Journal of Fluorine Chemistry, 4 (1974) 1–7

^{35}Cl NQR SPECTRA OF PENTAFLUOROPHENYLCHLOROMETHANES. THE ELECTRONIC INFLUENCE OF THE PENTAFLUOROPHENYL GROUP

T. A. BABUSHKINA, E. V. BRYUKHOVA AND G. K. SEMIN

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

V. M. VLASOV AND G. G. YAKOBSON

Institute of Organic Chemistry, Siberian Division of the Academy of Sciences, Novosibirsk, 630090 (U.S.S.R.)

(Received March 21, 1973)

SUMMARY

^{35}Cl NQR spectra of pentafluorophenylchloromethanes $C_6F_5CH(R)Cl$ (R = H, CH_3, Cl, $COOC_2H_5$, C_6F_5) have been studied to obtain information on the electronic influence of the C_6F_5 group. On the basis of the data thus obtained and literature data, the electronic influence of the C_6F_5 group is discussed.

INTRODUCTION

One of the important trends in the rapidly developing chemistry of polyfluoroaromatic compounds is research into the behaviour of the functional groups adjacent to polyfluorinated aromatic nuclei. In this connection, in order to estimate the reactivity of functional groups information is essential on the electronic influence of the polyfluorinated aromatic nucleus and, in particular, of the C_6F_5 group.

RESULTS AND DISCUSSION

In recent publications[1–7] a quantitative estimation of the electronic influence of the C_6F_5 group has been given in terms of the σ constants of the C_6F_5 group.

The various methods which have been employed for determining Hammett's σ_m and σ_p constants or Taft's σ_I, σ_R^0 and σ^* constants are summarised in Table 1.

As can be seen from Table 1, the electronic influence of the C_6F_5 group may be characterised by the Hammett σ_m or σ_p constants all of which are fairly

TABLE 1

MAGNITUDES OF THE VARIOUS σ CONSTANTS FOR THE C_6F_5 GROUP

Method of determination (Compound)	σ_m	σ_p	σ_I	σ°_R	Reference
pK_a value (m-, p-$C_6F_5.C_6H_4COOH$)	—0.12	—0.03	—	—	1
pK_a value (p-$C_6F_5.C_6F_4COOH$)	—	+0.45[a]	—	—	2
pK_a value (m-, p-$C_6F_5.C_6H_4\overset{+}{N}H(CH_3)_2$)	+0.34	+0.41	—	—	1
pK_a value ($C_6F_5CH_2COOH$)	—	—	+0.31	—	3
pK_a value ($C_6F_5CR^1R^2OH$)	—	—	+0.18[b]	—	4
^{19}F NMR spectroscopy (m-, p-$C_6F_5.C_6H_4F$)	+0.26	+0.27	+0.25	+0.02	1
^{19}F NMR spectroscopy ($C_6F_5.C_6F_5$)	—	—	+0.15	0.00	1
	—	—	—0.3	+0.1	5
^{19}F NMR spectroscopy (C_6F_5PXY)	+0.22	—	—	—	6
Correlation of reaction rates between C_6F_5X and C_6F_5ONa	—	+0.4	—	—	7

[a] Calculated from the data published in ref. 2.

[b] Calculated from a value of $\sigma^* = 1.1$ obtained from the equation $\sigma_I = \sigma^*/6.23$.

close in magnitude with the exception of one reactive centre (*cf.* ref. 3). However a better method of characterisation may be provided by the various σ_I constants listed for the C_6F_5 group which show some variability in value depending on the reactive centres involved (Table 1). For this reason it was considered of interest to obtain further quantitative data concerning the inductive influence of the C_6F_5 group through the use of a different method in order to obtain a more complete picture regarding the influence of various reactive centres on the C_6F_5 group.

Thus, in the present paper we have studied the ^{35}Cl NQR spectra of the various pentafluorophenylchloromethanes, $C_6F_5CH(R)Cl$ (R = H, CH_3, Cl, $COOC_2H_5$ and C_6F_5), listed in Table 2.

