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Conformational Structure of *N*-(Silylmethyl)anilines $PhNHCH_2SiMe_n(OEt)_{3-n}$ ($n = 0–3$)

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Abstract—As show the data of IR spectroscopy and quantum-chemical calculations (B3LYP/6-311+G**), *N*-(silylmethyl)anilines $PhNHCH_2SiMe_n(OEt)_{3-n}$ in inert media have an intramolecular hydrogen bond NH···OSi. *N*-[(Trimethylsilyl)methyl]aniline $PhNHCH_2SiMe_3$ in inert solvents exists as a mixture of two conformers close in energy.

Keywords: *N*-(silylmethyl)anilines, IR spectroscopy, quantum-chemical calculations, intramolecular hydrogen bond

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The constant interest to *N*-(silylmethyl)amines $RR^1R^2SiCH_2NR^3R^4$ is due to the fact that the geminal fragment N–CH_2–Si combines the basic (N) and acidic (Si) centers and as a result these compounds possess specific physicochemical properties [1–3]. They are promising synthons for organic and organoelemental synthesis and possess biological activity (see [1] and references therein). The first representatives of *N*-(silylmethyl)anilines $PhNHCH_2SiMe_n(OEt)_{3-n}$ ($n = 0–3$) were synthesized in 1951 by the reaction of the corresponding α-halomethylsilanes $HalCH_2SiMe_n(OEt)_{3-n}$ (Hal = Cl, Br) with aniline [4]. The basicity of the nitrogen atom in *N*-(silylmethyl)amines is notably higher than in the isostructural carbon analogs [5–11] that agrees with a stronger electron-donating effect of the silyl groups [12–14]. Recently we have found that *N*-(silylmethyl)amines readily react with polyhalomethanes, phenols [15–18] and alcohols, which were used as solvents or proton donors at measuring the bacisity of these amines. It cannot be ruled out that a decrease in the basicity of *N*-(silylmethyl)amines with respect to that expected from the dependence of the basicity of *N*-(silylalkyl)amines on the inductive constants of the silylalkyl substituents (the so-called α-effect, see [2, 3] and references therein) can be caused by the chemical reactions occurring during the determination of the basicity and distorting the results of measurements. Therefore, it was necessary to obtain new reliable data on the basicity of N-silylmethylamines. We planned to obtain such data for *N*-(silylmethyl)anilines $PhNHCH_2SiMe_n(OEt)_{3-n}$ [**I** ($n = 0$), **II** ($n = 1$), **III** ($n = 2$), **IV** ($n = 3$)]. As a proton donor, pyrrole was chosen due to the low degree of its self-association in solutions, rather high acidity (pK_a = 17.5 [19]), and inertness to organosilicon amines. However, the IR spectroscopic study has shown that compounds **I–IV** do not form H-complexes with pyrrole and their behavior in solutions completely depends on their structure. Therefore, the aim of this work was to investigate the structure of these compounds using the methods of IR spectroscopy and quantum chemistry. We have used polyhalomethanes as solvents. It was possible because they react with compounds **I–IV** much slower than with *N*-(silylmethyl)alkylamines: we did not observe any products of the reaction of *N*-(silylmethyl)anilines with polyhalomethanes in solution after spectral measurements.

N-Methylaniline, like other amines, forms self-associates in solution [20, 21]. In contrast, the shape and position of the ν_{NH} absorption band in the IR spectra of *N*-(silylmethyl)anilines **I–III** are practically identical in thin layer and in solutions in CCl_4 of various concentrations (Table 1). The absence of concentration dependence means that these compounds do not form self-associates. This is due to the formation of

Table 1. Calculated (B3LYP/6-311+G**) and experimental characteristics of compounds **I**–**III**

Comp. no.	ν_{NH}, cm^{-1}	ν_{NH}, cm^{-1} (CCl_4)		*l*, Å	–*E*, kcal/mol
		experiment	calculated		
I	3419	3423	3600	2.372	0.52
II	3414	3419	3601	2.325	0.83
III	3413	3421	3584	2.415	0.40

