR of the phenyl ring have also been correlated. The compounds correlated are 4-chlorobenzenesulphonamide, N-methyl,4-chlorobenzenesulphonamide, N-ethyl-4-chlorobenzenesulphonamide, N-phenyl-4-chlorobenzenesulphonamide, 4-chlorobenzenesodiumsulphoxide, 4-chloroaniline, 4-chlorophenol, 4-chlorobenzoic acid, 4-chloroanisole, 4-chloromethylbenzoate, 4-chlorobenzaldehyde, 4-chloroacetophenone, 4-chloroacetanilide, 1,4-dichlorobenzene and chlorobenzene. The formulae are given in Table 3.

Table 1. Melting points of arylsulphonamides, sodium salts of N-chloroarylsulphonamides and N,N-dichloroarylsulphonamides.

Arylsulphonamides	m.p. (°C) obs(lit.)	N-Chloroarylsulphonamides	m. p. (°C) obs(lit.)	N,N-Dichloroarylsulphonamides	m.p. (°C)
4-$C_2H_5C_6H_4SO_2NH_2$	99-101	4-$C_2H_5C_6H_4SO_2NCl(Na)\cdot H_2O$	194	4-$C_2H_5C_6H_4$-SO_2NCl_2	58
4-$FC_6H_4SO_2NH_2$	125 (124-125)	4-$FC_6H_4SO_2$-$NCl(Na)\cdot H_2O$	198	4-$FC_6H_4SO_2NCl_2$	55-56
4-$ClC_6H_4SO_2NH_2$	143 (142-143)	4-$ClC_6H_4SO_2$-$NCl(Na)\cdot H_2O$	191 (190)	4-$ClC_6H_4SO_2NCl_2$	81
4-$BrC_6H_4SO_2NH_2$	162 (161.5)	4-$BrC_6H_4SO_2$-$NCl(Na)\cdot H_2O$	179 (178)	4-$BrC_6H_4SO_2NCl_2$	102
2,3-$(CH_3)_2C_6H_3SO_2NH_2$	138-140	2,3-$(CH_3)_2$-$C_6H_3SO_2NCl(Na)\cdot H_2O$	167	2,3-$(CH_3)_2C_6H_3SO_2NCl_2$	58
2,4-$(CH_3)_2C_6H_3SO_2NH_2$	140-142	2,4-$(CH_3)_2$-$C_6H_3SO_2NCl(Na)\cdot H_2O$	154	2,4-$(CH_3)_2C_6H_3SO_2NCl_2$	63
2,5-$(CH_3)_2C_6H_3SO_2NH_2$	149-151	2,5-$(CH_3)_2$-$C_6H_3SO_2NCl(Na)\cdot H_2O$	192	2,5-$(CH_3)_2C_6H_3SO_2NCl_2$	68
2-CH_3,4-$ClC_6H_3SO_2NH_2$	180-182 (184-185)	2-CH_3,4-Cl-$C_6H_3SO_2NCl(Na)\cdot H_2O$	172	2-CH_3,4-$ClC_6H_3SO_2NCl_2$	70
2-CH_3,5-$ClC_6H_3SO_2NH_2$	139-141 (142-143)	2-CH_3,5-Cl-$C_6H_3SO_2NCl(Na)\cdot H_2O$	188	2-CH_3,5-$ClC_6H_3SO_2NCl_2$	66
3-CH_3,4-$ClC_6H_3SO_2NH_2$	132-134 (126)	3-CH_3,4-Cl-$C_6H_3SO_2NCl(Na)\cdot H_2O$	174	3-CH_3,4-$ClC_6H_3SO_2NCl_2$	62
2,4-$Cl_2C_6H_3SO_2NH_2$	178-180 (179-180)	2,4-Cl_2-$C_6H_3SO_2NCl(Na)\cdot H_2O$	210	2,4-$Cl_2C_6H_3SO_2NCl_2$	67
3,4-$Cl_2C_6H_3SO_2NH_2$	141-143 (134-135)	3,4-Cl_2-$C_6H_3SO_2NCl(Na)\cdot H_2O$	192	3,4-$Cl_2C_6H_3SO_2NCl_2$	55

