Based on the data obtained (see Table 1), the following values of the quenching coefficients of alkyl radicals can be used: $\varepsilon_{\dot{R}}^{max} = (1.28 \pm 0.21)\cdot 10^3$ liters/(mole·cm) and $\varepsilon^{max}_{C_6H_{11}\dot{S}O_2} = (0.89 \pm 0.06)\cdot 10^3$ liters/mole·cm for the cyclohexylsulfonyl radical.

CONCLUSIONS

Methods of determination were proposed and the quenching coefficients of a series of alkyl and cyclohexylsulfonyl radicals were measured by the method of pulsed photolysis.

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^{19}F NMR STUDY OF THE TRANSMISSION CAPACITY OF BINUCLEAR —N(X)SO_2— BRIDGING GROUPS

S. I. Pombrik, L. S. Golovchenko,
A. S. Peregudov, É. I. Fedin,
and D. N. Kravtsov

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In a study of the efficiency of the transmission of substituent electronic effects (SEE) in systems such as $ArHgN(SO_2Ph)C_6H_4F$-4 (I) [1] and $ArHgN(SO_2Ph)C_6H_3Br$-2-F-4 [2], we found that the transmission capacity (TC) of the Hg—N binuclear bridging group (BBG) depends significantly on the participation of the mercury atom in inter- and intramolecular coordination. The TC of the system decreases with increasing coordination strength.

Hence, it was of interest to elucidate whether this behavior is retained when the mercury atom is formally within the bridging group but does not directly participate in bonding the variable Ar group and indicator group (C_6H_4F-4). In the present work, we carried out an ^{19}F NMR study of the effect of coordinating solvents on the efficiency of the transmission of SEE in $ArN(HgPh)SO_2C_6H_4F$-4 (II) systems. In addition, in the framework of this model, independent interest was found in a comparative study of the behavior of organomercury systems (II) with the corresponding unsubstituted proton donor analogs $ArNHCO_2C_6H_4F$-4 (III) under identical conditions, especially since there is no information in the literature on the TC or the organic NH—SO_2 BBG.

In order to determine the nature and efficiency of the transmission of SEE through the $N(HgPh)SO_2$ and $NHSO_2$ BBG, we synthesized two series of model compounds (IIa-i) and (IIIa-i), where Ar = 4-$MeOC_6H_4$ (a), 4-MeC_6H_4 (b), 3-MeC_6H_4 (c), Ph (d), 4-FC_6H_4 (e), 3-FC_6H_4 (f), 3-ClC_6H_4 (g), 4-ClC_6H_4 (h), and 3,4,5-$Cl_3C_6H_2$ (i) and determined the ^{19}F NMR chemical shifts

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A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1263-1267, June, 1986. Original article submitted January 21, 1985.

TABLE 1. ^{19}F NMR Chemical Shifts for $ArN(X)SO_2C_6H_4F\text{-}4$ in PhCl, Me_2SO, and MeOH (ppm)

Series	Solvent	Compound								
		a	b	c	d	e	f	g	h	i
(II)	PhCl	−5,57	−5,73	−5,86	−5,98	−6,12	−6,64	−6,67	−6,45	−7,58
	DMSO	−4,87	−5,06	−5,21	−5,29	−5,18	−5,71	−5,81	−5,69	−6,45
(III)	PhCl	−7,80	−7,89	−7,99	−8,18	−8,41	−8,88	−8,77	−8,68	−9,47
	DMSO	−6,78	−6,98	−7,15	−7,21 *	−7,26	−7,63	−7,79	−7,55	−8,44
(IV)	MeOH	−2,36	−2,44	—	−2,59	−2,67	—	—	−2,95	—

