Cl^{35} NUCLEAR QUADRUPOLE RESONANCE SPECTRA OF SOME CARBOXYLIC ACID CHLORIDES

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It is known that the Cl^{35} nuclear quadrupole resonance (NQR) frequency of aliphatic acid chlorides (RCOCl, where R is alkyl or haloalkyl) changes in accordance with the induction constants of the substituents [1]. In addition, this sort of dependence cannot be considered to be a sign of the absence of double bond character in the C–Cl bond of the acid chloride group since the asymmetry parameter (η) for CH_3COCl is 27% [2], which, according to [3], corresponds to 9.8% double bond character. A similar estimate for $COCl_2$ [4] (η = 25%) gives 10.8% double bond character. The magnitude of the double bond character in this series apparently remains approximately constant.

It was of interest to investigate the behavior of the Cl^{35}NQR frequencies in the COCl group for a wider range of carboxylic acid chlorides. The experimental results are presented in Table 1. Our own data and, in part, literature data enabled us to examine the character of the changes in the NQR frequencies for the acid chlorides of meta- and para-derivatives of benzoic acid (1,3- and 1,4-RC_6H_4COCl). It turned out that a linear dependence between the NQR frequencies of the chlorine atom in the COCl group (ν_{COCl}) and the frequencies of chlorine in the benzene ring (ν_{benz}) of the corresponding chlorobenzene derivatives (1,3- and 1,4-RC_6H_4Cl) is observed in both cases. The following equation was obtained for the meta-derivatives (1,3-RC_6H_4COCl and 1,3-RC_6H_4Cl, where R = H, CH_3, Cl, COCl, and NO_2):

$$\nu_{COCl} = [(1.19\nu_{benz} - 11.34) \pm 0.20]\text{MHz};\ r = 0.92. \quad (1)$$

The "para-series" (R = H, Cl, Br, I, CH_3, OCH_3, NO_2) is described by the equation

$$\nu_{COCl} = [(0.74\ \nu_{benz} + 4.17) \pm 0.20]\ \text{MHz};\ r = 0.90. \quad (2)$$

The existence of this sort of linear dependence indicates the analogous character of the effects of transmission of the effect to the chlorine atom, both in the benzene ring and in the COCl group. However, the range of changes in the NQR frequencies for the Cl atom in the benzene ring is considerably greater than in the COCl group. It has already been noted that the primary change in the electron density apparently occurs in the carbonyl group rather than in the C–Cl bond in the case of carboxylic acid chlorides [1].

The correlation of ν_{COCl} with the substituent constants makes it possible to make a more definitive judgment regarding the nature of the changes in the Cl^{35}NQR frequencies. The most satisfactory correlation is observed with substituent induction constants (σ_I) [6]. For 1,3-RC_6H_4COCl (R = H, Cl, I, CH_3, COCl, NO_2), the Cl^{35}NQR frequency is determined as

$$\nu_{COCl} = [(29.79 + 2.14\sigma_I) \pm 0.22]\ \text{MHz};\ r = 0.92. \quad (3)$$

Similarly, for 1,4-RC_6H_4COCl (R = H, Cl, Br, I, OCH_3, CH_2, NO_2),

$$\nu_{COCl} = [(29.90 + 0.74\sigma_I) \pm 0.06]\ \text{MHz};\ r = 0.94. \quad (4)$$

In comparing Eqs. (3) and (4), attention is directed to the fact that the coefficient of σ_I for meta-substitution is somewhat higher than for the para-derivatives, i.e., the induction conductivity from the meta-position is high than from the para-position; this is completely natural.

Thus one can conclude that the change in the Cl^{35}NQR frequencies in the acid chlorides of meta- and para-derivatives of benzoic acid is due to the substituent induction effect. If there is double bond character,

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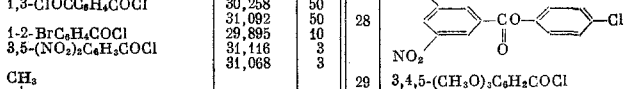
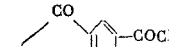
TABLE 1. Cl^{35}NQR Spectra of Carboxylic Acid Chlorides

