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THE EFFECTS OF FLUORINE SUBSTITUTION ON THE ^{35}Cl NQR SPECTRA OF FLUOROAROMATIC COMPOUNDS CONTAINING ELEMENT-CHLORINE BONDS

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SUMMARY

The ^{35}Cl NQR spectra of pentafluorosubstituted derivatives of benzene $\text{C}_6\text{F}_5\text{X}$ ($\text{X} = \text{N}=\text{PCl}_3, \text{CON}=\text{PCl}_3, \text{SO}_2\text{N}=\text{PCl}_3, \text{N}=\text{CCl}_2, \text{SCl}, \text{COCl}, \text{SO}_2\text{NCl}_2, \text{CONCl}_2, \text{PCl}_2, \text{SO}_2\text{Cl}$) and phosphazocompounds (dimers, $[\text{RN}=\text{PCl}_3]_2$; $\text{R} = \text{C}_6\text{F}_5, \text{C}_6\text{H}_5, 2,3,5,6\text{-tetrafluoropyridyl}$) have been recorded and interpreted. On passing from phenyl to pentafluorophenyl derivatives, the ^{35}Cl NQR frequencies increased. The influence of the relative numbers and positions of the fluorine atoms in the benzene ring on the ^{35}Cl NQR frequencies of fluoro-containing benzoyl chlorides has been discussed. The results are explained in terms of charge alteration on chlorine under the influence of the aromatic fluorine atoms. A linear correlation has been found between ^{35}Cl NQR frequencies of pentafluorophenyl derivatives and those of their hydrocarbon analogues. A relationship between electro-negativity of the element and the ionic character of the element-chlorine bond has been revealed. The reactivities of pentafluorophenyl and phenyl derivatives containing element-chlorine bonds have been predicted using the ν_{Cl} values.

INTRODUCTION

^{35}Cl NQR spectroscopy has been widely used to investigate the character of element-chlorine bonds, including those in organic compounds [1]. However, only episodic ^{35}Cl NQR data exist for polyfluoroaromatic derivatives of group V and VI elements, and no systematic investigation of the influence of fluorine atoms in the

benzene ring on the nature of element-chlorine bonds has been carried out [2]. Nevertheless, knowledge about the character of E-Cl bonds (E - element) is important to define the pattern of nucleophile substitution of chlorine atoms bonded with E in the various organic compounds of group V and VI elements. The influence of the substituents in the aromatic ring on the E-Cl bond can also be investigated by ^{35}Cl NQR spectra. The presence of electron-withdrawing substituents in the benzene ring (such as NO_2 , CF_3) has been shown to lead in some cases to the increase of ^{35}Cl NQR frequencies [1]. The influence of fluorine atoms in the aromatic ring has been found by us recently [3-5] to lead to the shielding of the nuclei of the elements (directly bonded with the aromatic ring) in NMR spectra; at the same time the β -atom of the multiple bond in that situation is deshielded. That led us to suppose that in the polyfluoroaromatic series of compounds the covalence of multiple bonds containing group V and VI elements should increase with respect to hydrocarbon analogues. The change of the ionic character of the E-Cl bond depending on the presence of fluorine atoms in the aromatic ring can also apply. The presence of chlorine atoms within these molecules provides us with a probe that gives information not only about the structural position of this element but also about the nature of the bond in which it is involved. In the present work we have compared the influence of the phenyl and pentafluorophenyl fragments on the ^{35}Cl NQR frequencies in the aromatic derivatives of the same type containing E-Cl bonds.

RESULTS AND DISCUSSION

^{35}Cl NQR spectral data for polyfluoroaromatic compounds and their hydrocarbon analogues are presented in the Table. The assignment of the frequencies in the case of the compounds containing non-equivalent chlorine atoms can be made without difficulties. The phosphorus atom in phenyl-, pentafluorophenyl- and trifluoromethyltetrachlorophosphoranes has the trigonal bipyramidal geometry of bonds, chlorine atoms being in axial and equatorial positions, with the Ar group occupying the remaining axial position. These compounds have been investigated by the ^{35}Cl NQR method. The high frequency lines have been shown to correspond to equatorial chlorine atoms and the low frequency lines - to axial ones [5-7]. The penta-

fluorophenyl compounds are characterized by higher frequencies relative to their hydrocarbon analogues (see Table). That difference is substantially greater in the case of phosphines (≈ 4 MHz) than for phosphoranes.

