NUCLEAR QUADRUPOLE RESONANCE SPECTRA OF SOME ARYLSULFENYL CHLORIDES

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To study the transfer of the influence of substituents through a –PhS– system and the effects of the coordination of a sulfur atom with ortho substituents, we have studied the NQR spectra of a number of substituted arylsulfenyl chlorides. The Cl^{35} NQR frequencies of the compounds studied are given in Table 1.

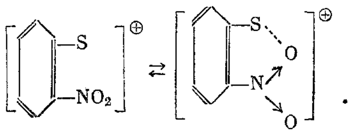
The closeness of the NQR frequency of chlorine bound directly to the ring in p-chlorophenylsulfenyl chloride (p-chloro-PSC) (34.979) to the frequency in p-dichlorobenzene (34.780) [6] permitted the assumption that in its donor-acceptor properties the SCl group is similar to a chlorine atom. The correlation of the NQR frequencies of chlorine with the constants of para substituents was carried out by means of formula $\nu = \nu_0 + \alpha\sigma_I + \beta\sigma_R$, where σ_I is the induction constant of the para substituent; σ_R is the conjugation constant, and α and β are the transmission coefficients characterizing the conduction of the influence of the substituent through the –PhS– system. After averaging the results by the method of least squares, the expression obtained has the form

$$\nu = 37.25 + 2.04\sigma_I + 1.23\sigma_R \qquad (r = 0.97).$$

The ratio of the transmission coefficients $\alpha:\beta = 2.04:1.23 = 1.66$ shows that the –PhS– system conducts the influence of substituents better by the inductive mechanism, although the contribution of conjugation is fairly large. This is also shown by the lower correlation coefficient of the NQR frequencies with σ^*, which reflects only the inductive effect of the substituent, the relationship being described, after treating the results by the method of least squares, by the equation

$$\nu = 36.17 + 1.84\sigma^* \qquad (r = 0.93).$$

On comparing our data with the rates of hydrolysis of arylsulfenyl chlorides in aqueous $CHCl_3$ [7], it was found that for derivatives having H, CH_3, Cl, or an NO_2 group in the para position, log k is connected linearly with the NQR frequency in the SCl group. In the same investigation [7] it was found that all ortho substituents retard the hydrolysis reaction, the o-NO_2 group having the greatest effect and retarding the reaction by a factor of 6000 as compared with the p-NO_2 group. It is known that arylsulfenyl chlorides containing a o-NO_2 group differ from other derivatives of this series of compounds by their capacity for giving electrically conducting solutions in 100% H_2SO_4 [8]. This characteristic is ascribed to their capacity for ionizing under the conditions mentioned, and it has been assumed that the sulfenium ion formed is stabilized by intramolecular coordination interaction with the oxygen of the o-NO_2 group. This can be represented by the following equilibrium



We have found that such a coordination is actually observed in solid o-nitro-PSC. It can be seen from the table that the NQR frequency of the chlorine in the o-nitro derivative is lower than in the unsubstituted phenylsulfenyl chloride (36.15 and 37.016 MHz, respectively). Since an electron-accepting group must raise the NQR frequency of chlorine, the observed lowering of the frequency with the introduction of an NO_2 group into the molecule means that in this case the o-NO_2 group is an electron donor with respect to the SCl group. The condradiction mentioned can be resolved by assuming an intramolecular coordination of the sulfur atom with the oxygen of the o-NO_2 group. The NQR frequency of the chlorine in p-nitro-PSC is 38.738 MHz. Because of the stronger acceptor action from the ortho position for the o-nitro derivative, a figure of the order of 39.5 MHz might have been expected. The observed difference of ~3.5 MHz is such that it exceeds