*In MeOH FCS = −7.35

(FCS) in dilute solutions of these compounds in PhCl and DMSO (Table 1). Correlation of the FCS data for (II) and (III) in PhCl relative to the σ_p and σ_p° substituent constants [3] which take account of the presence or absence of direct polar conjugation between the substituents varied and the indicator fluorine atom, respectively, showed that the better agreement (r) for series (II) is obtained in going from σ_p° to σ_p, while for series (III), the agreement is the same for both types of constants (Table 2, Nos. 1-4). Thus, the very moderate direct polar conjugation (R_π [4]) makes a definite contribution to the overall mechanism for the transmission of SEE on the FCS in (III) in addition to the π-inductive conjugation (F_π [4]). The role of R_π is greater in the case of PhHg-substituted compounds (II). We should note that our data for (III) are in accord with the conclusions of Dauphin [5] and Lutskii [6] on the existence of "slight resonance between the Ar π-electron system and the sulfur 3d orbitals, considerable conjugation between nitrogen and the SO_2 group, and a weak interaction of the nitrogen n-electrons with the Ar π-electron system" (i.e., weak direct resonance interaction between Ar and Ar') which were based on studies of the acidity and IR spectra of a broad range of model compound series.

In order to evaluate the relative contribution of the F_π and R_π effects to the transmission of the SEE in systems (II) and (III), we carried out a two-parameter correlation of the FCS with the polar (σ_I) and resonance (σ_R, σ_R°, and $\sigma_{\overline{R}}$) substituent parameters according to the Taft method [7] (Table 3, Nos. 1-4). Analysis of the equations obtained showed that the σ_R resonance parameters best describe the resonance component of the overall mechanism for the transmission of SEE in both (II) and (III). In addition with the values $\lambda < 1$ (see Table 3, Nos. 2 and 4), which characterize the relative contribution of resonance effects to the overall mechanism for the transmission of SEE, we may conclude that the dominant type of transmission of SEE both in (II) and (III) is the F_π effect. About 40% of the SEE $[((\rho_R)/(\rho_I + \rho_R))\cdot 100\%]$ is transmitted in these compounds by the R_π mechanism. The role of this mechanism somewhat increases in going from the unsubstituted benzenesulfonanilides (III) ($\lambda = 0.78$) to their PhHg analogs (II) ($\lambda = 0.89$). This finding, in all likelihood, may be related to an increase in the capacity for conjugation of the unshared electron pair of the nitrogen atom with the π-electron system of the adjacent aromatic ring and the sulfur atom 3d orbitals due to an increase in the polarity of the $N^{\delta-}\text{—}X^{\delta+}$ bond (X = H, Hg) upon replacing the H atom in (III) by the PhHg group. In such a case, we should expect a further increase in the contribution of the R_π effects to the overall mechanism for the transmission of SEE for analogous

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

Number	x	y	n	$s\rho$	$\rho\pm\Delta\rho\,(L=95\%)$	s	r	c
1	FCS (III)	σ_p^{0}	5	0,130	−1,89±0,36	0,050	0,993	−8,14
2	FCS (III)	σ_p	5	0,149	−1,87±0,41	0,057	0,991	−8,24
3	FCS (II)	σ_p^{0}	5	0,245	−1,74±0,67	0,094	0,972	−5,92
4	FCS (II)	σ_p	5	0,070	−1,77±0,19	0,027	0,998	−6,01
5	FCS (II)	FCS (III)	9	0,067	1,12±0,15	0,104		3,19
6	FCS (II) (DMSO)	FCS (II) (PhCl)	9	0,047	0,77±0,11	0,083	0,987	−0,62
7	FCS (I) (DMSO)	FCS (I) (PhCl)	7	0,060	0,28±0,14	0,080	0,911	5,38

TABLE 3. Correlation Parameters of Equations $y = \rho_I\sigma_I + \rho_{\overline{R}}x + c$

Number	y	x	ρ_I	$\rho_{\overline{R}}$	$\lambda \equiv \rho_{\overline{R}}/\rho_I$	c	R
1	XCΦ(III)	σ_R°	−1,87	−2,00	1,07	−8,20	0,992
2	XCΦ(III)	σ_R	−1,75	−1,36	0,78	−8,16	0,998
3	XCΦ(II)	σ_R°	−1,72	−2,02	1,17	−6,02	0,981
4	XCΦ(II)	σ_R	−1,60	−1,39	0,89	−5,98	0,995
5	XCΦ(IV)	σ_R°	−1,11	−1,28	1,15	−2,62	0,944
6	XCΦ(IV)	σ_R	−1,04	−0,90	0,87	−2,60	0,971
7	XCΦ(IV)	σ_R^-	−1,29	−1,34	1,04	−2,62	0,991

systems with negative change on the nitrogen atom (N^-X^+).

