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COMPARATIVE STUDY BY THE ^{19}F METHOD OF THE INFLUENCE OF POLAR AND COORDINATING SOLVENTS ON THE EFFICACY OF TRANSFER OF THE ELECTRONIC INFLUENCES OF SUBSTITUENTS IN N-ARYLMERCURI- AND SUBSTITUTED N-BENZYL DERIVATIVES OF 4'-FLUOROBENZENESULFANILIDE

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The present work was devoted to a further quantitative study by the ^{19}F NMR method of the electronic transmission properties of the binuclear bridge grouping (BNG) Hg—N. To answer the question of the reasons for the appearance of the anomalously high efficacy of transfer of the electronic influence of substances through an Hg—N BNG and the considerable influence on it of the nature of the solvent which we have discussed previously [1], considerable interest was presented by a comparison of the results obtained with analogous results for corresponding compounds containing the CH_2—N BNG. With this aim, we have investigated a series of substituted N-benzyl-4'-fluorobenzenesulfanilides of the type of

$$ArCH_2N(PhSO_2)C_6H_4F\text{-}4\ (I);\ Ar = 4\text{-}Me_2NC_6H_4,\ 4\text{-}MeOC_6H_4,\ 4\text{-}MeC_6H_4,\ Ph,\ 4\text{-}FC_6H_4,\ 4\text{-}ClC_6H_4,\ 3\text{-}ClC_6H_4,\ 3\text{-}FC_6H_4,\ 3\text{-}CF_3C_6H_4,\ 3,4\text{-}Cl_2C_6H_3,\ 3,5\text{-}Cl_2C_6H_3,\ 3,4,5\text{-}Cl_3C_6H_2.$$

For compounds (I) we determined the chemical shifts of the fluorine atoms (δF) in relation to PhF as internal standard in the inert relatively specific solvation of PhCl, in the proton-donating $CHCl_3$, and in a series of aprotic coordinating solvents — C_5H_5N, C_4H_8O, and Me_2SO (Table 1). A positive sign of δF corresponds to an upfield shift. Analysis of the results obtained in the PhCl shows that δF in (I) changes according to the nature of the substituents but the range of change $\Delta\delta F$ (1.40 ppm) is somewhat smaller than $\Delta\delta F$ (1.67 ppm) in the corresponding series of N-arylmercuri-4'-fluorobenzenesulfanilides $ArHgN(SO_2Ph)C_6H_4F$-4 (II) [1]. It must be mentioned that the comparison of these magnitudes is completely justified,

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TABLE 1. Values of δF for Compounds (I) and (III) in Various Solvents (ppm)

Ar	(I)					(III)
	$CHCl_3$	PhCl	C_5H_5N	THF	DMSO	PhCl
$4\text{-}Me_2NC_6H_4$	0,25	0,51	0,71	1,32	0,91	−2,05
$4\text{-}MeOC_6H_4$	−0,06	0,21	0,44	1,09	0,78	−2,28
$4\text{-}MeC_6H_4$	0,01	0,24	0,47	1,08	0,76	−2,29
Ph	−0,18	0,13	0,39	1,01	0,65	−2,41
$4\text{-}FC_6H_4$	−0,45	−0,17	0,19	0,77	0,54	−2,48
$4\text{-}ClC_6H_4$	−0,53	−0,27	0,11	0,71	0,50	−2,61
$3\text{-}ClC_6H_4$	−0,53	−0,28	0,06	0,65	0,44	−2,62
$3\text{-}FC_6H_4$	−0,50	−0,23	0,13	0,72	0,50	−2,67
$3\text{-}CF_3C_6H_4$	−0,71	−0,45	−0,04	0,51	0,40	−2,72
$3,4\text{-}Cl_2C_6H_3$	−0,89	−0,59	−0,13	0,41	0,28	—
$3,5\text{-}Cl_2C_6H_3$	−0,97	−0,67	−0,24	0,31	0,20	−2,73
$3,4,5\text{-}Cl_3C_6H_2$	−1,19	−0,89	−0,34	0,17	0,06	—

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

y	x	n*	$\rho \pm \Delta\rho$	s	r	c
δF (II)	δF (I)	12	1,17 ±0,08	0,06	0,993	4,22
δF (III)	δF (II)	10	0,51 ±0,13	0,08	0,950	4,57

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*n is the number of compounds in the series.

since in the present study, as previously, we used the $^{19}F\{^1H\}$ NMR method giving an error of the determination of δF of ∿1% with respect to the total range ΔδF in the series of compounds studied. Thus, this fact alone indicates the somewhat greater sensitivity of the indicator F atom to the contribution of substituents in the organomercury compound (II) as compared with their carbon analogs.