2. Experimental Section

2.1. Preparations, Purifications, and Characterisation of the Compounds

The substitutedbenzenesulphonamides were prepared by the chloro-sulphonation of substitutedbenzenes to the corresponding sulphonylchlorides and subsequent conversion of the latter to the respective substitutedbenzenesulphonamides by the procedures reported earlier [9 – 11, 21 – 25]. The sulphonamides were recrystallised to constant melting point (Table 1) from dilute ethanol and dried at 105 °C. The purity of all the compounds was further checked by recording their infrared spectra. The sulphonamides were then N-chlorinated to obtain sodium salts of N-chloroarylsulphonamides by bubbling pure chlorine gas through clear aqueous solutions of substituted benzenesulphonamides in 4M NaOH at 70 °C for about 1 hr. The precipitated sodium salts of N-chlorosubstitutedbenzenesulphonamides (CASB) were filtered, washed, dried and recrystallised from water. The purity of all the reagents was checked by determining the melting points (Table 1) and by estimating iodometrically, the amounts of active chlorine present in them [25]. N,N-Dichloroarylsulphonamides were prepared by further chlorination of N-chloroarylsulphonamides in aqueous solution. Pure chlorine gas was bubbled through the solution to ensure complete chlorination. The fine white precipitates formed were filtered off, dried on the filter paper by sucking dry air through it, and then dried in a blackened vacuum desiccator for 24 hours. The N,N-dichloroarylsulphonamides so obtained were recrystallised from chloroform. The purity of the compounds was checked by estimating the amount of active chlorine present in them by the iodometric method. They were further characterised by recording their infrared spectra. All other reagents employed in the preparations and purification of reagents were of analytical grade.

Table 2. ^{35}Cl NQR spectra of N-chloroarylsulphonamides and N,N-dichloroarylsulphonamides.

Compound	γ(N-^{35}Cl/C-^{35}Cl) (MHz)
$C_6H_5SO_2NClNa\cdot H_2O$	45.73 [12]
4-$CH_3C_6H_4SO_2NClNa\cdot H_2O$	45.72 [13]
4-$C_2H_5C_6H_4SO_2NClNa\cdot H_2O$	45.528 (77 K, Present)
4-$ClC_6H_4SO_2NClNa\cdot H_2O$	45.474, 45.690, 35.235, 35.278 (77 K, Present) 44.756, 44.884, 34.719, 34.841 (298 K, Present)
4-$BrC_6H_4SO_2NClNa\cdot H_2O$	45.398 (77 K, Present)
2,4-$(CH)_3C_6H_3SO_2NClNa\cdot H_2O$	44.963 (77 K, Present)
$C_6H_5SO_2NClK\cdot H_2O$	45.35 (77 K, Present)
$C_6H_5SO_2NCl_2$	52.606, 52.254 [12]
4-$CH_3C_6H_4SO_2NCl_2$	51.6 [13]
4-$ClC_6H_4SO_2NCl_2$	52.038, 35.53 [13]
4-$BrC_6H_4SO_2NCl_2$	52.951, 53.010 (77 K, Present), 51.738 (298 K, Present)

2.2. ^{35}Cl NQR Frequency Measurements

Polycrystalline samples of the title compounds were employed. The ^{35}Cl NQR of the sodium and potassium salts N-chlorosubstituted benzenesulphonamides and N,N-dichlorosubstituted benzenesulphonamides were measured at 77 K. The spectra 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 at the sample site were measured by copper-constantan thermocouples to ± 1 K. The resonance frequencies were measured via a frequency counter to an accuracy of ± 5 kHz. The latter accuracy was determined by the line width of the resonances, which was between 10 and 20 kHz.

^{35}Cl NQR frequencies of 4-chlorobenzenesulphonamide, N-methyl-4-chlorobenzenesulphonamide, N-ethyl-4-chlorobenzenesulphonamide, N-phenyl-4-chlorobenzenesulphonamide, 4-chlorobenzeneso-

