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Spectroscopic Study of Proton-Transfer Interaction between Methylbis(1-silatranylmethyl)amine and Phenols

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Abstract — Acid–base interaction of phenol and 4-nitrophenol with methylbis(1-silatranylmethyl)amine in acetonitrile is completely shifted toward formation of solvation-separated ion pairs. The unusually high electron-donor power of the exocyclic nitrogen atom in the amine is due to the presence of two silatranylmethyl groups exhibiting a super-electron-donor inductive effect.

In hydrocarbon solvents, trialkylamines form with phenol a hydrogen bond PhO–H···NR_3 [1–3]. In acid–base interaction of trialkylamines with 4-nitrophenol, three types of complexes can form depending on the dielectric permittivity of the solvent: hydrogen-bonded complex ArO–H···NR_3 (C_nH_{2n+2}), contact ion pair $ArO^-\cdots N^+HR_3$ ($ClCH_2CH_2Cl$), and solvation-separated ion pair $ArO^-(Solv)N^+HR_3$ (MeCN) [4, 5]. Successive introduction of CH_2SiX_3 groups at the nitrogen atom enhances its electron-donor power. For example, the ionization potentials of the lone electron pair of the nitrogen atom in $Me_mN[CH_2SiMe_3]_{3-m}$ regularly decrease as *m* is decreased from 2 to 0 (7.93, 7.82, and 7.66 eV, respectively [6]). Addition of phenol to a solution of dialkylaminomethyltriethoxysilane $R_2N\cdot CH_2Si(OEt)_3$ [R_2 = Me_2, $(CH_2)_5$] in heptane results in formation of a hydrogen bond [7]. On mixing solutions of phenol with *N*-methyl-*N*,*N*-bis[methyl(ethoxy)silylmethyl]amines $MeN[CH_2SiMe_m(OEt)_{3-m}]_2$ (*m* = 0–2) in heptane results in ether interchange of the ethoxy groups with phenols, yielding compounds of the general formula $MeN[CH_2SiMe_m(OPh)_n\cdot(OEt)_{3-m-n}]_2$ [8]. The $CH_2Si(OCHRCH_2)_3N$ group, being an intramolecular donor–acceptor complex, exhibits a super-electron-donor inductive effect (σ* –2.24 [9–11]). Introduction of even one silatranylmethyl group $CH_2Si(OCHRCH_2)_3N$ at the nitrogen atom considerably enhances its electron-donor power. The hydrogen bond of phenol with piperidinomethyl-3,7,10-trimethylsilatrane $(CH_2)_5N_{CH_2Si(OCHMe\cdot CH_2)_3N}$ in heptane is much stronger than with triethylamine (*K* 1100 and 52 l mol^{-1}, respectively [7, 12]). A considerable low-frequency shift of the symmetrical stretching band of the Me(N) group (2730 cm^{-1}) in the IR spectra of methylbis(1-silatranylmethyl)amines $MeN[CH_2Si(OCHRCH_2)_3N]_2$ (R = H, Me), compared to the position of this band in the spectra of aliphatic methylamines (2780–2830 cm^{-1}), is indicative of increased electron density at the exocyclic nitrogen atom [13].

For quantitative evaluation of the electron-donor power of the exocyclic nitrogen atom, we studied by UV spectroscopy the interaction of phenol and 4-nitrophenol with methylbis(1-silatranylmethyl)amine $MeN[CH_2Si(OCHRCH_2)_3N]_2$ [R = H (**I**), Me (**II**)] and dimethyl(aminomethyl)silatrane $Me_2NCH_2Si(OCH_2\cdot CH_2)_3N$ (**III**).

When solutions of phenol and **II** in heptane are combined, a white precipitate is formed immediately even at the molar ratio of 1 : 1. The IR spectrum of the isolated reaction product contains absorption bands of the 3,7,10-trimethylsilatranyl group and benzene ring, and new bands appear at 2490 and 2590 cm^{-1}, indicative of the presence of the N^+H group [14]. In the UV spectra of acetonitrile solutions containing phenol and **I**, along with the bands of free phenol (short-wave λ_2 at 216 nm and long-wave λ_1 with the vibronic structure and maxima at 267, 273, and 279 nm), new maxima appear at 244 and 299 nm (Fig. 1, Table 1). These peaks coincide with those observed in the spectrum of tetraethylammonium phenolate in MeCN [245 (ε 12500) and 298 nm (ε 800)] and in the spectrum of the complex of phenol with **II**, precipitated from heptane and then dissolved in acetonitrile. Considerable bathochromic shifts of the short-wave and long-wave bands of phenol ($\Delta\lambda_2$ 5300 and $\Delta\lambda_1$ 2300 cm^{-1}, respectively) and coincidence of these bands with those of tetraethylammonium phenolate suggest partial proton transfer with the formation of the PhO^- ion incorporated in an ion pair [15]. According to [4, 5], in acetonitrile the equilibrium ArOH + NR_3 $\rightleftarrows$ $ArO^-(Solv)N^+HR_3$ is virtually completely shifted to the right.