Previously, linear correlations had been shown to exist between the frequencies of the ^{35}Cl NQR spectra of the substituted chloromethanes RCH_2Cl, R^1R^2CHCl, $R^1R^2R^3CCl$ and $RCHCl_2$ on the one hand and the pK_a values of the carboxylic acids, RCH_2COOH, and the amines, RCH_2NH_2, as well as the Taft σ^* constants for the RCH_2 groups[8] and for the sum of the R^1, R^2 and R^3 groups[9] on the other hand. We have used these correlations for calculating the frequencies of the ^{35}Cl NQR spectra of compounds (I)–(V) and for comparing the calculated values with

TABLE 2

^{35}Cl NQR SPECTRA OF PENTAFLUOROPHENYLCHLOROMETHANES, $C_6F_5CH(R)Cl$ (I)–(V), AT 77 K

R	Compound	Value of ν(C–Cl) obtained from experimental spectrum/MHz	Average value of frequency ν_e/MHz	Calculated value of frequency ν_c/MHz	Deviation $\Delta\nu = \nu_e - \nu_c$/MHz
H	(I)	35.756	35.76	35.60[a] 35.41[b] 35.36[c]	+0.16 +0.35 +0.40
CH_3	(II)	35.266	35.27	34.52[d]	+0.75
Cl	(III)	38.367 38.192	38.28	37.47[d]	+0.81
$COOC_2H_5$	(IV)	38.031 37.891	37.96	36.67[d]	+1.29
C_6F_5	(V)	38.738	38.74	36.48[d]	+2.26

[a] Obtained from the equation $pK_a = 17.47 - 0.3930\nu$[8], where $pK_a = 3.48$ for $C_6F_5CH_2COOH$[3].
[b] Obtained from the equation $pK_a = 39.79 - 0.9061\nu$[8], where $pK_a = 7.70$ for $C_6F_5CH_2NH_2$[11].
[c] Obtained from the equation $\nu = 33.017 + 1.214\sigma^*$[9], where $\sigma^* = 1.93$ for the C_6F_5 group may be calculated from $\sigma^* = 6.23\sigma_I$ when $\sigma_I = 0.31$[3].
[d] Obtained from the equation $\nu = 32.05 + 1.019\Sigma\sigma^*$[9], where $\sigma^* = 1.93$ for the C_6F_5 group (see footnote c above), $\sigma^*_{Cl} = 2.9$, $\sigma^*_{COOC_2H_5} = 2.11$, $\sigma^*_H = 0.49$, $\sigma^*_{CH_3} = 0$.

those determined experimentally (Table 2). As may be seen from the data, for pentafluorobenzyl chloride (I) the calculated frequencies of the ^{35}Cl NQR spectrum are in satisfactory agreement with the experimental values when a value of $\sigma_I = 0.31$[3] is used for the induction constant of the C_6F_5 group in the correlation equation (see footnotes c and d in Table 2). Excluding the values of $\sigma_I = +0.15$ and -0.3 (Table 1) which were obtained from a correlation with the chemical shifts of the fluorine atoms in decafluorodiphenyl[1,5] and which are too low, the interesting value is that of $\sigma_I = +0.18$ obtained from the correlation of the pK_a values of the tertiary alcohols $C_6F_5CR^1R^2OH$[4]. Since the NQR frequency value of the chlorine atom in pentafluorobenzyl chloride correlates well with the pK_a values of pentafluorophenylacetic acid or pentafluorobenzylamine (Table 2), the pK_a value of pentafluorobenzyl alcohol may be calculated through the use of a correlation of the type $pK_a(XCH_2OH)$–$\nu(XCH_2Cl)$ given by the equation[8]:

$$pK_a = 39.10 - 0.7209\nu \quad (1)$$

The calculated value of $pK_a = 13.30$ for $C_6F_5CH_2OH$ may be introduced into the equation which links the value of the σ^* constant with the pK_a values of the alcohols RCH_2OH[12]:

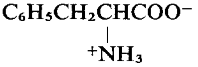
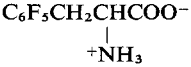
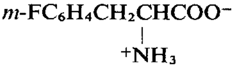
$$pK_a = -1.316\sigma^* + 16.23 \quad (2)$$

The calculated value of $\sigma^* = 2.22$ and the value of $\sigma_I = 0.36$ recalculated through the use of the equation $\sigma_I = \sigma^*/6.23$ lead to satisfactory agreement with the values of σ_I for the C_6F_5 group obtained from the data given in Tables 1 and 2. The accuracy of a value of $\sigma_I \sim 0.3$ for the C_6F_5 group is also confirmed by the fact that the calculated magnitudes of 14.9 and 15.44 for the pK_a value of $C_6H_5CH_2OH$ obtained from an application of equations (1) and (2) using $\nu(C_6H_5CH_2Cl) = 33.63$ MHz and $\sigma^*(C_6H_5) = 0.6$ respectively are also in satisfactory agreement with the experimentally determined value of p$K_a = 15.4$[12]. A number of deviations from the correlation for alcohols containing the C_6F_5 group pointed out by earlier authors[4] may be attributed to the low value previously assumed for the σ^* constant for the C_6F_5 group.

