INVESTIGATION OF THE TRANSMISSION OF THE ELECTRONIC EFFECTS OF SUBSTITUENTS IN 4- AND 4'-FLUOROBENZYL ETHERS BY THE ¹⁹F NMR METHOD

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Earlier [1] for the case of the binuclear bridging group $-NH-CH_2-$ it was established that the enhanced electron conduction characteristic of metal-containing binuclear bridging groups of the -M-X-type (M = Sn, Hg; X = S, N(SO₂Ph), CH₂) [2-4] can also appear in the case of purely organic binuclear bridging groups containing a heteroatom with an unshared electron pair. The present work was undertaken, first, in order to check this suggestion for a different organic subject, i.e., the binuclear bridging group $-CH_2-O-$. Second, it was interesting to study the matter for an organic analog in the light of our previously obtained [3, 4] contradictory data for Hg-containing binuclear bridging groups Hg-X (X = N, S) on the effect of the direction of transmission of the electronic effects of the substituents on the transmission power of the respective systems. Third, quantitative data on the transmission power of the binuclear bridging group $-CH_2O-$ and the effect of the nature of the solvents on it are essential for our current investigation into the transmission power of the binuclear bridging group -Sn-O-.

In order to solve these questions we synthesized two series of substituted aryl benzyl ethers $ArCH_2OC_6H_4F-4$ (Ia-f, h-k) and $ArOCH_2C_6H_4F-4$ (IIa-h, k) with the "forward" and "reverse" arrangement of the units in the binuclear bridging group $-CH_2O-$, where $Ar = 4-MeOC_6H_4$ (a), $4-MeC_6H_4$ (b), $3-MeC_6H_4$ (c), Ph (d), $4-ClC_6H_4$ (e), $4-FC_6H_4$ (f), $3-ClC_6H_4$ (g), $3-FC_6H_4$ (h), $3-CF_3C_6H_4$ (i), $3, 4-Cl_2C_6H_3$ (j), $4-NO_2C_6H_4$ (k).

For all the compounds (I) and (II) we determined the chemical shift of the fluorine (δF) in relation to internal PhF in proton-donating (chloroform) and aprotic solvents with various polarities (chlorobenzene, pyridine, DMSO) (Table 1). A positive sign for δF corresponds to an upfield shift.

The obtained data (Table 1) indicate that in all the series of compounds δF varies according to the nature of the substituents in the aromatic rings, i.e., the transition from electron-donating to electron withdrawing substituents is accompanied by descreening of the indicator fluorine nucleus. Then, in accordance with a "rough" estimate of the electronic conductivity of the systems from data on the ranges of variations of δF ($\Delta \delta F$) in chlorobenzene the substituents in series (II) ($\Delta\delta F$ = 1.25 ppm) have a rather stronger effect on the fluorine atom than in (I) ($\Delta\delta F$ = 1.06 ppm). For a quantitative assessment of the difference in the transmission power with the "forward" and the "reverse" arrangement of the units in the binuclear bridging group $-CH_2O-$ in relation to the indicator group C_6H_4F a correlation of δF was made for (I) and the corresponding of values for (II) (Table 2, No. 1). Here we obtained a correlation line (r = 0.99), the tangent of the slope of which was ≤ 1 , i.e., in the present case the effectiveness of the transmission of the electronic effects of the substituent depends on the direction of transfer and is rather higher when the oxygen atom is situated directly in the varied substituted aromatic ring [series (II)]. On the basis of the correlation coefficient (r) of the relationships establishing a relation between $\delta F(I)$ or $\delta F(II)$ and the Taft induction constants of the aromatic substituents (σ°) and the Hammett polar constants (σ) [5] (Table 2, Nos. 1-4) it can be concluded that there is no direct polar conjugation between the substituents in the Ar and the F atom both in (I) and in (II). At the same time, for the series of compounds (II) the differences in the quality of the obtained correlations using the whole set of substituents are very small (Table 2, Nos. 3 and 4) and only become perceptible if the correlations are realized without due regard to the δF value of such a strong resonance acceptor as the NO₂ group. Here r increases to 0.994