Phosphazo compounds $(\text{RNPCl}_3)_n$ are known to exist in monomer ($n=1$) or dimer ($n=2$) forms depending on the fragment R : ^{35}Cl NQR spectra of those forms have been investigated rather widely [8]. In the cases where R = PhCO, $\text{C}_6\text{F}_5\text{CO}$ and polyfluoroaryl containing NO_2 or CF_3 groups, as has been shown by us on the basis of ^{31}P and ^{15}N NMR, Raman and mass-spectra, the phosphazo compounds are monomeric. Their ^{35}Cl NQR spectra contain 5 signals with intensity ratio 2:1:1:1:1 interpreted in terms of the presence of two crystallographically non-equivalent molecules in the elementary unit of the crystal [9] (see Table).

Phosphazo compounds $(\text{RNPCl}_3)_n$ containing C_6F_5 and 2,3,5,6-tetrafluoropyridyl groups exist as dimers in the crystalline state. The ^{35}Cl NQR spectra of the latter are characterized by singlet and doublet signals of substantially different frequencies assigned to axial and equatorial chlorine atoms (1:3 respectively) (see Table)[9]. These phosphazo compounds are monomeric in organic solvents or in the liquid state [10]. Conditions have been found [9] to observe the transformation of 2,2,2,4,4,4-hexachloro-1,3-bis(pentafluorophenyl)-1,3-diaza-2,4-diphosphacyclobutane (I) into the less stable monomeric form of (p,p,p-trichlorophosphazo)-pentafluorobenzene (II) in the solid state. Thus, the crystal structure obtained by fast crystallization of the melted dimer form of (I) (temperature 250°C) under liquid nitrogen temperature, consists only of the monomeric form (II). In ^{35}Cl NQR spectra, the frequencies of chlorine atoms of (I) are absent and 5 new signals are observed (intensity ratio 2:1:1:1:1) interpreted as above. The assignment of the signals of form (II) has been made in [8].

The comparison of ^{35}Cl NQR data for monomer and dimer forms of the phosphazo compounds $(\text{C}_6\text{H}_5\text{NPCl}_3)_n$ and $(\text{C}_6\text{F}_5\text{NPCl}_3)_n$ shows an increase of frequencies of c.a. 1 MHz for pentafluorophenyl derivatives. Hence, the direction of the effect (the increase of ^{35}Cl NQR frequency) in the case of polyfluorinated compounds does not depend on the element and its valence state, but the magnitude of the effect varies in the wide range. A linear correlation dependence between

TABLE
 ^{35}Cl NQR spectral data and q_{Cl} for aromatic compounds of ArX type containing E-Cl bonds

X	q_{Cl}	$\nu_{\text{Cl}}^{\text{C}_6\text{F}_5}$, MHz (relative intensity)	q_{Cl}	$\nu_{\text{Cl}}^{\text{C}_6\text{H}_5}$, MHz (relative intensity)
PCl_2	-0.85	30.442, 29.930	-0.43	26.24, 26.54
PCl_4	-0.37	34.480 ^a , 34.380 ^a , 34.290 ^a , 25.300 ^b [7]	-0.40	33.74 ^a (3), 25.06 ^b (1) [6]
$\text{N}=\text{PCl}_3^{\text{c}}$	-0.35	31.166 ^a (2), 31.018 ^a (1), 29.252 ^a (1), 29.005 ^b (1), 28.901 ^b (1)		
$\text{CON}=\text{PCl}_3$	-0.36	29.573 ^a (2), 30.873 ^a (1), 30.742 ^a (1), 29.812 ^b (1), 29.421 ^b (1)	-0.38	28.420 ^a (2), 29.352 ^a (1), 29.645 ^a (1), 28.042 ^b (1), 28.200 ^b (1)
$\text{N}=\text{PCl}_3$	-0.37	30.639 ^a (2), 29.531 ^a (1), 29.190 ^a (1), 29.351 ^b (1), 29.250 ^b (1)	-0.39	29.533 ^a (2), 28.515 ^a (1), 28.013 ^a (1), 28.410 ^b (1), 28.105 ^b (1)
$\text{N}=\text{CCl}_2$	-0.20	38.031 ^a (2), 36.727 ^b (1), 35.548 ^b (1)	-0.22	36.128, 37.047 [21]
$\begin{array}{c} \text{-N-PCl}_3 \\ \\ \text{Cl}_3\text{P-N-} \end{array}$	-0.36	31.093 ^a , 30.903 ^a , 27.750 ^b	-0.37	30.53 ^a , 30.74 ^a , 26.28 ^b [22]
$\begin{array}{c} \text{-N-PCl}_3 \\ \\ \text{-N-PCl}_3 \\ \\ \text{Cl}_3\text{P-N-} \end{array}^{\text{d}}$	-0.34	31.898 ^a , 31.184 ^a , 29.374 ^b		
SO_2NPCl_3	-0.34	30.919	-0.35	30.375 ^a (2), 29.912 ^b (1)
CH_2Cl	-0.23	35.756	-0.28	33.627 [1]
CHCl_2	-0.18	38.192, 38.367 [2]	-0.23	36.373, 35.77 [1]
SO_2NCl_2	-0.02	53.632	-0.04	52.606 [23]
CONCl_2	0.02	56.278	-0.04	56.061