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Table 1. UV spectra of solutions of ArOX in MeCN

Compound	λ_1 (ε), nm	λ_2 (ε), nm
$MeN[CH_2Si(OCH_2CH_2)_3N]_2$	≤210	
$PhOSi(OCH_2CH_2)_3N$	267 (1550), 273 (1900), 279 (1450)	222 (9100)
$PhOSi(OEt)_3$	262 (750), 267 (1000), 276 (800)	213 (6400)
$PhO^-(Et_4N)^+$	298 (800)	245 (12500)
PhOH	267 (1750), 273 (2300), 279 (1900)	216 (7900)
p-$NO_2C_6H_4OSi(OCH_2CH_2)_3N$	310 (6500)	
p-$NO_2C_6H_4OH$	308 (11900)	

Based on these data, the complex of phenol with **II** has probably the following structure: $PhO^-(Solv)\cdot N^+HMe[CH_2Si(OCHRCH_2)_3N]_2$. The equilibrium constant of the complexation is 27 ± 2 l mol^{-1} at 20°C. In the spectra of solutions of phenol in MeCN containing **III**, even at its tenfold excess, only a weak absorption at about 300 nm is observed (Fig. 1). These results show that compounds **I** and **II** are considerably stronger bases than dimethyl(aminomethyl)silatrane **III**.

For comparative quantitative evaluation of the basicity of the exocyclic nitrogen atom in **I** and **III**, we studied by UV spectroscopy their interaction with 4-nitrophenol in acetonitrile. The UV spectra of solutions of 4-nitrophenol and **III** contain, along with the band of the $\pi\rightarrow\pi^*$ transition in free 4-nitrophenol at 308 nm, also a band at 426 nm belonging to the solvation-separated ion pair, as in the similar complexes with trialkylamines [4, 5]. The contact ion pair should have an absorption band at 390 nm [4, 5], but this band is not revealed in the spectrum (Fig. 2); the overall spectrum is described as a sum of the bands at 308 and 426 nm. The dependence of the optical characteristics of the spectrum on the relative concentration of 4-nitrophenol and amine and on the degree of dilution shows that there are no equilibria other than that suggested in [4, 5]. An increase in the volume and polarizability of cations derived from amines **I** and **III** additionally stabilizes the solvation-separated ion pairs [15]. The equilibrium constant for **III**, determined as described in [16], is 1400 ± 70 l mol^{-1} (Table 2).

The UV spectrum of a mixture of 4-nitrophenol and methylbis(1-silatranylmethyl)amine **I** does not contain a $\pi\rightarrow\pi^*$ absorption band of free 4-nitrophenol even at the molar ratio of 4-nitrophenol to **I** of 1 : 1.4; only the band at 430 nm is observed (Fig. 2). At the molar ratio of the amine to phenol increased by a factor of 2–7, the intensity of this band does not noticeably change. These facts show that, even at the equimolar ratio of the components, the proton transfer from 4-nitrophenol to the amine is virtually complete, yielding a solvation-separated ion pair, $ArO^-(Solv)\cdot N^+HMe[CH_2Si(OCHRCH_2)_3N]_2$. The equilibrium constant was determined by the procedure suggested in [4, 5], and also from the equation $K = c_b/(c_{ph}c_B)$ (c_B is the concentration of the freee amine; c_b, that of the complex; and c_{ph}, that of the free phenol), and both approaches give the value of 2700 ± 120 l mol^{-1} (Table 2). This very large equilibrium constant of interaction of 4-nitrophenol with methylbis(1-silatranyl)methylamine is indicative of unique super-electron-donor properties of the exocyclic nitrogen atom in this compound, due to the presence of two silatranylmethyl groups.