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TABLE 1. The δF Values of (I) and (II) in Relation to C_6H_5F in Various Solvents (δ , ppm)

Compound	CH Cl ₃	PhCl	Ру	DMSO	Com- pound	CHCl3	PhCl	Ру	DMSO	
(lb) (Ic) (Id) (le) (If) (Ig) (Ii) (Ij) (Ik) (Il)	$\begin{array}{c} 10,73\\ 10,75\\ 10,69\\ 10,62\\ 10,23\\ 10,34\\ 10\\ ,24\\ 10,09\\ 9,82\\ 9,67 \end{array}$	10,89 10,87 10,82 10,76 10,38 10,50 10,37 10,20 9,97 9,83	$\begin{array}{c} 10,91\\ 10,87\\ 10,84\\ 10,73\\ 10,52\\ 10,62\\ 10,48\\ 10,32\\ 10,14\\ 10,10\end{array}$	$\begin{array}{c} 10,82\\ 10,78\\ 10,74\\ 10,73\\ 10,50\\ 10,61\\ 10,48\\ 10,43\\ 10,22\\ 10,20\\ \end{array}$	(Ilb) (Ilc) (IId) (Ilf) (IIf) (IIf) (Ilf) (IIh) (IIi) (II1)	1,34 1,34 1,29 1,25 0,85 1,01 0,81 0,84 0,32	1.62 1,60 1,53 1,48 1,10 1.27 1,03 1.09 0,37	$\begin{array}{c} 1,58\\ 1,59\\ 1,53\\ 1,49\\ 1,27\\ 1,29\\ 1,09\\ 1,16\\ 0,65\\ \end{array}$	1,61 1,53 1,48 1,26 1,36 1,17 1,17 0,70	

TABLE 2. The Parameters of the Correlation Equations $y = \rho x + c$

No.	n	у	x	φ±Δρ	$s_{ m ho}$	S	r	c
1 2 3 4 5 6 7 8 9 10	10 10 9 9 8 6 7 7 10 10 10	$ \begin{array}{c} \delta F(I) \\ \delta F(I) \\ \delta F(I) \\ \delta F(II) \\ \delta F(I) (PhCl) \\ \delta F(I) (PhCl) \\ \delta F(I) (PhCl) \\ \end{array} $	σ [°] σ [°] δF(II) δF(II) δF(IV) δF(IV) δF(I)(CHCl _s) δF(I)(Py) δF(I)(Py)	$\begin{array}{c} 1,17\pm0,09\\ 1,09\pm0,16\\ 1,33\pm0,20\\ 1,20\pm0,20\\ 0,86\pm0,09\\ 0,75\pm0,27\\ 1,00\pm0,25\\ 0,66\pm0,17\\ 1,01\pm0,05\\ 1,28\pm0,11\\ 1,68\pm0,16\end{array}$	$\begin{array}{c} 0,039\\ 0,069\\ 0,086\\ 0,089\\ 0,039\\ 0,102\\ 0,099\\ 0,066\\ 0,020\\ 0,051\\ 0,051\\ 0,070\end{array}$	$\begin{array}{c} 0,037\\ 0,071\\ 0,071\\ 0,082\\ 0,043\\ 0,099\\ 0.940\\ 0.076\\ 0,019\\ 0.041\\ 0.041\\ 0.046\end{array}$	0,996 0,984 0,986 0,981 0,965 0,976 0,977 0,999 0,995 0,994	10,72 10,67 1,45 1,40 9,46 7,56 4,25 12,06 0,24 3,3 7,30

for the $\delta F(II)/\sigma_r^0$ relation and decreases to 0.971 for the $\delta F(II)/\sigma$ relation. In all probability, the obtained data indicate that the quantity of the correlations for $\delta F/\sigma^0$ or $\delta F/\sigma$, which are normally employed as tests for the presence of fully conjugated systems, can be affected significantly even by the presence of only a conjugated fragment in the molecule, as occurs in (II). In turn, the presence of polar conjugation between the substituents in Ar and the oxygen atom in (II) and the absence of such conjugation in (I) are in our opinion responsible for the greater effectiveness of the transmission of the electronic effects of the substituents in (II).