SCl	-0.17	39,317, 38,409	-0.21	37,016
SO ₂ Cl	-0.25	35,154	-0.30	32,892, 32,538, 32,470, 32,538 [1]
				32,808 ^e [1]
				33,446 ^f [1]
COCl	-0.31	32,06	-0.36	29,918
			-0.31	30,368 ^g
			-0.35	30,48 ^h
			-0.356	30,058 ^e
				30,790 ⁱ
				30,900 ^f
			-0.33	31,109 ^j
			-0.32	31,866 ^k
			-0.30	31,820 ^l

NOTES : a ν_{Cl} , b ν_{Cl} , c 2-nitro-5-(trifluoromethyl)-3,4,6-trifluorophenyl, d 2,3,5,6-tetrafluoropyridyl, e 4-fluorophenyl, f 2,5-difluorophenyl, g 2-fluorophenyl, h 3-fluorophenyl, i 2,6-difluorophenyl, j 2,3,4,5-tetrafluorophenyl, k 2,4,5,6-tetrafluorophenyl, l 2,3,5,6-tetrafluorophenyl.

the frequencies of pentafluorophenyl derivatives and their hydrocarbon analogues exists :

$$\nu_{\text{C}_1^{\beta}\text{H}_5\text{X}} = 0,96 \nu_{\text{C}_1^{\beta}\text{F}_5\text{X}}$$

$$r = 0,994, s = 0,8, n = 16$$

This observation can be explained by the decrease of the ionic character of E-Cl bonds in the case of pentafluorophenyl-containing compounds and indicates the changes in the hybridization of the element E and its orbital population.

This could be assigned either to the special influence of fluorine or to the known effect connected with the increase of electron-withdrawing properties of aryl substituent under the action of fluorine atoms. A choice between these possibilities can be based on the ^{35}Cl NQR spectra of fluoro-containing benzoyl chlorides. The analysis of the data of Table allows us to note the following regularities :

a. Meta- ($\Delta\nu_{\text{Cl}} = 0,562$ MHz) and ortho- ($\Delta\nu_{\text{Cl}} = 0,45$ MHz) fluorine atoms exert greater influences on ^{35}Cl NQR frequencies in monofluorosubstituted benzoyl chlorides (in respect to the non-substituted one), than the para-fluorine atom ($\Delta\nu_{\text{Cl}} = 0,14$ MHz). The observed shift to the higher frequencies corresponds in these cases to the inductive effects of fluorine atoms as substituents in the benzene ring.

b. The values of ^{35}Cl NQR frequencies, calculated by the simple additive scheme, are in rather satisfactory accordance with the experimental ones.

Hence, the influence of fluorine atoms on the ^{35}Cl NQR frequencies can be concluded to obey the usual regularity - i.e., the fluorine atoms in the benzene ring do not possess any special effects towards ^{35}Cl NQR frequencies of the chlorine atoms of element-chlorine bonds in the functional groups.

The reason for the described increase of ^{35}Cl NQR frequencies can be found in the change of the charge on the chlorine atom. The presence of fluorine atoms in the aromatic ring leads to an increase of the positive charge on the element bonded with the aryl fragment. The effective charges on the chlorine atoms calculated from ^{35}Cl NQR frequencies are more positive in polyfluoroaromatic compounds than in their hydrocarbon analogues (see Table). The value of charge on the chlorine atoms was calculated by Townes and Dailey [11] from ^{35}Cl NQR frequencies. In that case the value of charge

q_{Cl} is calculated through the number of non-balanced p-electrons (n_p) [12] and therefore its precision is equal as for fluorinated as for hydrocarbon series of compounds. The values of q_{Cl} , obtained by that way, are in good agreement with those obtained from CNDO/2 calculations and X-ray ClK_{α} shifts (see [13]). The greater electronegativity of the pentafluorophenyl group leads to an increase of electron-withdrawing ability of the element E accompanied by the X-ray photoelectron shift of the inner levels of element E to higher energies, indicating the increase of positive charge on E [14,15]. The same conclusion follows directly from X-ray K_{α} - shifts of phosphorus and sulphur [16,17]. Hence the positive charge on chlorine atoms bonded with the element E also increases, leading to the more effective overlap of element and chlorine orbitals and to the decrease of ionic character of E-Cl bonds.