If the relative effectiveness of the inductive influence of the fluorine atoms in pentafluoro derivatives of benzene of the type $C_6F_5CH_2X$ are compared (Table 3), it may be concluded that the inductive influence of the C_6F_5 group in such compounds is only slightly dependent on the nature of the reactive centre X and may be evaluated through the use of the constants $\sigma_I \sim 0.3$ or $\sigma^* \sim 1.9$.

TABLE 3

RELATIVE INFLUENCE OF FLUORINE ATOMS ON THE ACIDITY OF THE PENTAFLUORO DERIVATIVES OF BENZENE

Compound	pK_a	$\dfrac{\Delta pK_a(C_6F_5CH_2X - C_6H_5CH_2X)}{\Delta pK_a(m\text{-}FC_6H_4CH_2X - C_6H_5CH_2X)}$
$C_6H_5CH_2OH$	14.86[a]	
$C_6F_5CH_2OH$	13.30[a]	4.0
m-$FC_6H_4CH_2OH$	14.47[a]	
$C_6H_5CH_2NH_3^+$	9.33[a]	
$C_6F_5CH_2NH_3^+$	7.40[a]	3.9
m-$FC_6H_4CH_2NH_3^+$	8.84[a]	
$C_6H_5CH_2COOH$	4.31	
$C_6F_5CH_2COOH$	3.48	4.6[3]
m-$FC_6H_4CH_2COOH$	4.13	
 $C_6H_5CH_2\underset{^+NH_3}{\underset{\vert}{C}}HCOO^-$	2.16 (COO^-)	
	9.12 (NH_3^+)	
 $C_6F_5CH_2\underset{^+NH_3}{\underset{\vert}{C}}HCOO^-$	1.88 (COO^-)	4.6 (COO^-)[3]
	8.47 (NH_3^+)	4.6 (NH_3^+)[3]
 $m\text{-}FC_6H_4CH_2\underset{^+NH_3}{\underset{\vert}{C}}HCOO^-$	2.10 (COO^-)	
	8.98 (NH_3^+)	

[a] Calculated using the equation p$K_a = 39.10 - 0.7209\nu$ for $ArCH_2OH$[8] and p$K_a = 39.79 - 0.9061\nu$ for $ArCH_2NH_2$[8], where ν is the NQR frequency of chlorine in the corresponding $ArCH_2Cl$ compound.

It should be noted that the value of the NQR frequency of chlorine in pentafluorobenzyl chloride ($\nu_e = 35.76$ MHz) is substantially higher than that calculated on an additive basis ($\nu_c = 34.45$ MHz) using the NQR frequencies of chlorine in *o*-, *m*- and *p*-monofluorobenzyl chlorides [ν(*o*-F) $= 33.602$[13], ν(*m*-F) $= 34.168$[13], ν(*p*-F) $= 33.524$[13] and 33.511 MHz[14]] and in benzyl chloride ($\nu = 33.63$ MHz[14]). This is somewhat unexpected, since the calculated value of pK_a for pentafluorophenylacetic acid, obtained from the corresponding pK_a values of monofluorophenylacetic acids on a similar additive basis, is in good agreement with the value obtained experimentally[3]. In contrast, the calculated NQR frequencies for the chlorine atoms in *m*- and *p*-monofluorobenzyl chlorides as calculated from the equation[8] p$K_a = 17.47 - 0.3930\nu$, where p$K_a = 4.13$ and 4.22 for *m*- and *p*-monofluorophenylacetic acids respectively[3], are in good agreement with the experimental values. A similar calculation for *o*-fluorobenzyl chloride using p$K_a = 4.07$ for *o*-fluorophenylacetic acid[3], however, gives a higher value for the calculated NQR frequency of the chlorine atom ($\nu_c = 34.10$ MHz) in comparison to the experimental value ($\nu_e = 33.602$ MHz)[13]. These variations indicate that the experimental value for the NQR frequency of chlorine obtained for *o*-FC_6H_4-CH_2Cl should be accepted only with caution.