In order to check this hypothesis, we determined the FCS for a series of corresponding $ArN^-(Na^+)SO_2C_6H_4F$-4 (IVa, b, d, e, h) in methanol (see Table 1). The statistical analysis of the FCS for (IV) (see Table 3, Nos. 5-7) indicate that, in this case, the transition from σ_R° to σ_R is indeed accompanied by an increase in the correlation coefficient R which reaches a maximum using the σ_R^- nucleophilic constants. In addition, the transmission of SEE in (IV) is accomplished both by the F_π and R_π mechanism, whose contributions are virtually identical (λ = 1.04, No. 7).

Thus, the effect of the polarity of the $N^{\delta-}$—$X^{\delta+}$ bond affects the mechanism for the transmission of SEE in $ArN(X)SO_2C_6H_4F$-4 systems. An increase in this polarity leads to an increase in the contribution of the direct polar conjugation and, as indicated in Table 2 (No. 5), to an increase in the TC of the bridging $N(X)$—SO_2 group.

In order to determine the possible effect of the nature of the solvent on the TC of the $N(PhHg)SO_2$ BBG, we compared the efficiency of the transmission of SEE in systems (II) and (III) in PhCl which is inert relative to specific solvation (E_T = 37.5 kcal/mole [8]) and coordinating DMSO (E_T = 45 kcal/mole [8]) (see Table 1). Analysis of the data for the range of change in the FCS (ΔFCS) for (II) and (III) showed that going from PhCl to DMSO has virtually no effect on the efficiency of the transmission of SEE in (III) ($\Delta FCS_{PhCl} - \Delta FCS_{DMSO}$ = 0.01 ppm) and is accompanied by only a slight drop in the electronic transmission in the case of (II) ($\Delta FCS_{PhCl} - \Delta FCS_{DMSO}$ = 0.43 ppm). Thus, hydrogen bonding with the solvent has virtually no effect on the TC of the $NHSO_2$ BBG, while specific solvation leads to some decrease in the TC of the $N(PhHg)SO_2$ group. For a quantitative evaluation of the effect of coordination interactions with DMSO on the TC in (II), we correlated the FCS for (II) in DMSO relative to these values in PhCl (see Table 2, No. 6).

Comparison of the ρ_{II} value with the previously determined slope ρ_I [1] from the analogous equation for series (I) (see Table 2, No. 7) showed that coordination with DMSO leads to an only extremely slight drop in the TC of the $N(HgPh)SO_2$ BBG relative to the $N(SO_2Ph)Hg$ BBG. This finding indicates that the specific solvation of the metal in metal-containing BBG has a significant effect on their TC only when the metal is directly in the chain of transmission of the SEE.

EXPERIMENTAL

The ^{19}F—{^1H} NMR spectra were taken on a Bruker WP-200 spectrometer at 188.3 MHz at 27°C and 0.2 and 0.1 M sample concentrations. The experimental error in the determination of the FCS did not exceed 0.1 ppm. The solvents used were purified according to standard procedures. The FCS for (IV) were determined for solutions of the corresponding (III) in methanolic MeONa.

The substituted N-phenylmercuro-4-fluorobenzenesulfonanilides (II) were prepared by the reaction of phenylmercuric hydroxide with the corresponding 4-fluorobenzenesulfonyl chlorides (III), which, in turn, were obtained by the action of 4-fluorobenzenesulfonyl chloride [9] on substituted anilines. The physical constants and elemental analysis data for the new compounds are given in Table 4. Typical examples of the synthesis of the compounds studied are given below.