Table 2. Calculated total energies of neutral molecules of molecules **I**–**IV** and their forms protonated at nitrogen (E_t, a.e.), nitrogen atom proton affinity (PA, kcal/mol), acidity (–Δ*G*, kcal/mol)

Molecule	$-E_t$	$-E_t$ (ZPE)	PA[a]	ΔG[b]
I	1079.5378651	1079.189938		
I-NH^+	1079.9186958		238.97	
I-N^-	1078.9538970			366.44
II	964.9352072	964.621716		
II-NH^+	965.3166406		239.35	
II-N^-	964.3481888			368.35
III	850.3367549	850.057197		
III-NH^+	850.7156993		237.79	
III-N^-	849.7494416			368.54
IV	735.7370128	735.491667		
IV-NH^+	736.1039541		230.26	
IV-N-	735.1442033			371.99

[a] PA was determined as the difference of the energies of the protonated and neutral forms. [b] Δ*G* calculated as the difference of the energies of the neutral molecule and its anion.

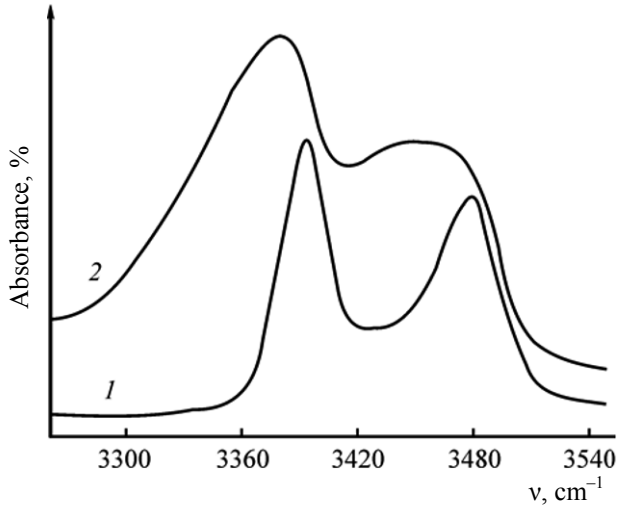
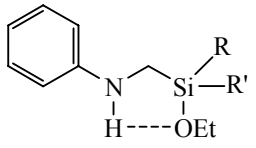
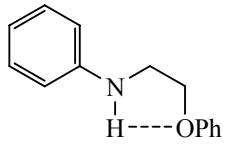


Fig. 1. IR spectrum of *N*-[(trimethylsilyl)methyl]aniline in CCl_4: (a) *C* = 0.0028 mol/L; *d* = 2 cm; (b) *C* = 8.6 mol/L; *d* = 0.0011 cm.

an intramolecular hydrogen bond (IHB) N–H···O–Si in the molecules of *N*-(silylmethyl)anilines **I–III** (**A**), as it is the case in the structurally similar *N*-(2-phenoxyethyl)aniline $PhO(CH_2)_2NHPh$ (**B**), where the formation of the intramolecular hydrogen bond N–H···O–R has been proved [22].



A



B

The structure of compounds **I–III** was studied at the DFT level of theory using the basis set B3LYP/6-311+G**, and theoretical vibration spectra of the monomeric molecules as well as their structure and energy were calculated. The results of the IR spectroscopic study, quantum-chemical calculations,

Table 3. Effect of temperature and concentration on the position of the ν_{NH} band of *N*-[(trimethylsilyl)methyl]aniline in different media

Temperature, K	Thin layer	CCl_4	CH_2Cl_2	Heptane
298	3422, 3358	3481, 3396 (d = 10 cm) 3460, 3380 (d = 0.011 mm)	3462, 3384	3482, 3397
203			3455, 3378	3482, 3446, 3418, 3396, 3330, 3295
353				3482, 3397

