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INFLUENCE OF SUBSTITUENTS ON THE CHEMICAL SHIFT OF FLUORINE IN CERTAIN FLUOROSUBSTITUTED ARYLPHENYLMERCURY COMPOUNDS AND N-ARYLMERCURY DERIVATIVES OF BENZENESULFONANILIDE

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Earlier [1], in a <sup>19</sup>F NMR investigation of the electronic influence of substituents (EIS) on the chemical shifts of fluorine (CSF) in fluorosubstituted phenyl benzyl ethers  $ArCH_2OC_6H_4F-4$  (2), (3), it was established that with respect to the effectiveness of the transmission of the EIS in the benzyl group to the indicator fluorine atom, the 3-fluorophenyl group is less informative than the 4-fluorophenyl group, whereas the CSF in the 2-fluorophenyl group is virtually independent of the nature of the substituent. In accordance with this, it seemed interesting to determine the degree of generality of the principles detected for structurally similar organic and organometallic compounds, and also to compare the behavior of mono- and binuclear bridge systems in this sense.

To determine the relative sensitivity of the shielding of F in various positions of the indicator fluorophenyl group to the EIS in an aromatic ring, separated from the indicator by a mono- or binuclear bridge group, in the present work we investigated the following series of model compounds:  $ArHgC_6H_4F-3$  (Ia-k),  $ArHgC_6H_4F-2$  (IIa, c, d, e, h),  $ArHgN(SO_2Ph)C_6H_4F-3$  (IIIa, c, e, f, i, k), and  $ArHgN(SO_2Ph)C_6H_4F-2$  (IVa-f, h, k), where  $Ar = 4-Me_2NC_6H_4$  (a),  $4-MeOC_6H_4$  (b),  $4-MeC_6H_4$  (c), Ph (d),  $4-ClC_6H_4$  (e),  $4-FC_6H_4$  (f),  $3-ClC_6H_4$  (g),  $3-CF_3C_6H_4$  (h),  $3,4-Cl_2C_6H_3$  (i),  $3,5-Cl_2C_6H_3$  (j), and  $3,4,5-Cl_3C_6H_2$  (k), for which the CSF were determined with respect to PhF in PhC1 (Table 1). A positive sign of the CSF corresponds to a strong-field shift.

In connection with the tendency for symmetrization of nonsymmetrical arylmercury compounds, the compounds of type (I) and (II) were generated in solution by exchange reactions  $Ar_2Hg + Hg(C_6H_4F-3(2))_2 \rightleftharpoons ArHgC_6H_4F-3(2)$ 

which, as was established, are slow in the NMR time scale.

From the data (see Table 1) it follows that for both the 3-fluorophenyl-substituted series of compounds (I) and (III) the changes in the CSF corresponds to the nature of the substituents in Ar. However, the range of variation of the CSF of (III) ( $\sim 0.5$  ppm) is somewhat smaller than for (I) ( $\sim 0.75$  ppm). For series (II) the electron-donor group Me<sub>2</sub>N has the same influence on the CSF as H, while the transition to acceptor substituents is accompanied by a

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Compound	CSF, ppm	Compound	CSF, ppm	Compound	CSF, ppm
(Ia) (Ib) (Ic) (Id) (If) (Ig) (Ih) (Ii) (Ij) (k)	$\begin{array}{c} 0,13\\ 0,03\\ 0,06\\ -0,11\\ -0,17\\ -0,19\\ -0,27\\ -0,34\\ -0,46\\ -0,61\\ \end{array}$	(IIa) (IIc) (IId) (IIh) (IIIa) (IIc) (IIId) (IIIe) (IIIe) (IIIf)	$\begin{array}{c} -19,46\\ -19,40\\ -19,47\\ -19,71\\ -1,56\\ -1,77\\ -1,76\\ -1,80\\ -1,89\\ -1,91\end{array}$	(IIIk) (IVa) (IVc) (IVd) (IVe) (IVf) (IV h) (IV k)	$\begin{array}{r} -2,05\\12,49\\12,61\\12,72\\12,78\\12,78\\12,70\\12,61\\12,48\end{array}$