For a quantitative assessment of the relative transmission power of the binuclear bridging group $-CH_2-O-$ we made a correlation of the δF values for the compounds of series (I) with the δF values for the previously investigated corresponding mononuclear analogs ArCH₂C₆H₄F-4 (III) [6], on the one hand, and the δF values of $ArCH_2NHC_6H_4F-4$ (IV) [1], on the other (Table 2, Nos. 6 and 7). From the obtained data it follows that within the accuracy limits achieved in the determination of the coefficients ρ , characterizing the relative transmission power of the investigated binuclear bridging groups, the systems containing the -CH2O- and -CH2NH- bridges have practically the same electron conductivity. In addition, the introduction of an additional unit (the O atom) to the CH_2 group in (III) leads to a significantly smaller decrease in the effectiveness of transmission of the electronic effects of the substituents than occurs in the transition from (III) to the dibenzyl systems ArCH2CH2C6H4F-4 [7]. Thus, to summarize the results from the present and the previous work, it can be concluded that the exaltation of the transmission power can show up both in the case of metal-containing binuclear bridging groups of the $-CH_2-M-$ type (where M is the atom of a heavy nontransition metal) and in the case of purely organic binuclear bridging groups containing a heteroatom with an unshared electron pair of the $-CH_2-Q-$ type (where Q = N, 0). However, the most favorable condition for the manifestation of this effect is the presence in the system of a binuclear bridging group of the -M-Q- type, an illustration of which is provided by the large transmission power of the binuclear bridging group -Hg-H- compared with the bridging atom -Hg- [3].

In order to determine the effect of the nature of the solvents on the transmission power of the binuclear bridging group $-CH_2-O-$ quantitatively we made a correlation between the data

Compound	Yield, %	mp, deg C (sol- vent)	bp, deg C (p, mm Hg)	n_{D}^{20}	Found/calculated, %		
					С	н	
4-MeOC ₆ H ₄ CH ₂ OC ₆ H ₄ F-4	75	82-83 (CH₃OH)	-	-	$\frac{72,66}{72.40}$	5,36	
$4\text{-}\mathrm{MeC}_{6}\mathrm{H}_{4}\mathrm{CH}_{2}\mathrm{OC}_{6}\mathrm{H}_{4}\mathrm{F}\text{-}4$	85	56-57 (CH ₃ OH)	-	-	77,48	5,74	
$3-MeC_6H_4CH_2OC_6H_4F-4$	90	32-33 (CH₃OH)	-	-	77,59	<u>6,04</u>	
$4-FC_6H_4CH_2OC_6H_4F-4$	71	42-43 (CH-OH)	-	-	70,92	4,51	
3-FC ₆ H ₄ CH ₂ OC ₆ H ₄ F-4	55	-	144-145	1,5384	70,45	4,38	
3-CF ₃ C ₆ H ₄ CH ₂ OC ₆ H ₄ F-4	42	-	123-126	1,5350	<u>62.10</u>	4,58	
$3,4-Cl_2C_6H_3CH_2OC_6H_4F-4$	84	29-30	(2) 190–192	-	57,57	3,13	
$3-NO_2C_6H_4CH_2OC_6H_4F-4$	64	52-53 (CH-0H)	-	-	<u>63.01</u>	4,03	
4-MeOC ₆ H ₄ OCH ₂ C ₆ H ₄ F-4	55	64-65 (CH.OH)	-	-	72,31 72,31	4,08	
4-MeC ₆ H ₄ OCH ₂ C ₆ H ₄ F-4	70	57-58		-	72,40	5,64 <u>5,70</u>	
3-MeC ₆ H ₄ OCH ₂ C ₆ H ₄ F-4	45	(CH30H) -	133-135	1,5527	77,75	6,06 <u>5,63</u>	
3-ClC ₆ H ₄ OCH ₂ C ₆ H ₄ F-4	52	-	(3)	1,5649	77,75 <u>65,86</u>	6,06 <u>4.32</u>	
4-NO ₂ C ₆ H ₄ OCH ₂ C ₆ H ₄ F-4	95	112-113	(1)	_	65,96 <u>62,93</u>	4,26 4,19	
3-FC ₆ H₄OCH₂C ₆ H₄F-4	60	(CH30H) ~	$\left \begin{array}{c} 109-113\\(1-2)\end{array}\right $	1,5350	63,16 70,58 70,90	4,08 4.55 4.58	