The qualitative connection between the electronegativity of the element and the ionic character of the bond E-Cl has been established [12]. We have obtained the linear correlation dependence between these values (see Table).

$$G = 3,1 - 2,1 I$$

$$r = 0,97, s = 0,1, n = 18$$

where G - the electronegativity of the element E;

I - the ionic character of the E-Cl bond calculated ^{35}Cl NQR frequencies by [18].

The ionic character of the bond E-Cl depends on the nature of the element E : in the aliphatic derivatives of nitrogen, sulphur and phosphorus it is equal to 5, 28 and 47% respectively. The greater ionic character leads to a decrease of ^{35}Cl NQR frequency. That fact corresponds to our conclusion that the presence of fluorine atoms in the aromatic ring leads to less ionic character of bonds in the functional group bonded with that ring.

The difference ν_{Cl} for the compounds of the same type (Table) correlates qualitatively with the ionic character of the E-Cl bond. Thus, for the pairs of the compounds $C_6F_5SO_2NCl_2-C_6H_5SO_2NCl_2$; $C_6F_5SCl-C_6H_5SCl$; $C_6F_5PCl_2-C_6H_5PCl_2$, ν_{Cl} is 1; 2,3; 4,2 MHz respectively, indicating the different influence of the C_6F_5 -ring on the ionic character of the E-Cl bonds. Hence, the influence of the C_6F_5 group on the reactivities of similar compounds of various elements in the reactions involving E-Cl bonds also can be different. E.g., in the case of $RNCl_2$ compounds, reactions occur similarly when $R = C_6H_5$

or C_6F_5 and the most characteristic are those of homolytic cleavage of N-Cl bonds. Thus N,N-dichloropentafluoroanilines have been shown [19,20] to possess highly chlorinating properties and participate in the oxidative imination reactions, *i.e.* the most usual type of reactions for that class of compounds. Heterolytic cleavage nevertheless, is characteristic for S-Cl and P-Cl bonds and for the compounds containing those bonds the influence of the aryl fragment on the rates of reactions can be observed.

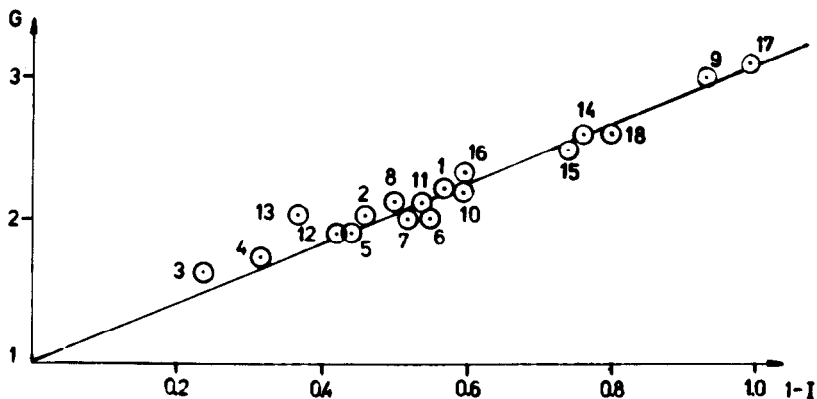


Fig. The dependence between the electronegativity of the elements and the ionic character of E-C bonds : 1 - PCl_3 ; 2 - BCl_3 ; 3 - $AlCl_3$; 4 - $GaCl_3$; 5 - $SiCl_4$; 6 - $GeCl_4$; 7 - $SnCl_4$; 8 - $PbCl_4$; 9 - NCl_3 ; 10 - $SbCl_5$; 11 - $AsCl_3$; 12 - $SbCl_3$; 13 - $BiCl_3$; 14 - S_2Cl_2 ; 15 - $SeCl_4$; 16 - $TeCl_4$; 17 - Cl_2 ; 18 - ICl .

EXPERIMENTAL

All ^{35}Cl quadrupole resonance spectra were recorded on a pulse spectrometer ISSh-1. Searches were conducted in the frequency range from 20 to 45 MHz at the standard temperature of liquid nitrogen (77 K). The experimental frequencies are listed in the Table. Compounds have been obtained as in [24]. The known compounds obtained in this work were identified by the IR and ^{19}F NMR spectra; mixing with authentic samples did not depress the melting points.

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