For a quantitative evaluation of the relative transmission capability (TC) of the Hg—N and CH_2—N BNGs a correlation was made of the values of δF in PhCl found for (II) [1] with the values of δF for the corresponding compounds (I) (Table 2). This gave a straight line of which the tangent of the angle of slope, characterizing the relative TCs of the BNGs under consideration, was somewhat greater than unity. Thus, in view of the magnitude of the error in determining the coefficient ρ($\Delta\rho$ = ±0.08), within the framework of the approach used for the 95% confidence level the probability of the TC of a Hg—N BNG is somewhat higher than that for a CH_2—N BNG. Previously [2], in a comparison of the efficacy of the transfer of electronic effects of substituents in mononuclear bridge systems it was established that the TC of the Hg atom was little more than half that of the CH_2 group. Consequently, the introduction of an additional link — a N atom attached to the Hg or to the C — leads to an inversion of the electronic transmission capacity — the Hg-containing group becomes a better conductor.

To ascertain the possible reasons for such inversion we studied in detail the nature of the electronic interactions at different bonds in the binuclear bridge systems considered. With this aim, we synthesized N-phenylmercuri-4(3)-fluorobenzenesulfanilides and N-[4(3)-fluorophenylmercuri]benzenesulfanilides, and also their carbon analogs.

From the δF values for these compounds (Table 3) using the Taft equations for the corresponding correlations [4], we determined the inductive (σ_I) and resonance (σ_R^o) constants of the groupings given in Table 4. Analysis of the results obtained shows that the interactions at the Hg—C_{ar}, N—C_{ar}, and C_{al}—C_{ar} bonds in both bridge systems have basically an inductive nature. However, in contrast to (I), for (II) a substantial contribution to the interaction through the N—C_{ar} bonds of resonance effects due to the conjugation of the unshared pair of N electrons or of the Hg—N σ-bond with the π-electronic system of the aromatic ring of the p_π—p_π- or the σ,π type, respectively, is observed. The considerably smaller relative contribution of such interactions in the case of the carbon-containing analogs is apparently connected with

TABLE 3. δF Values of N-Phenylmercuri-4(3)-fluoro- and N-[4(3)-Fluorophenylmercuri]benzenesulfanilides and their Carbon Analogs in $CHCl_3$

Compound	δF, ppm	Compound	δF, ppm
$PhHgN(PhSO_2)C_6H_4F$-4	3,6	$PhN(PhSO_2)CH_2C_6H_4F$-4	1,46
$PhHgN(PhSO_2)C_6H_4F$-3 [3]	−2,0	$PhN(PhSO_2)CH_2C_6H_4F$-3	−0,15
$PhCH_2N(PhSO_2)C_6H_4F$-4	−0,18	$PhN(PhSO_2)HgC_6H_4F$-4	−2,98
$PhCH_2N(PhSO_2)C_6H_4F$-3	−1,68	$PhN(PhSO_2)HgC_6H_4F$-3	−2,07

TABLE 4. Polar Constants of the Substituents

Substituent	σ	σ_R°
$PhHgN(PhSO_2)$	0,37	−0,19
$PhN(PhSO_2)Hg$	0,38	0,03
$PhCH_2N(PhSO_2)$	0,32	−0,05
$PhN(PhSO_2)CH_2$	0,11	−0,06

conformational factors leading to a disturbance of the coplanarity of the p-orbitals of the N atom and of the π-orbitals of the ring in these systems, and also to a smaller capacity of the C–N σ-bond for σ,π-conjugation. Thus, according to what has been stated, the greater transmission capacity of the Hg–N BNG as compared with the CH_2–N BNG can be explained by a considerable contribution of resonance interactions to the common mechanism of the transmission of electronic effects through $N–C_{ar}$ bonds in organomercury systems.