N-Phenylmercuro-4-fluorobenzenesulfonanilide (IId). A solution of 1.26 g (5 mmoles) 4-fluorobenzenesulfonanilide in 20 ml abs. ethanol was added to a hot solution of 1.47 g (5

TABLE 4. Elemental Analysis Data and Physical Indices of Substituted 4-Fluorobenzenesulfonanilides and N-Phenylmercuro-4-fluorobenzenesulfonanilides

Number	Compound	Chemical formula	Yield, %	Mp, °C	Found/calculated, %		
					C	H	N(Hg) *
1	4-$MeOC_6H_4NHSO_2C_6H_4F$-4	$C_{13}H_{12}FNO_3S$	62	91–92 (aq. MeOH)	55,53/55,52	4,27/4,30	4,98/4,98
2	4-$MeC_6H_4NHSO_2C_6H_4F$-4	$C_{13}H_{12}FNO_2S$	85	83–85 (aq. MeOH)	59,11/58,87	4,71/4,56	5,15/5,28
3	3-$MeC_6H_4NHSO_2C_6H_4F$-4	$C_{13}H_{12}FNO_2S$	36	88–90 (aq. EtOH)	58,60/58,87	4,64/4,56	5,30/5,28
4	$C_6H_5NHSO_2C_6H_4F$-4	$C_{12}H_{10}FNO_2S$	90	117–119 (aq. MeOH)	57,42/57,37	3,84/4,01	5,66/5,57
5	4-$FC_6H_4NHSO_2C_6H_4F$-4	$C_{12}H_9F_2NO_2S$	92	86–87 (aq. MeOH)	53,86/53,54	3,17/3,36	5,45/5,20
6	4-$ClC_6H_4NHSO_2C_6H_4F$-4	$C_{12}H_9ClFNO_2S$	73	91–93 (aq. EtOH)	50,31/50,44	3,02/3,17	4,92/4,90
7	3-$FC_6H_4NHSO_2C_6H_4F$-4	$C_{12}H_9F_2NO_2S$	84	94–95 (aq. EtOH)	53,58/53,54	2,90/3,36	5,10/5,20
8	3-$ClC_6H_4NHSO_2C_6H_4F$-4	$C_{12}H_9ClFNO_2S$	68	100–102 (aq. EtOH)	50,74/50,44	3,17/3,17	4,61/4,90
9	3,4,5-$Cl_3C_6H_2NHSO_2C_6H_4F$-4	$C_{12}H_7Cl_3FNO_2S$	56	183–185 (EtOH)	40,72/40,63	1,97/1,99	4,13/3,95
10	4-$MeOC_6H_4N(HgPh)SO_2C_6H_4F$-4	$C_{19}H_{16}FHgNSO_3$	79	153–155 (EtOH)	40,96/40,94	3,05/2,89	35,87/35,89
11	4-$MeC_6H_4N(HgPh)SO_2C_6H_4F$-4	$C_{19}H_{16}FHgNSO_2$	66	140–142 (MeOH)	41,98/42,15	2,80/2,98	37,01/36,95
12	3-$MeC_6H_4N(HgPh)SO_2C_6H_4F$-4	$C_{19}H_{16}FHgNSO_2$	70	139–141 (EtOH)	41,93/42,15	2,97/2,98	–
13	$C_6H_5N(HgPh)SO_2C_6H_4F$-4	$C_{18}H_{14}FHgNSO_2$	87	163–164 (EtOH)	40,72/40,99	2,62/2,68	37,96/37,94
14	4-$FC_6H_4N(HgPh)SO_2C_6H_4F$-4	$C_{18}H_{13}F_2HgSO_2N$	62	134–136 (MeOH)	39,29/39,60	2,40/2,40	36,56/36,75
15	4-$ClC_6H_4N(HgPh)SO_2C_6H_4F$-4	$C_{18}H_{13}ClFHgNSO_2$	85	160–161 (EtOH)	38,34/38,43	2,62/2,42	–
16	3-$FC_6H_4N(HgPh)SO_2C_6H_4F$-4	$C_{18}H_{14}F_2HgNSO_2$	79	140–142 (EtOH)	39,35/39,60	2,48/2,40	36,60/36,75
17	3-$ClC_6H_4N(HgPh)SO_2C_6H_4F$-4	$C_{18}H_{13}ClFHgNSO_2$	82	149–151 (EtOH)	38,33/38,43	2,33/2,42	35,60/35,67
18	3,4,5-$Cl_3C_6H_2N(HgPh)SO_2C_6H_4F$-4	$C_{18}H_7Cl_3HgNSO_2$	93	183–185 (PrOH)	40,72/40,63	1,97/1,99	4,13/3,95