Thus, in the compounds $Me_nN(CH_2SiX_3)_{3-n}$, the electron-donor power of the nitrogen atom considerably grows in going from SiX_3 = $Si(OAlk)_3$ to

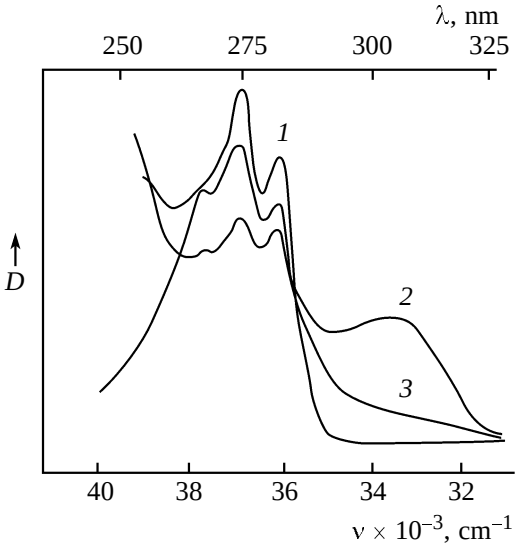

Fig. 1. UV spectra (l 0.1 cm) of acetonitrile solutions of phenol (c_{ph} 4.1×10^{-3} M): (*1*) no amine added, (*2*) in the presence of bis(1-silatranylmethyl)amine (c_B 1.1×10^{-2} M), and (*3*) in the presence of 1-dimethyl(aminomethyl)silatrane (c_B 4.36×10^{-2} M).

Table 2. UV absorption spectra of reaction mixtures and equilibrium constants (K, l mol^{-1}) of interaction of 4-nitrophenol (ArOH) with trialkylamines in acetonitrile

Amine	ArOH [λ, nm (ε)]	ArO(*Solv*)N^+HR_3 [λ, nm (ε)]	K
I	308 (12000)	430 (37800)	2700 ± 120[a]
III	308 (12000)	426 (35100)	1400 ± 70[a]
Et_3N	308,[b] 310[c]	426	270,[b] 230[c] ± 8
Bu_3N	310	420	300 ± 20
Oct_3N	310	420	126 ± 5[c]

[a] At 22°C. [b] At 20°C [4]. [c] At 26°C [5].

$Si(OCHRCH_2)_3N$ and with increasing number of these substituents. Therefore, the reactivity of these compounds toward electrophiles should also substantially increase.

EXPERIMENTAL

The equilibrium constants of interaction of phenols with **III** in MeCN were determined according to [16] with a Specord UV-Vis spectrophotometer; for **I**, c_{ph} 3.7×10^{-4}, c_B $(5.1–25.5) \times 10^{-4}$ M; for **III**, c_{ph} 5.0×10^{-4}, c_B $(1.1–3.2) \times 10^{-3}$ M; l 0.05 cm; the solutions were prepared in a dry atmosphere.

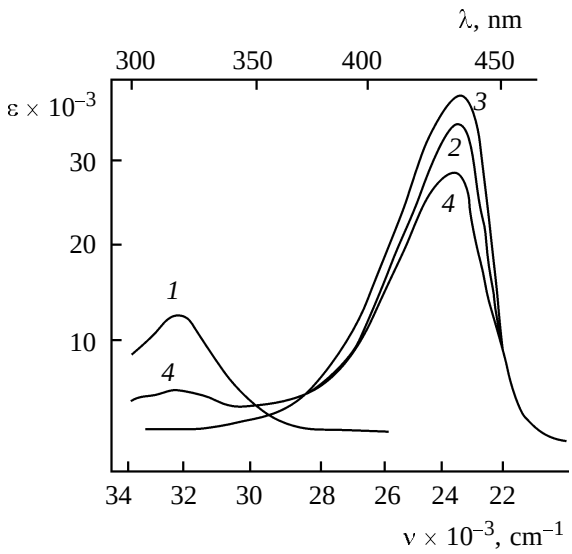

Fig. 2. Electronic absorption spectra (l 0.05 cm) of solutions of 4-nitrophenol (c_{ph} 3.6×10^{-4} M) in MeCN in the presence of various amounts of bis(1-silatranylmethyl)amine [(*1*) 0, (*2*) 5.1×10^{-4}, and (*3*) 1.0×10^{-3} M] and dimethyl(aminomethyl)silatrane [(*4*) 1.1×10^{-3} M, c_{ph} 5.0×10^{-4} M].

Methylbis(1-silatranylmethyl)amine was prepared as described in [13].

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