Number	Compound	Cl^{35} NQR frequency, MHz	Signal /noise	Number	Compound	Cl^{35} NQR frequency, MHz	Signal /noise
1	C_6H_5COCl	29,918 [5]	50	20	1,2-ClC_6H_4COCl	29,900 c	10
2	1,4-$CH_3OC_6H_4COCl$	30,144	30			29,690	10
3	1,4-IC_6H_4COCl	29,988	3	21	cis- $COClC_6H_{10}COCl$	29,000	30
		30,372	3	22	trans- $COClC_6H_{10}COCl$	28,990	50
4	1,4-BrC_6H_4COCl	30,105	2	23	4-4'-$COClC_6H_4$—O—C_6H_4COCl	30,120	5
5	1,4-ClC_6H_4COCl	30,28 a	10			29,870	5
6	1,4-$NO_2C_6H_4COCl$	30,113	5	24	4,4'-$COClC_6H_4$—C_6H_4—$COCl$	29,900	5
		30,575	5			29,680	5
7	1,4-$CH_3C_6H_4COCl$	29,800	10	25	4,4'-$COClC_6H_4$—CH_2—C_6H_4COCl	29,994	3
8	1,4-$C_6H_5CH_2C_6H_4COCl$	30,480	15	26	4,4'-$COClC_6H_4$—C(=O)—C_6H_4COCl	30,762	30
9	1,3-JC_6H_4COCl	30,650	50				
10	1,3-$NO_2C_6H_4COCl$	31,404	10				
		31,200	10	27	3,3'-$COClC_6H_4N$ = NC_6H_4COCl	30,69	3
11	1,3-$CH_3C_6H_4COCl$	29,610	3				
12	1,3-ClC_6H_4COCl	30,250 b	5		NO_2		
13	1,3-$ClOCC_6H_4COCl$	30,258	50				
		31,092	50	28		35,098 d	3
14	1-2-BrC_6H_4COCl	29,895	10				
15	3,5-$(NO_2)_2C_6H_3COCl$	31,116	3		NO_2		
		31,068	3				
16		33,17 32,94	4 4	29	3,4,5-$(CH_3O)_3C_6H_2COCl$	30,120	10
				30	1,2,4,5-$(COCl)_4C_6H_2$	32,220	20
						31,500	20
				31	2,2'-$COClC_6H_4$—C_4H_4COCl	29,885	10
				32	trans-C_6H_5CH=$CHCOCl$	29,100	4
				33	CH_2=CH—$COCl$	30,190	4
						29,950	15
							17
		31,428 31,092	5 5	34		30,130 29,870	40
17				35	ClOC (CH_2) COCl	30,564	5
18	1,3,5-$(COCl)_3C_6H_3$	31,188	5			30,780	5
		31,158	5			30,810	5
		30,888	5	36	ClOC (CH_2)$_3$COCl	31,200	5
19	1,2-ClOC—C_6H_4COCl	30,240	10			28,770	5
		31,290	50			29,340	5

Note: The frequencies of the chlorine in the benzene ring are as follows (MHz):
a) 34.860; b) 35.532; c) 36.750 and 36.792; d) the line is a very closely knit doublet.

it either changes slightly within the limits of the examined series or does not have a substantial effect on the q_{ZZ} component of the electrical field gradient along the axis of the C–Cl bond.

It should be noted that the state of the chlorine atom of the COCl group in the investigated series of double acid chlorides of dicarboxylic acids (ClOC–  –X–  –COCl, where X = –, O, CH_2, CO) depends only slightly on the character of the X bridging group. In the double acid chlorides that we studied the Cl^{35}NQR frequency changes within the limits of 1 MHz in the following sequence: X = – < CH_2 ≃ O < CO (see Table 1, compounds 23-26).

The NQR frequencies for cis- and trans-$COCl-C_6H_{10}COCl$ (compounds 21 and 22) were practically identical, i.e., in this case the chlorine atoms of the COCl groups have little senstivity to the conformation of the molecule.

EXPERIMENTAL METHOD

The Cl^{35}NQR spectra were obtained with an IS-2 pulse NQR spectrometer at 77°K. The acid chlorides were obtained by reaction of the corresponding carboxylic acids with thionyl chloride and were purified by fractional distillation in vacuo or by recrystallization from organic solvents. The constants of the investigated compounds were in agreement with the reported values.

CONCLUSIONS

1. The Cl^{35}NQR spectra of a number of carboxylic acid chlorides were investigated.

2. The change in the Cl^{35}NQR frequencies in the series of acid chlorides of meta- and para-derivatives of benzoic acid is due to the inductive effect of the substituent.

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