and the energies of IHBs estimated using the NBO analysis [23, 24] are given in Table 1. We have also estimated the acidic and basic properties of the NH group in compounds **I–IV** (Table 2). There is a direct relationship between such characteristics of substituted anilines as their basicity determined experimentally in the gas phase or in solution, and the calculated values of proton affinity (PA), and the theoretical values calculated taking into account the solvent effects are in good agreement with the experiment [25–27]. In review [28], various methods for calculation of PA values (HF, MP2, MP4) are compared for a wide series of amines, but the most close to the experiment were the results obtained at the B3LYP level with the basis set 6-311+G(d,p). The results obtained by us (Table 2) suggest that the value of PA in the molecules of compounds **I–III** increases with the number of the ethoxy groups. The PA values for the ethoxy-substituted compounds **I–III** are by 7.5–9.0 kcal/mol larger than that of compound (**IV**). The calculated acidity (ΔG) of *N*-(silylmethyl)anilines decreases in the order **IV** > **III** > **II** > **I** (Table 2).

N-[(Trimethylsilyl)methyl]aniline $PhNHCH_2SiMe_3$ (**IV**) demonstrates quite different behavior in solutions. In the IR spectra of its diluted solutions in inert solvents (CCl_4, CH_2Cl_2, heptane) two absorption bands of the NH group are observed. To elucidate the nature of these bands we have studied the effect of concentration of (**IV**) in CCl_4 solution on their position and intensity. It turned out that the two absorption bands of the NH groups exist even in diluted solutions, which is indicative of the presence of two conformers in the solution. Small low-frequency shift and broadening of the two bands upon a large increase in concentration is indicative of self-association of these conformers (Fig. 1).

In order to investigate the conformational transformations in molecule **IV** we have measured the temperature dependence in CH_2Cl_2 and heptane solutions (Table 3). In dichloromethane, the decrease in the temperature causes a small low-frequency shift ($\Delta\nu \sim 6–7$ cm^{-1}), but the character of the bands is not changed (Fig. 2). The IR spectrum of compound **IV** in

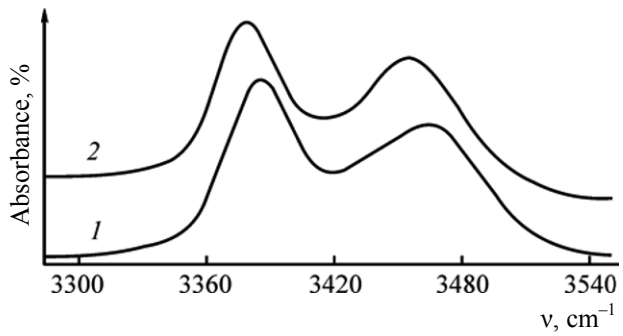


Fig. 2. IR spectrum of *N*-[(trimethylsilyl)methyl]aniline in CH_2Cl_2, c = 0.0058 mol/L; d = 0.507 mm; (*1*) T = 298 K; (*2*) T = 203 K.

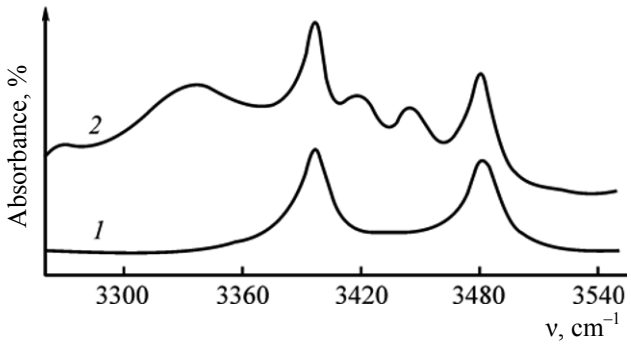
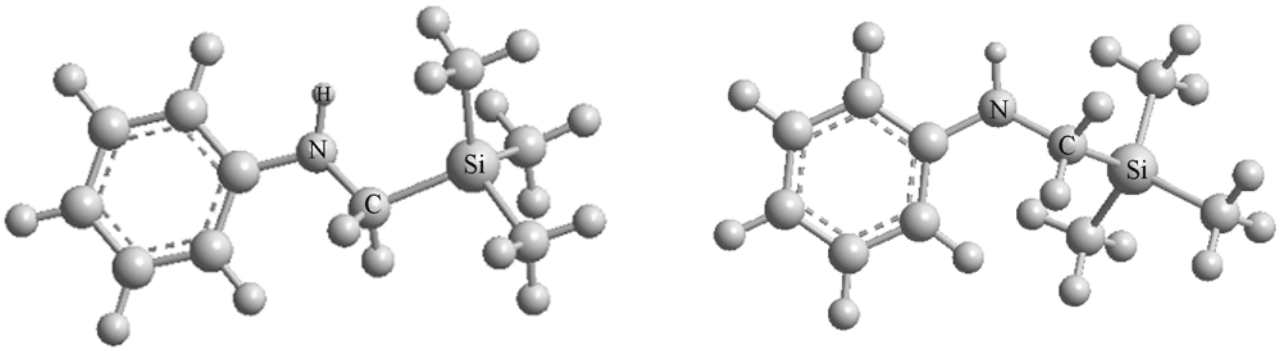