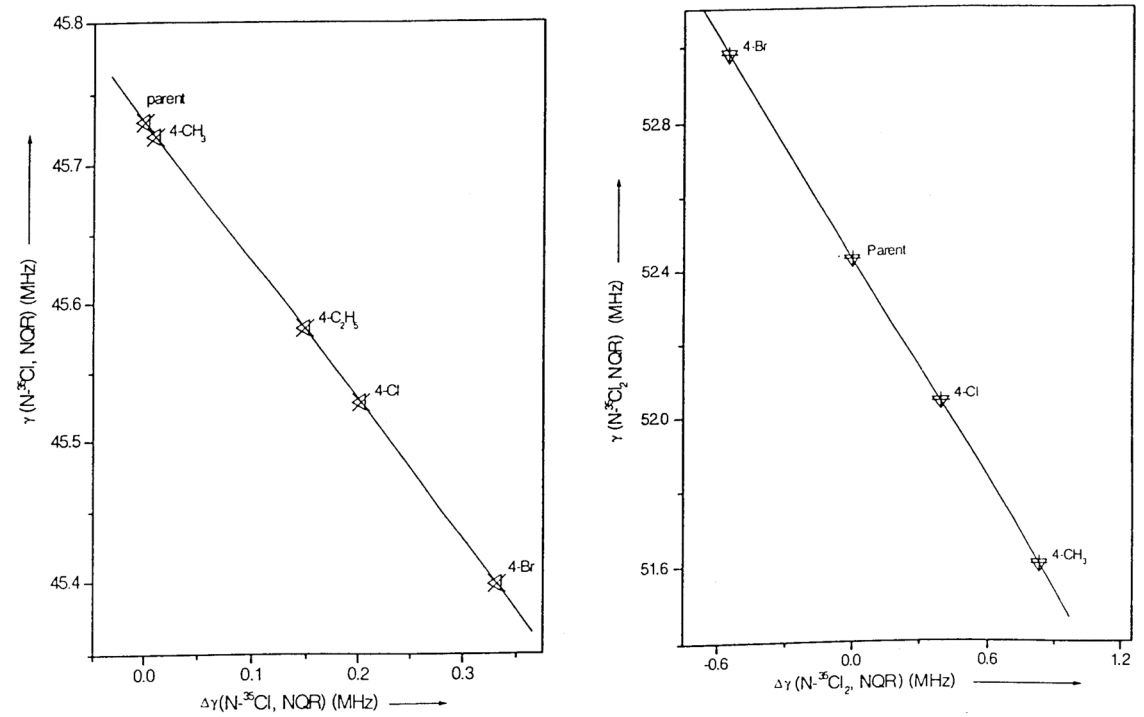
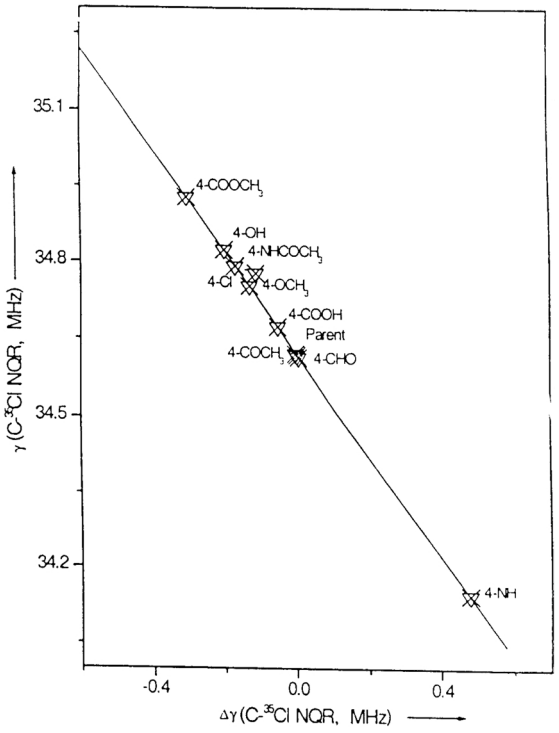


Fig. 1. Plots of γ(N-^{35}Cl, NQR) vs. $\Delta\gamma$(N-^{35}Cl, NQR) of *i*-X-$C_6H_4SO_2NCl(Na) \cdot xH_2O$ (left) and γ(N-$^{35}Cl_2$, NQR) vs. $\Delta\gamma$(N-$^{35}Cl_2$, NQR) of *i*-X-$C_6H_4SO_2NCl_2$ (right).



⟵ Fig. 2. Plots of γ(C-^{35}Cl, NQR) vs. $\Delta\gamma$(C-^{35}Cl, NQR) of 4-^{35}Cl-C_6H_4-X.

Table 3. Effect of substitution on the C-^{35}Cl NQR frequencies of 4-chloro-1-substitutedbenzenes.

Compound	γ (C -^{35}Cl NQR) in MHz
C_6H_5Cl	34.622 [17]
4-ClC_6H_4Cl	34.778 (77K, present)
4-ClC_6H_4OH	34.700, 34.945 [15]
4-$ClC_6H_4OCH_3$	34.753 [15]
4-ClC_6H_4-CHO	34.607, 34.623 [16]
4-ClC_6H_4COOH	34.673 [15]
4-$ClC_6H_4COOCH_3$	34.928 [18]
4-$ClC_6H_4COCH_3$	34.618 [16]
4-$ClC_6H_4NH_2$	34.146 [15]
4-$ClC_6H_4NHCOCH_3$	34.792 [15]
4-$ClC_6H_4SO_2NH_2$	35.094, 35.113 (77K, Present)
4-$ClC_6H_4SO_2NHCH_3$	No Resonance
4-$ClC_6H_4SO_2NHC_2H_5$	35.094, 35.113 (77K, Present)
4-$ClC_6H_4SO_2NHC_6H_5$	35.237, 35.090 (77K, Present)
4-$ClC_6H_4SO_2Na$	35.137 [17]

diumsulphoxide were measured under identical conditions for comparison. In fact all the other compounds were prepared, characterised and their ^{35}Cl NQR frequencies measured.