In order to determine a possible influence of the mutual positions of the links of the Hg–N BNG relative to indicator fluorophenyl grouping on the TC of the system, we synthesized a series of 4-fluorophenylmercuri- derivatives of substituted benzenesulfanilides of the type of $ArN(SO_2Ph)HgC_6H_4F$-4 (III), for which we determined the values of δF in PhCl (see Table 1). A comparison of the values of ΔδF in series (II) (ΔδF = 1.67 ppm) and (III) (ΔδF = 0.68 ppm) with the direct (Hg–N) and the reverse (N–Hg) arrangements of the links in the BNG, respectively, shows that the sensitivity of the F indicator atom to the influence of the substituents that were varied is higher in the first case than in the second, and a quantitative treatment of the results obtained (see Table 2) gives a substantial difference (ρ = 0.51 ± 0,13). Thus, the efficacy of the transmission of electronic influences of substituents in binuclear bridge systems containing the Hg–N BNG depends to a large extent on the direction of transmission. In order to ascertain the reasons for the observed effect in the light of the results that we obtained previously on the different TCs of the Hg–S BNGs in the two directions [5], we subsequently investigated Hg–O and $Hg–CH_2$ BNGs.

It has been established previously [1] that for compounds containing Hg–N BNGs, a transition from an inert solvent (PhCl) to a proton-donating solvent ($CHCl_3$) or to aprotic coordinating solvents (C_5H_5N, C_4H_8O, Me_2SO) is accompanied by a substantial fall in electronic conductivity. This may be a consequence both of dipole–dipole [6] and of coordination interactions of the model compounds (II) investigated with the solvents. Consequently, in the present investigation to evaluate the relative contributions of each of these types of interactions we studied the influence of the nature of the solvents on the transmission of electronic effects of substituents in the structurally related carbon analogs (I), specific solvation in which is definitely absent (see Table 2).

An analysis of the results on δF shows that ΔδF for the series of compounds considered in the PhCl which we selected as standard, comparatively weakly polar but possessing a good dissolving capacity (E_T = 37.5 kcal/mole [7], ε = 5.7 [8]), and in the proton-donating $CHCl_3$ (E_T = 39.1 kcal/mole, ε = 4.8) are practically identical.

The passage from PhCl to C_4H_8O (E_T = 39.1, ε = 4.8), C_5H_5N (E_T = 40.2, ε = 9.0) and on to the most polar Me_2SO (E_T = 45.0, ε = 46.4) was accompanied by a decrease in ΔδF. Thus, an increase in the polarity of the medium leads to a fall in the degree of dependence of δF on the nature of the substituents which is probably connected with the effects of dipole–dipole interactions that were observed previously for systems with other carbon-containing bridge groupings [6]. For a quantitative estimate of the influence of this factor on the transmission capacity of the CH_2—N BNG, a correlation of δF for (I) in each of the above-mentioned solvents in relation to δF for the corresponding compounds in PhCl was made (Table 5).

It can be seen from a comparison of the calculated values of ρ_{CH_2-N} characterizing the relative transmission capacities of the CH_2—N BNG in various solvents with the corresponding values of ρ_{Hg-N} for the Hg—N BNG that we obtained previously, and also with δF in the corresponding series of compounds in various solvents, that the passage from PhCl to Me_2SO, with the highest polarity and the greatest coordination capacity, led to a fall in the efficacy of the transmission of electronic influences of substituents in systems (I) by ~40% and in (II) by ~75%. Consequently, to a first approximation within the framework of the approach used it may be concluded that the "quenching" of the transmission capacity of the Hg—N BNG in coordinating solvents takes through both dipole—dipole and coordination interactions with the solvents with the participation of the vacant 6p-orbitals of the Hg atom, the relative contributions of these interactions being practically identical.

It must be mentioned that the results obtained in the investigation showing the absence of an influence of $CHCl_3$ on the TC of the CH_2—N BNG and the lowering of the TC of the Hg—N BNG in this medium show that the comparison of the efficacy of transmission of electronic influences for these BNGs must be carried out only in PhCl, which is inert for both systems. Consequently, the preliminary results that we have obtained on this question in $CHCl_3$ [9] must be considered with a correction for this fact.

Subsequently, for a more detailed elucidation of the role of the vacant orbitals of the Hg atom in the transmission of the electronic influences of substituents in bridge system (II), it will be of interest to investigate the dependence of the transmission capacity of the Hg—N BNG on intramolecular coordination in model systems of the type of N-arylmercuri-2'-bromo-4'-fluorobenzenesulfanilides.

EXPERIMENTAL

The ^{19}F NMR spectra were obtained on a RYa-2309 spectrometer (84.56 MHz) at 25°C using concentrations of the samples of 0.2 and 0.05 M. The experimental error in the determination of δF did not exceed ±0.01 ppm. The solvents used were purified by standard methods and were additionally redistilled in a current of dry Ar.