TABLE 3. The Analytical Data and Physical Characteristics of the Synthesized Compounds

on δF for (I) in the aprotic weakly polar solvent chlorobenzene ($E^T = 37.5$ kcal/mole [8], $\pi^* = 0.709$ [9]), in relation to δF of (I) in the proton-donating chloroform similar in polarity ($E_T = 39.1$ kcal/mole, $\pi^* = 0.710$) and also δF of (I) in the aprotic polar solvents pyridine ($E_T = 40.2$ kcal/mole, $\pi^* = 0.867$) and DMSO ($E_T = 45.0$ kcal/mole, $\pi^* = 1.00$) (Table 2, Nos. 8-10). Here it was found (Nos. 9-11) that in accordance with the obtained slopes of the correlation lines chloroform has practically no effect on the transmission power of (I), in spite of the presence of a potential donor of an unshared electron pair in the bridging group. The transition to more polar media leads to a decrease in the effective ness of the transmission of the electronic effects of the substituents by 20% in pyridine and 60% in DMSO on account of dipole-dipole interactions [9].

EXPERIMENTAL

The ¹⁹F-{¹H} NMR spectra were obtained on a Tesla BS-497 spectrometer at 94.075 MHz and 25°C for dilute solutions (c = 0.2 M). The experimental error of the δ F measurement was ±0.01 ppm. The solvents were purified by standard procedures. The substituted ary1 benzy1 ethers (I) and (II) were obtained by the reaction of the corresponding substituted benzy1 chlorides with substituted sodium phenolates. The described compounds (I) [10] and (II) [11] were identified by their melting and boiling points. The constants and analytical data for the new compounds are given in Table 3. Typical examples of the synthesis of the compounds obtained in the present work are given below.

4-Fluorobenzyl 4-Fluorophenyl Ether (If). To a solution of 0.01 mole of sodium 4fluorophenolate [obtained from 1.12 g (0.01 mole) of 4-fluorophenol and 0.23 g (0.01 g-atom) of sodium] in 50 ml of absolute ethanol we added a solution of 1.44 g (0.01 mole) of 4fluorobenzyl chloride in 30 ml of absolute ethanol. After boiling under a reflux condenser for 2 h the reaction mixture was evaporated under vacuum. The residue was washed with water and with a weak solution of sodium hydroxide. We obtained 1.7 g of a shiny colorless crystalline substance melting at 42-43°C (from methanol, on cooling with acetone and dry ice). 3-Fluorobenzyl 4-Fluorophenyl Ether (Ic). A solution of 2.68 g (0.02 mole) of sodium 4-fluorophenolate and 2.9 g (0.02 mole) of 3-fluorobenzyl chloride in 80 ml of absolute ethanol was boiled under a reflux condenser for 2 h. The solvent was evaporated under vacuum. The residue was dissolved in ether, and the solution was washed with water and with a weak solution of sodium hydroxide and dried with sodium sulfate. After vacuum distillation we obtained 2.5 g of a colorless liquid boiling at 144-145°C (5 mm Hg).

CONCLUSIONS

1. The ¹⁹F-{¹H} spectra of a series of 4- and 4'-fluoroaryl benzene ethers $ArCH_2OC_6H_4F-4$ and $ArOCH_2C_6H_4F-4$ were investigated.

2. The transmission power of the binuclear bridging group $-CH_2O-$ differs little from that of the CH₂ group.

3. The effectiveness of the transmission of the electronic effects of the substituents in $ArCH_2OAr'$ depends on the direction of transfer and is highest in the case where the oxygen atom is near the variable substituent.

4. Unlike the proton-donating chloroform, aprotic polar solvents reduce the electron conduction of $ArCH_2OC_6H_4F-4$.

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