Fig. 3. IR spectrum of *N*-[(trimethylsilyl)methyl]aniline in heptane, c = 0.0032 mol/L; d = 1 mm; (*1*) T = 353 K; (*2*) T = 203 K.



IVA **IVB**

Fig. 4. Conformers of the molecule of *N*-[(trimethylsilyl)methyl]aniline (B3LYP/6-311+G**).

CH_2Cl_2 (low-temperature dependence, variation of temperature from 298 to 203 K, Fig. 2) is similar to its spectrum in CCl_4 (concentration dependence, Fig. 1). A low-frequency shift and a broadening of the absorption bands suggest that upon the temperature decrease the self-associates of the conformers of compound **IV** in dichloromethane solution are stabilized, as well as upon the increase of concentration in the solution in carbon tetrachloride.

Quite different is the temperature dependence of the IR spectrum of compound **IV** solution in heptane in the region of NH absorption in the temperature range of 203–353 K. While the ν_{NH} bands do not change their shape and position upon heating to 353 K, cooling to 203K results in appearance of new absorption bands, both monomeric (3418, 3396 cm^{-1}) and associated (3330, 3295 cm^{-1}) (Fig. 3). This might suggest the presence of at least four types of stable conformers and two types of their associates at low temperatures.

Similar integral intensities of the ν_{NH} bands of *N*-[(trimethylsilyl)methyl]aniline **IV** both in the spectra of concentration dependence (Fig. 1) and the spectra of temperature dependence (Figs. 2, 3) suggest similar energies of the conformers of compound **IV**. B3LYP/6-311+G** calculations revealed the presence of two minima on the potential energy surface corresponding to the conformers presented in Fig. 4.

Table 4. Calculated parameters (B3LYP/6-311+G**) of the conformers of molecule **IV**

Parameter	**IVA**	**IVB**
ν(NH), cm^{-1}	3604	3630
Angle C_{Ph}–N–C–Si, deg	179.3	103.8
Δ*E*, kcal/mol	0	2.0
μ, D	2.25	1.97

The geometry optimization showed that the N–H bond in the molecule of *N*-[(trimethylsilyl)methyl]-aniline lies practically in the plane of the benzene ring. Conformer **IVA** where the dihedral angle C_{arom}–N–C–Si is equal to ~180° is by 2.0 kcal/mol more stable than conformer **IVB**, in which this angle is equal to ~104°, and has a larger dipole moment (2.25 and 1.97 D, respectively). The ν_{NH} frequency in conformer **IVB** is by 26 cm^{-1} higher than the corresponding frequency in conformer **IVA**. The calculated characteristics of the conformers of compound **IV** are shown in Table 4. Comparison of the IR spectroscopy data and the calculated vibration spectrum of molecule **IV** allowed us to assign the low-frequency band ν_{NH} in the spectra in Figs. 1–3 to conformer **IVA**, and the high-frequency one, to conformer **IVB**.

EXPERIMENTAL

IR spectra were recorded on a FTIR Varian 3100 spectrophotometer. Quantum-chemical calculations were performed using the GAUSSIAN-09 program package [29]. Compounds **I–IV** were synthesized as described previously [4].

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