The considerable differences observed between the calculated NQR frequencies for the chlorine atoms in compounds (II)–(V) and the experimental data (Table 2) may be indicative of the considerably reduced contribution of π–σ conjugation to the values of the NQR frequencies for chlorine in these compounds relative to $C_6F_5CH_2Cl$ (*cf.* refs. 13 and 14). It is possible that the smaller contribution of π–σ conjugation is governed by the interaction of the C_6F_5 group with the substituent R, leading to a conformation of the molecule $C_6F_5CH(R)Cl$ such that the overlap of the p orbital of the carbon atom nearest to the aromatic ring with the σ orbital of the C–Cl bond is at a minimum (*cf.* ref. 14). Support for this supposition is obtained from the following facts. Firstly, the NQR frequency of chlorine in compounds of the type $RCHCl_2$, where R = CF_3 ($\nu = 38.69$ MHz[15]), CCl_3 ($\nu = 38.74$ MHz[16]), COOH ($\nu = 38.39$ MHz[17]), correlates well with the corresponding σ^* constants[9], in contrast to the NQR frequency of chlorine in $C_6F_5CHCl_2$ (III) ($\nu = 38.28$ MHz). Secondly, it is not unexpected that close agreement is observed between the NQR frequencies of chlorine atoms in compounds of the type $C_6F_5CH(R)Cl$, where R = $COOC_2H_5$ (IV) and C_6F_5 (V), since the compounds $C_6F_5CH_2Cl$ and $ClCH_2COOC_2H_5$ have very similar values of the NQR frequency for chlorine, *i.e.* 35.76 and 35.96 MHz respectively[8].

Similar values of $\Delta\nu$ for the compounds (II)–(IV) (Table 2) are indicative of a similar acceptor influence for the C_6F_5 group in these compounds. A sharp increase in the value of $\Delta\nu$ for $(C_6F_5)_2CHCl$ (V) may be accounted for in terms of an increased acceptor effect of the C_6F_5 group resulting from the occurrence of a maximum decrease in the π–σ interaction in this compound. This effect runs parallel to the increase in the NQR frequency of the chlorine atom due to the presence of two phenyl groups in $(C_6F_5)_2CHCl$ ($\nu = 34.36$[13] or 34.21 MHz[10]) in comparison with the one phenyl group in $C_6H_5CH_2Cl$ ($\nu = 33.63$ MHz[14]). Since the calculated value of the ^{35}Cl NQR frequency for $(C_6H_5)_2CHCl$ is in fair agreement with the experimental value[9, 10] and in view of the fact that no noticeable additional influence of the crystalline field is observed for polyfluorinated compounds in comparison with their non-fluorinated analogues[18], the considerable differences between the calculated and experimental values of the NQR frequencies for chlorine in $(C_6F_5)CHCl$ must be attributed mainly to the electron-acceptor inductive influence of the C_6F_5 group. Hence the electronic influence of the C_6F_5 group is probably dependent on the number of these groups present at a given reactive centre. This effect could lead to the observed variation of the σ^* constant for the C_6F_5 group from a value of ~1.9 in $C_6F_5CH_2Cl$ to one of ~2.4 in $(C_6F_5)_2CHCl$. However this supposition must be subjected to further quantitative experimental checking.

EXPERIMENTAL

^{35}Cl NQR spectra were recorded on a pulse NQR spectrometer at 77 K whilst IR spectra were recorded on a UR-20 instrument employing 5% solutions in CCl_4. Compounds (I)–(III) and (V) were prepared by following the procedures described in the literature.