The 4-fluorophenylmercuri- derivatives of the substituted benzenesulfanilides were obtained by the reaction of 4-fluorophenylmercury acetate with the Na derivatives of the substituted benzenesulfanilides [1]. The substituted N-benzyl derivatives of the benzenesulfanilides were obtained by the reaction of benzenesulfonyl chloride with the appropriate N-benzylanilines, which, in their turn, were obtained by the reaction of the corresponding anilines with benzyl chlorides [10].

The known initial compounds were identified by their melting and boiling points. The purity of the compounds obtained was checked from ^{19}F NMR and their mass spectra. The constants and results of analysis for the new compounds are given in Table 6. Typical examples of the synthesis of the compounds studied are given below.

N-4-Fluorophenylmercuri-3'-fluorobenzenesulfanilide. With stirring, a mixture of solutions of 0.65 g (2.5 mmole) of benzenesulfo-3-fluoroanilide in 10 ml of hot methanol and of 0.1 g (2.5 mmole) of NaOH in 2 ml of distilled water were added to a solution of 0.9 g (2.5 mmole) of 4-fluorophenylmercury acetate in 10 ml of hot methanol, the mixture was heated to the boil (10-15 min) and filtered, and the filtrate was left overnight. Then it was evaporated and the residue was washed with water and dried. This gave 1.2 g of a substance with mp 167-168°C (from MeOH).

TABLE 5. Parameters of the Correlation Equations $\delta F(L) = \rho\delta F(PhCl) + c$ for (I) and (III)

L	n	ρ±Δρ(I)	s	r	c	ρ±Δρ(II) [4]
$CHCl_3$	11	1,03±0,06	0,03	0,997	−0,26	0,76±0,09
C_5H_5N	11	0,75±0,04	0,02	0,998	0,30	0,58±0,05
C_4H_8O	11	0,84±0,04	0,02	0,999	0,90	0,54±0,09
Me_2SO	10	0,61±0,07	0,03	0,995	0,63	0,28±0,15

TABLE 6. Analytical Results and Physical Properties of the Compounds Investigated

Compound	Yield, %	mp or bp, °C (p. mm Hg)	Found/calculated, %	
			C	H
$4\text{-}FC_6H_4HgN(SO_2Ph)C_6H_4NMe_2\text{-}4$	90	171–172 methanol	41,83/42,06	3,24/3,36
$4\text{-}FC_6H_4HgN(SO_2Ph)C_6H_4OMe\text{-}4$	82	151–152 methanol	40,47/40,89	2,82/2,90
$4\text{-}FC_6H_4HgN(SO_2Ph)C_6H_4Me\text{-}4$	80	146–147 methanol	42,21/42,10	3,01/2,98
$4\text{-}FC_6H_4HgN(SO_2Ph)Ph$	84	175–176 methanol	40,55/40,95	2,62/2,68
$4\text{-}FC_6H_4HgN(SO_2Ph)C_6H_4Cl\text{-}4$	68	155–157 methanol	38,08/38,44	2,40/2,34
$4\text{-}FC_6H_4HgN(SO_2Ph)C_6H_4Cl\text{-}3$	65	161–163 methanol	38,42/38,44	2,33/2,34
$4\text{-}FC_6H_4HgN(SO_2Ph)C_6H_4CF_3\text{-}3$	98	167–168 methanol	38,63/38,29	2,16/2,20
$4\text{-}FC_6H_4HgN(SO_2Ph)C_6H_4F\text{-}3$	84	152–153 methanol	39,57/39,60	2,38/2,41
$4\text{-}FC_6H_4HgN(SO_2Ph)C_6H_3Cl_2\text{-}3,5$	78	226–227 methanol	36,23/36,22	1,99/2,03
$3\text{-}FC_6H_4N(SO_2Ph)CH_2Ph$	74	81–83 hexane	66,93/66,84	4,79/4,73
$3\text{-}FC_6H_4HgN(SO_2Ph)Ph$	90	171–172 methanol	41,15/40,95	2,84/2,68
$3\text{-}FC_6H_4CH_2N(SO_2Ph)Ph$	88	83–84 heptane	66,84/66,84	4,88/4,10
$4\text{-}FC_6H_4CH_2N(SO_2Ph)Ph$	96	110–111 heptane	66,60/66,84	4,69/4,73
$4\text{-}FC_6H_4CH_2NHPh$	92	145 (1)	77,62/77,58	6,08/6,02
$3\text{-}FC_6H_4CH_2NHPh$	90	142 (1)	76,61/77,58	5,81/6,02

N-(3-Fluorobenzyl)aniline. A mixture of 14.5 g (0.1 mmole) of 3-fluorobenzyl chloride, 37.3 g (0.4 mole) of aniline, and 10.6 g of Na_2CO_3 was heated with stirring to 110°C for 1 h, followed by cooling, washing with water, extraction with ether, and drying with Na_2SO_4. After elimination of the ether, the residue was distilled in vacuum in an atmosphere of Ar. This gave 10.2 (90%) of a light yellow liquid with bp 142-144°C (2 mm).