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*N for compounds 1–9 and 18 and Hg for compounds 10–17.

mmoles) PhHgOH in 20 ml abs. ethanol. The reaction mixture was heated to reflux. Solvent removal in vacuum and crystallization of the residue from ethanol gave 2.3 g white crystalline (IId), mp 163-164°C.

4-Fluorobenzenesulfonanilide (IIId). A solution of 4.85 g (25 mmoles) 4-fluorobenzenesulfonyl chloride in 20 ml methanol was added to a solution of 0.86 g (20 mmoles) aniline in 30 ml methanol and 2 ml pyridine. Spontaneous warming was noted in the reaction mixture, which turned bright red. After 1 h, the reaction mixture was evaporated in vacuum and washed with water. The residue was filtered off and heated at reflux with activated charcoal in methanol until the color disappeared. A white fibrous precipitate separated from the cold filtrate. Crystallization from aq. methanol gave 4.5 (IIId), mp 117-119°C.

CONCLUSIONS

1. A comparative ^{19}F NMR study of a series of model $\mathrm{ArN(X)SO_2C_6H_4F}$-4 compounds (X = H, HgPh, and Na) showed that the mechanism for the transmission of the substituent electronic effects in these compounds depends on the polarity of the $\mathrm{N^{\delta-}{-}X^{\delta+}}$ bond. An increase in this polarity leads to an increase in the relative contribution of direct polar conjugation.

2. The specific solvation of the mercury atom in the binuclear bridging $\mathrm{N(HgPh)SO_2}$ group has only a slight effect on its transmission capacity.

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PENTACOORDINATION OF THE SILICON ATOM IN (2-ORGANYLSULFINYLETHYL)TRIFLUOROSILANES

M. G. Voronkov, L. V. Klyba,
T. N. Aksamentova, G. A. Gavrilova,
M. S. Sorokin, V. Yu. Vitkovskii,
V. B. Modonov, N. N. Chipanina,
and Yu. L. Frolov

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The capacity of the silicon atom to form an intramolecular $\mathrm{Si \leftarrow O{=}C}$ coordination bond was studied in detail in our previous work in the case of (aroyloxyalkyl)fluorosilanes [1-3]. Methyl(aroyloxymethyl)fluorosilanes $\mathrm{4\text{-}XC_6H_4CO_2CH_2SiMe_{3-n}F_n}$ (n = 1, 2; X = H, Me, Br, Cl) and (acylthiomethyl)trifluorosilanes $\mathrm{RCOSCH_2SiF_3}$ (R = Me, Ph) exist in solution as equilibrium mixtures of forms with and without an intramolecular $\mathrm{Si \leftarrow O{=}C}$ coordination bond. The strength of the intramolecular coordination bond of the silicon atom to the oxygen atom of the carbonyl group in (aroyloxymethyl)trifluorosilanes $\mathrm{4\text{-}XC_6H_4CO_2CH_2SiF_3}$ (X = MeO, H, Me, F, Cl, Br, $\mathrm{O_2N}$) is significantly greater. In solution, these compounds exist only in the form with a pentacoordinated silicon atom. The $\mathrm{Si \leftarrow O}$ coordination is retained even in the gaseous state at 420°K.

We study the formation of the intramolecular coordination bond of silicon with the

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