Ethyl pentafluoromandelate (nc) (VI)

3 g (0.0124 mol) of pentafluoromandelic acid[19] were boiled in a solution consisting of 6 cm^3 of alcohol and 1 cm^3 of concentrated H_2SO_4. The mixture was then cooled and poured into water. It was then extracted with ether, the extract washed with water and dried over $CaCl_2$. The ether was distilled off and the residue vacuum-distilled to yield 2.2 g (65%) of compound (VI), b.p. 96–98 °C/11 mmHg, m.p. 45–46.5 °C (petroleum ether 40–60 °C). Analysis: Found: C, 44.25, 44.30; H, 2.45, 2.49; F, 34.93, 35.05%. $C_{10}H_7F_5O_3$ requires C, 44.42; H, 2.59; F, 35.20%. IR: ν_{max} 1010 (s) (C–F), 1535 (s) (polyfluoroaromatic ring), 1757 (s) (C=O), 2885 (w), 2918 (w), 2950 (w), 2995 (m) ($\geqslant$CH, >CH$_2$, –CH$_3$) and 3530 (m) (OH) cm^{-1}.

Ethyl α-chloropentafluorophenylacetate (nc) (IV)

6 g (0.0222 mol) of compound (IV) and 4.8 g (0.023 mol) of PCl_5 were heated for 1 h at 100 °C. The mixture was cooled, poured on to ice water and extracted with ether. The ether extract was washed with a 5% solution of $NaHCO_3$ and then water, and dried over $CaCl_2$. After distilling off the ether the residue was vacuum-distilled to yield 4.2 g (65%) of compound (IV), b.p. 65–67 °C/7 mmHg, n_D^{21} 1.4500. Analysis: Found: C, 41.93, 41.69; H, 2.19, 2.17; Cl, 12.28, 12.45; F, 32.90, 33.37%. $C_{10}H_6ClF_5O_2$ requires C, 41.60; H, 2.08; Cl, 12.30; F, 33.30%.

IR: ν_{max} 1010 (s) (C–F), 1522 (s), 1535 (s) (polyfluoroaromatic ring), 1750 (s), 1785 (s) (C=O), 2885 (w), 2920 (w), 2950 (w), 2980 (w) and 2995 (m) ($\gg$CH, $>$CH$_2$, –CH$_3$) cm^{-1}.

REFERENCES

1 W. A. Sheppard, *J. Amer. Chem. Soc.*, *92* (1970) 5419.
2 M. T. Ryan and K. J. Berner, *Spectrochim. Acta*, *25A* (1969) 1155.
3 V. P. Petrov and V. A. Koptyug, *Organic Chemistry, Tartu*, *3* (1966) 135.
4 I. S. Chang, J. T. Price, A. J. Tomlinson and C. J. Willis, *Can. J. Chem.*, *50* (1972) 512.
5 R. Fields, J. Lee and D. J. Mowthorpe, *J. Chem. Soc. (B)*, (1968) 308.
6 M. J. Barlow, M. Green, R. N. Haszeldine and H. G. Higson, *J. Chem. Soc. (B)*, (1966) 1025.
7 R. J. de Pasquale and C. Tamborski, *J. Org. Chem.*, *32* (1967) 3163.
8 E. K. Tsvetkov, G. K. Semin, D. I. Lobanov and M. I. Kabachnik, *Teoret. Eksper. Khim.*, *4* (1968) 452.
9 I. P. Biryukov and M. G. Voronkov, *Collect. Czech. Chem. Commun.*, *32* (1967) 830.
10 I. P. Biryukov, M. G. Voronkov and I. A. Saphin, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, (1966) 638.
11 J. Birchall and R. Haszeldine, *J. Chem. Soc.*, (1961) 3719.
12 S. Takahashi, L. A. Cohen, H. K. Miller and E. G. Peake, *J. Org. Chem.*, *36* (1971) 1205.
13 M. G. Voronkov, V. P. Feshin and E. P. Popova, *Teoret. Eksper. Khim.*, *7* (1971) 356.
14 J. S. Dewar and M. L. Herr, *Tetrahedron*, *27* (1971) 2377.
15 E. A. Lucken, *J. Chem. Soc.*, (1959) 2954.
16 R. Livingston, *J. Phys. Chem.*, *57* (1953) 496.
17 T. A. Babushkina, T. L. Khotsyanova and G. K. Semin, *Zh. Strukt. Khim.*, *6* (1965) 307.
18 G. K. Semin, T. A. Babushkina and G. G. Yakobson, *Application of NQR in Chemistry*, Khimiya Publishers, Moscow, 1972, p. 30.
19 A. K. Barbour, M. Buxton, P. Coe, R. Stephens and J. Tatlow, *J. Chem. Soc.*, (1961) 808.