TABLE 1. Chemical Shifts of Fluorine for (I)-(IV) Relative to PhF in PhCl

TABLE 2. Parameters of the Correlation Equations y = ox + c

No. in order	n *	y	x	ρ±Δρ	s <sub>ρ</sub>	s	r	c
1 2 3 4 5	9 7 9 7 7	CSF (I) CSF (III) CSF (I) CSF (III) CSF (III) CSF (III)	σ° σ° CSF (IV) CSF (V) CSF (I)	$ \begin{vmatrix} -0,50\pm 0,07\\ -0,29\pm 0,08\\ 0,51\pm 0,09\\ 0,33\pm 0,09\\ 0,57\pm 0,23 \end{vmatrix} $	0,032 0,035 0,039 0,039 0,039 0,096	$0,044 \\ 0,043 \\ 0,039 \\ 0,042 \\ 0,061$	0,986 0,967 0,980 0,968 0,947	-0,06 -1,74 0,03 -2,89 -1,71

\*n is the number of compounds in the series.

negligible unshielding of the fluorine ( $\sim 0.25$  ppm). In the case of (IV) the indicator o-F atom does not react at all to the electronic nature of the variable substituents in the aryl radical.

Thus, just as in the previously investigated fluorophenyl benzyl ethers [1], in the fluorophenyl derivatives of arylmercury (II) and N-arylmercuryfluorobenzenesulfonanilides (IV) studied in this work, the CSF of the indicator 2-fluorophenyl group is not sensitive to the real redistribution of electron density in the molecule under the influence of variable substituents in the aryl radical at the bridge atom or group.

Evidently, in this case also, the main factor determining the absence of a change in the shielding of fluorine is the direct eletrostatic interaction through space between the electron shells of F and the atoms of the bridge groups, the change in the electron density on which under the influence of substituents prevents an equivalent change in it on F, thereby equalizing the EIS transmitted along the bonds.

For a quantitative characterization of the qualitative principles detected in the changes in the CSF of the 3-fluorophenyl-substituted series of compounds on the nature of the variable substituents, we constructed a correlation of the CSF in (I) and (III) with the Taft inductive constants of aromatic substituents  $\sigma^{\circ}$  [2] (Table 2, Nos. 1 and 2). In this case, both for mono- (I) and for binuclear (III) bridge systems, satisfactory correlation functions (r = 0.967-0.986) were obtained. Since the relative arrangement of the substituents and the indicator in (I) and (III) is such that direct polar conjugation between them is impossible in principle, the existence of such correlations between the CSF-3 and  $\sigma^{\circ}$  is quite regular and is evidence that, in this case, the shielding of the indicator fluorine atom is determined chiefly by the EIS.

Consequently, a correct idea of the nature of the changes in the electron density in the molecules of the investigated organomercury systems can be obtained using fluorophenyl indicator groups containing a fluorine atom in the 3 position or, as was shown earlier [3, 4], in the 4 position of the phenyl radical.

To determine the relative effectiveness of the EIS on the shielding of fluorine in positions 3 and 4 of the phenyl radical in analogous mono- and binuclear Hg-containing bridge systems, we constructed the correlation of the data on the CSF for (I) or (III) relative to the CSF for the corresponding  $ArHgC_5H_4F-4$  (IV) (cf. [3]) or  $ArHgN(SO_2Ph)C_6H_4F-4$  (V) (cf. [4]) (see Table 2, Nos. 3 and 4).