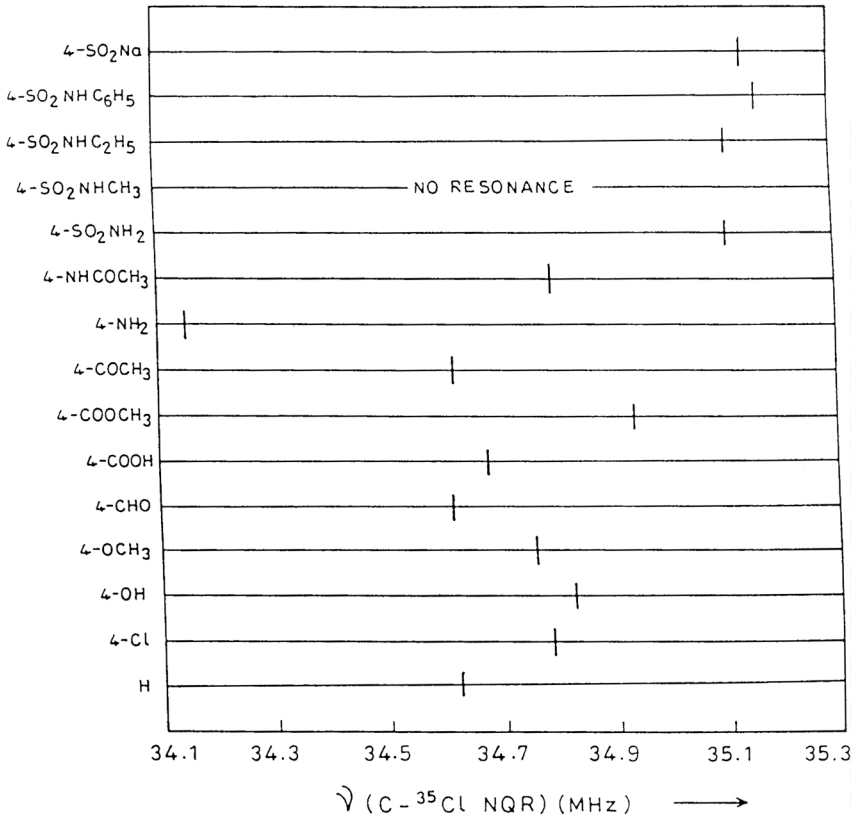


Fig. 3. Line diagram for the variation of γ(^{35}Cl, NQR) of phenyl C-^{35}Cl of Cl-C_6H_4-X with substitution.

3. Results and Discussion

^{35}Cl NQR frequencies of the compounds studied are shown in Table 2. There was no problem in assigning the frequencies as there are only either N-Cl or C-Cl NQR ^{35}Cl frequencies in all the N-chloroarylsulphonamides and N,N-dichloroarylsulphonamides, and N-^{35}Cl NQR is observed at higher frequency than that of C-^{35}Cl NQR. Further, N-^{35}Cl of N,N-dichloroarylsulphonamides resonate at higher frequencies than those of N-^{35}Cl of N-chloroarylsulphonamides.

^{35}Cl NQR spectra of both the N-chloro and N,N-dichloroarylsulphonamides have been compared and correlated (Fig. 1). Variations of γ (^{35}Cl (N) NQR) with substitution in the phenyl ring are correlated with the difference between the frequencies ($\Delta\gamma$) of the substituted N-chloroarylsulphonamides or N,N-dichloroarylsulphonamides and the parent N-chlorobenzenesulphonamide or N,N-dichlorobenzenesulphonamide, respectively. The correlation is exceedingly good, although there was no systematic variation in the frequencies with substituents in the phenyl ring.

The γ (^{35}Cl NQR) of C-Cl of the substituted chlorobenzenes are listed in Table 3 and have been correlated (Fig. 2). In the light of the fact that the effect of substitution is not immediately next to the C-Cl bond and it has to be transmitted through the phenyl ring, the deviations are understandable. The deviation is also not systematic. This is due to the fact that the chemically equivalent chlorine atoms may exhibit different NQR frequencies due to crystal field effect [18,20]. Finally, γ (C-^{35}Cl NQR) of all the 4-chloro-1-substitutedbenzenes have been correlated through the line diagram (Figure 3).

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