N-(3-Fluorobenzyl)benzenesulfanilide. A solution of 2.01 g (10 mmoles) of N-(3-fluorobenzyl)aniline in 7 ml of acetone was treated with 1 ml of pyridine and a solution of 1.8 g (10 mmoles) of benzenesulfonyl chloride in 5 ml of acetone, after which the mixture was kept for 12 h and was poured into water, and the resulting mixture was filtered. The crystallization of the residue from heptane gave 2.7 g (88%) of a colorless crystalline substance with mp 83-84°C.

CONCLUSIONS

1. In a comparative investigation by the ^{19}F NMR method of two series of model compounds of the type of $ArQN(SO_2Ph)C_6H_4F\text{-}4$ ($Q = Hg, CH_2$), it was established that the Hg–N binuclear bridge grouping (BNG) possesses a greater transmission capacity (TC) than the CH_2–N BNG.

2. The efficiency of the transfer of the electronic influence of substituents to an indicator F atom through the Hg–N BNG depends substantially on the direction of transmission.

3. The decrease in the TC of the Hg–N BNG in coordinating solvents is the result of both dipole–dipole and coordination interactions with the solvent the contributions of which are practically equal.

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A STUDY OF THE ELECTRON-DONATING CAPACITY OF TIN-CONTAINING AMINES BY THE IR-SPECTROSCOPIC METHOD

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The electron-donating capacity of compounds containing a bond between nitrogen and an element of the silicon subgroup (M) has been studied by the IR-spectroscopic method by a number of authors [1-4]. It has been established [5] that organo-Si and organo-Ge substituents in these compounds exhibits not only inductive but also conjugation effects (d_π—p_π interaction), and the influence of steric factors has scarcely been considered. Tin-containing amines have been investigated to a considerably smaller degree and here information on the existence of d_π—p_π interaction in the Sn—N fragment is contradictory [6].

The aim of the present investigation was to study the electron-donating capacity of the tin-containing amines as a function of the nature of the constituents at the N and Sn atoms, and also to compare the results obtained with those for related compounds of C, Si, and Ge. The donating capacity of the tin-containing amine was evaluated from the shift in the frequency ($\Delta\nu$) of the νC—D stretching vibrations in the IR spectrum of $CDCl_3$ (electron acceptor) on the formation of the $Cl_3CD\ldots N{-}Sn{<}$ hydrogen bond. As is well known [7], the values of $\Delta\nu$ are connected with the enthalpy of formation of the H-bond ($-\Delta H$) by a complex relationship. For weak H bonds (shifts $\Delta\nu$ up to 200 cm^{-1}), to which those which we are considering belong, a direct proportionality is observed between $\Delta\nu$ at $-\Delta H$ [7].

Taking into account information [8] on the high reactivity of the Sn—N bond, we have shown specially that during the performance of an experiment at ∿20°C with a volume ratio of $CDCl_3$ to tin-containing amine of 1:5, no reaction between these compounds is observed.

If follows from Table 1 that a variation in the substituents R in compounds of the type of R_3SnNEt_2 has an independent influence on the electron-donating capacity of the amines, which, in the light of the relatively close donor properties of alkyl radicals, shows the absence of a steric influence of the radicals attached to the Sn on the basicity of the tin-containing amine. The introduction of an acceptor vinyl group into the amine molecule leads to a lowering of the parameter $\Delta\nu$ to 81 cm^{-1} for (IV), as compared with 93-97 cm^{-1} for (I)-(III). The replacement of the electron-donating Me groups by the acceptor fragments NR_2 (R = Me, Et) in compounds of the type of $Me_{4-n}M(NR_2)_n$ (M = Si, Ge, Sn) also leads to a decrease in the electron-donating capacity of amines containing the elements mentioned (Table 2).

As follows from a comparison of the values of $\Delta\nu$ for compounds (V)-(VIII) and (XIII)-(XVII) (see Table 1), an increase in the length of the alkyl radical at the N atom leads to a decrease in the donor properties of tin-containing amine. This shows that the influence of

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