	Yield.		Found/calc., %			
Compound	%	mp′, °C*	C	н	N	
$4-\mathrm{Me}_{2}\mathrm{NC}_{6}\mathrm{H}_{4}\mathrm{HgN}\left(\mathrm{SO}_{2}\mathrm{C}_{6}\mathrm{H}_{5}\right)\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{F}\text{-}3$	94	149-150	$\frac{42,16}{42,06}$	$\frac{3,08}{3,36}$	$\frac{4,90}{4,91}$	
$4\text{-}MeC_{6}H_{4}HgN\left(SO_{2}C_{6}H_{5}\right)C_{6}H_{4}F\text{-}3$	96	181-182	$\frac{42,06}{42,10}$	$\frac{3,04}{2,98}$	$\frac{2,36}{2,59}$	
$C_6H_5HgN(SO_2C_6H_5)C_6H_4F-3$	84	134-135	$\frac{40,79}{40,95}$	$\tfrac{2,76}{2,68}$	$\frac{2.58}{2,65}$	
$-4\text{-}\mathrm{ClC}_{6}\mathrm{H}_{4}\mathrm{HgN}\left(\mathrm{SO}_{2}\mathrm{C}_{6}\mathrm{H}_{5}\right)\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{F}\text{-}3$	56	155-156	$\tfrac{38,43}{38,44}$	$\frac{2,\!44}{2,\!34}$	$\frac{2,40}{2,49}$	
$3,4\text{-}Cl_2C_6H_3HgN(SO_2C_6H_5)C_6H_4F\text{-}3$	52	213-214	$\tfrac{36,22}{36,22}$	$\frac{2,05}{2,03}$	$\frac{2,43}{2,35}$	
$3{,}4{,}5{-}Cl_{3}C_{6}H_{2}HgN\left(SO_{2}C_{6}H_{5}\right)C_{6}H_{4}F{-}3$	88	223-224	$\tfrac{34,17}{34,24}$	$\tfrac{1,64}{1,76}$	$\tfrac{2,17}{2,22}$	
$4\text{-}Me_2NC_6H_4HgN\left(SO_2C_6H_5\right)C_6H_4F\text{-}2$	98	120-121	$\tfrac{42,05}{42,06}$	$\frac{3,36}{3,36}$	$\frac{4,91}{4,91}$	
$4\text{-}MeC_{6}H_{4}HgN\left(SO_{2}C_{6}H_{5}\right)C_{6}H_{4}F\text{-}2$	80	206-207	$\begin{array}{r} \underline{42,04}\\ \underline{42,10} \end{array}$	$\tfrac{3,14}{2,98}$		
$C_6H_5HgN(SO_2C_6H_5)C_6H_4F-2$	83	157-163	$\frac{40,90}{40,95}$	$\tfrac{2,56}{2,68}$	$\frac{2,67}{2,65}$	
$4\text{-}\mathrm{FC}_{6}\mathrm{H}_{4}\mathrm{HgN}\left(\mathrm{SO}_{2}\mathrm{C}_{6}\mathrm{H}_{5}\right)\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{F}\text{-}2$	95	150-151	$\frac{39,62}{39,60}$	$\frac{2,39}{2,41}$	$\frac{2,52}{2,57}$	
$4\text{-}\mathrm{CIC}_{6}\mathrm{H}_{4}\mathrm{HgN}\left(\mathrm{SO}_{2}\mathrm{C}_{6}\mathrm{H}_{5}\right)\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{F}\text{-}2$	85	195-196	$\tfrac{38,49}{38,44}$	$\frac{2,33}{2,34}$	$\frac{2,42}{2,49}$	
3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> HgN (SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) C <sub>6</sub> H <sub>4</sub> F-2	8 <b>3</b>	127-128	$\frac{38,38}{38,29}$	$\frac{2,09}{2,20}$	$\frac{2,07}{2,35}$	
3,4,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> HgN (SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) C <sub>6</sub> H <sub>4</sub> F-2	94	223-224	$\frac{34,46}{34,24}$	$\frac{1,90}{1,76}$	$\frac{2,29}{2,22}$	

TABLE	3.	Analytical	Data	and	Physical	Properties	of	the
Invest	igat:	ted Compound	ls					

\*From MeOH.