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TABLE 1

Arylsulfenyl chloride	ν_{S-Cl}, MHz	ν_{C-Cl}, MHz	Mp or bp, °C (p, mm Hg)	Literature references
C_6H_5SCl	37,016		50—52 (1);	58—60 (3) [1]
p-Cl—C_6H_4SCl	37,947	34,979	79 (3);	94 (6) [2]
p-Br—C_6H_4SCl	37,760		85 (0,1);	91 (0,6) [3]
p-$CH_3C_6H_4SCl$	$\left.\begin{matrix}37{,}002\\37{,}212\end{matrix}\right\}37{,}11$		76—77 (2);	77,5—78 — 2,5 [1]
p-NO_2—C_6H_4SCl	38,738		51—52;	52 [2]
o-Cl—C_6H_4SCl	38,465	33,864	97 (7);	116 (17) [2]
o-Br—C_6H_4SCl	38,143		118,5—119,5 (9)	—
o-NO_2—C_6H_4SCl	$\left.\begin{matrix}35{,}966\\36{,}330\end{matrix}\right\}36{,}15$		73—74;	74,5—75 [4]
o-NO_2—*p*-Cl—C_6H_3SCl	37,332	35,826	99—100;	97,5—98 [5]
o-NO_2-*p*-NO_2—C_6H_3SCl	34,752		93,5—94,5	94—95 [4]

all changes in frequencies caused by para substituents of any nature. In confirmation of the strong donor–acceptor interaction of the sulfur with the oxygen of the o-NO_2 group may be adduced the results of an x-ray study of methyl o-nitrophenylsulfenate, which show that the distance between the sulfur and oxygen atoms (2.44 Å) is considerably smaller than the sum of their Van der Waals radii (3.25 Å) [9].

When a chlorine atom is introduced into the molecule of o-nitro-PSC in the para position with respect to the SCl group, the NQR frequency of the chlorine attached to the sulfur rises from 36.15 to 37.332 MHz, the shift in frequency of 1.18 MHz in this case being comparable in magnitude with the difference in the frequencies of unsubstituted PSC and its p-chloro derivative (0.931 MHz). However, when a second NO_2 group, a far stronger acceptor than a chlorine atom, is introduced into the para position of o-nitro-PSC, the frequency falls, completely unexpectedly, to 34.752 MHz. Apparently this unusual influence of a p-NO_2 group on the NQR frequency of the chlorine in the SCl group can be connected with additional intermolecular coordination of the sulfur atom with the oxygen of the p-NO_2 group of another molecule.

In the case of the o-chloro and o-bromo derivatives, the NQR frequencies of the chlorine in the SCl group are higher than those of the corresponding para isomers, but the frequency of the Cl in the ring is very similar (33.864 MHz). Since the SCl group is similar to a chlorine atom in its donor–acceptor properties, the considerable lowering of the NQR frequency of the chlorine atom attached to the ring can be explained by a coordination interaction of the ortho substituent with the sulfur atom which, however, has a different nature from the coordination in o-nitro-PSC.

EXPERIMENTAL

The p-H, p-CH_3, p-Cl, o-Cl, p-Br, and o-Br-PSCs were obtained by chlorinating the corresponding thiols with chlorine in CCl_4 at 0°. The substances were purified by vacuum distillation. The o-NO_2, p-NO_2, o-NO_2-p-Cl, and 2, 4-dinitro derivatives were obtained by chlorinating the corresponding disulfides and were purified by recrystallization from CCl_4. The constants of the compounds obtained are given in Table 1, together with literature figures.

The Cl^{35} NQR were recorded at 77°K on a IS-2 pulse spectrometer–relaxometer constructed by SKB IRÉ AN SSSR [Special Design Office, Institute of Radio and Electronics Technology, Academy of Sciences of the USSR].

CONCLUSIONS

1. The NQR frequencies are connected with the constants of para substitutents by the equation $\nu = 37.25 + 2.04\sigma_I + 1.23\sigma_R$, where σ_I is the induction constant and σ_R the conjugation constant.

2. A nitro group interacts with the sulfur atom, considerably lowering the NQR frequency of the chlorine in the SCl group.

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