An analysis of the values of  $\rho$ Hg and  $\rho$ Hg-N obtained in this case and characterization of the relative sensitivity of the shielding of the CSF in the 3-FC<sub>6</sub>H<sub>4</sub> group to the EIS in the mono- and binuclear bridge system, respectively, shows that in both types of systems the transition from the 4-FC<sub>6</sub>H<sub>4</sub> group to the 3-FC<sub>6</sub>H<sub>4</sub> group is accompanied by a substantial decrease in the sensitivity of the indicator to the influence of substituents. If we take into consideration the fact that the sensitivity of CSF-4 to the resonance effects of the substituents in substituted benzenes is more than three times the sensitivity of CSF-3 [5], and that a substantial contribution to the interaction along the N-Carom bonds in (V) can be made by resonance effects according to the  $p_{\pi}$ - $p_{\pi}$  and/or  $\sigma$ , $\pi$  types [6], then the causes of the observed decrease in the effectiveness of the EIS in the transition from (V) to (III) are evident. Less understandable are the sources of the detected phenomenon for mononuclear systems, since, as was established earlier [3], interactions along the Hg-Carom bonds in (IV) are chiefly of an inductive type, and the sensitivity of CSF-4 and CSF-3 to the inductive effect of substituents is approximately the same [5].

Earlier [4], on the basis of the slope ( $\rho = 1.18 \pm 0.08$ ) of the correlation straight line, which established the relationship between CSF (V) and CSF (IV), it was concluded that the binuclear bridge group Hg-N transmits the EIS more strongly than the bridge Hg atom. And yet, in an analogous comparison of the CSF of the systems (III) and (I), differing from (V) and (IV) only in the position of the indicator F atom, it was found (see Table 2, No. 5) that for the 95% probability level, considering the error in the determination of the value of  $\rho$ , the bridge Hg atom transmits the EIS more effectively than the Hg-N group. The conclusions obtained, mutually contradictory at first glance, actually are not, but are evidence that the term "transmission capacity of the bridge group" can be used only within the limits of series of compounds in which, with the exception of the bridges, all structural factors, including the indicator groups, are fixed. When this requirement is not observed, we should speak of the transmission capacity of the system as a whole. Therefore, transmission of the EIS is more effective in (III) than in (I), but the transmission capacity of (V) is higher than for its mononuclear analog (IV).

## EXPERIMENTAL

The <sup>19</sup>F-{<sup>1</sup>H} NMR spectra were obtained on a Tesla BS-497 spectrometer (working frequency 94.075 MHz) at 25°C for dilute solutions (concentration 0.2 M). The experimental error in the determination of the CSF is  $\leq \pm 0.01$  ppm. PhCl was purified according to the standard procedure.

N-Arylmercury derivatives of 3'(2')-fluorobenzenesulfonanilides (III) were produced by the reaction of arylmercury hydroxides or acetates with 3(2)-fluorobenzenesulfonanilides or with their Na derivatives. The known starting materials were identified according to melting or boiling points. The constants and analytical data for the new compounds are cited in Table 3. A typical example of the synthesis of the compounds studied is given below.

<u>N-4-Tolylmercury-2'-fluorobenzenesulfonanilide (IIIc).</u> A mixture of solutions of 0.63 g (2.5 mmoles) of benzenesulfo-2-fluoroaniline in 10 ml of hot MeOH and 0.1 g (2.5 mmoles) NaOH in 2 ml of water was poured into a solution of 0.82 g (2.5 mmoles) of 4-tolylmercury acetate in 10 ml of hot MeOH with mixing, heating to boiling, and filtered. The cold solution was evaporated, washed with water, and dried. Yield 1.2 g of a substance with mp 206-207°C (from MeOH).

## CONCLUSIONS

1. In a comparative investigation by the  ${}^{19}F-{}^{1}H$  NMR method of a series of mono- and binuclear bridge systems containing 3- and 2-fluorophenyl indicator groups  $ArHgC_6H_4F-3(2)$  and  $ArHgN(SO_2Ph)C_6H_4F-(2)$ , it was established that in both types of systems the chemical shift (CS) of fluorine in the 3 position, in contrast to the CS of fluorine in the 2 position, is determined chiefly by the electronic influence of the substituents.

2. The 3-fluorophenyl indicator group in the compounds studied is less sensitive to the electronic influence of substituents than the 4-fluorophenyl group.

3. In the presence of the effects of  $\pi$ - or  $\sigma,\pi$ -conjugation along the bonds of the bridge atom to the aromatic ring, the comparative transmission capacity of the bridge groups may vary with changing position of the indicator group in the aromatic ring.

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