# ORGANOSILICON COMPOUNDS. CV.*
# THE EFFECT OF STRUCTURE ON THE BASICITY OF SILYLALKYLAMINES**

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Fifteen methylethoxysilylalkylamines of the type $(CH_3)_{3-n}(C_2H_5O)_nSi(CH_2)_mNH_2$ ($n = 0-3$; $m = 1-4$) were prepared and their basicities were determined by IR spectroscopy using deuteriochloroform as proton donor. From the results of the measurements it follows that to explain anomalously low basicity of silylmethylamines, the effect of hyperconjugation should be considered. The basicity of higher silylalkylamines ($m = 2-4$) is sufficiently explained by inductive effects of silyl groups, so that within the precision of the method used the coordination of the nitrogen of the amino group to central silicon atom cannot be proved.

In our studies on the effect of structure on the reactivity and physical properties of carbofunctional silicon derivatives we have so far systematically investigated particularly the derivatives containing oxygeneous functional groups[1-3]. In these works we were concerned with the effect of the distance between a functional group and silicon and of its substitution upon the electronic configuration of carbofunctional silanes and made an attempt to examine the possibility of the coordination of basic functional atoms to silicon as well as the possibility of the operation of hyperconjugation in α-carbofunctional derivatives. As, according to present knowledge, both phenomena may be expected to occur especially in the compounds with nitrogen-containing functional groups[4,5], in the present work we performed systematic measurements of the basicity of methylethoxysilylalkylamines of the type $(CH_3)_{3-n}.(C_2H_5.O)_nSi(CH_2)_mNH_2$.

Coordination of nitrogen to silicon was proved by IR measurements and by X-ray analysis in triethanolamine derivatives of the type $RSi(OCH_2CH_2)_3N$ (refs[6-10]). In contrast, Graham and Thompson[11] found that in diethanolamine derivatives of the type $R_2Si(OCH_2CH_2)_2NR'$ the nitrogen is not coordinated to the silicon. In similar compounds, such as 1-ethoxy-2,8-dioxa-5-aza-1-silabicyclo-(3,3,3)undecane[12] or methyl-(2,2',3-cyanodiethoxypropyl)silane[13,14], trans-anular coordination bond of the type Si ← N has not been detected. Of silylalkylamines, the

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basicity of trimethylsilylpropylamine[15] and of several methylethoxysilylmethylamines[16] has so far been measured. The measurements were carried out, however, in aqueous medium, in which these compounds are readily hydrolysed.

## EXPERIMENTAL

(*Chloromethyl*)*methylchlorosilanes* were prepared analogously as in our previous work[17]. A similar procedure was also used to prepare (chloromethyl)methylethoxysilanes[17] by reaction of appropriate chlorosilanes with ethanol.

*Methylethoxysilylmethylamines.* The autoclave cooled to −80°C was charged with c. 0·2 mol of an appropriate methylethoxysilylmethyl chloride. Then 100—110 ml of liquid ammonia (20—22 fold excess) was added while cooling the reaction mixture. It was then heated to 95 to 125°C (pressure 70—115 atm) for 6 h. After cooling to ambient temperature the excess ammonia was removed and the reaction mixture was extracted with dry ether. Fractional distillation of the ether portion afforded the pure primary amine. The so prepared trimethylsilylmethylamine had b.p. 93·5—94°C/740 Torr; $d_{25}^{25}$ 0·7667 ($d_4^{25}$ 0·7646) (ref.[18]); $n_D^{25}$ 1·4143 (ref.[18] 1·4139). Dimethylethoxysilylmethylamine was obtained in 38% yield as fraction boiling 134·5—135°C : : 740 Torr (ref.[18] 131·8°C/740 Torr); $d_{25}^{25}$ 0·8540 ($d_4^{25}$ 0·849) (ref.[18]); $n_D^{25}$ 1·411). Methyldiethoxysilylmethylamine (41% yield) had b.p. 60·5°C/14 Torr (ref.[18] 67·5°C/24 Torr); $d_{25}^{25}$ 0·9153 ($d_4^{25}$ 0·914—0·916) (ref.[18]); $n_D^{25}$ 1·4127 (ref.[18] 1·4120—6). Triethoxysilylmethylamine (31% yield) boiled at 80·5°C/14 Torr (ref.[18] 93°C/26 Torr); $d_{25}^{25}$ 0·9576 ($d_4^{25}$ 0·955) (ref.[18]); $n_D^{25}$ 1·4082 (ref.[18] 1·4080).

*Triethoxysilylethylamine.* Ethyltrichlorosilane was prepared by the direct synthesis[19] and was chlorinated by sulfuryl chloride[20]. The obtained 2-chloroethyltrichlorosilane (b.p. 151—152°C) was reacted with ethanol[21] to give 2-chloroethyltriethoxysilane in 85% yield as fraction boiling 93·5—94°C/14 Torr (ref.[21] 89·9°C/9 Torr); $d_{25}^{25}$ 1·0102 ($d_4^{25}$ 1·0090) (ref.[21]); $n_D^{25}$ 1·4139 (ref.[21] 1·4130). On using the lesser than stoichiometric amount of ethanol, the following partially esterified products were isolated and identified: ethoxydichlorosilylethyl chloride, b.p. 66—68°C/13 Torr, $d_{25}^{25}$ 1·2008, $n_D^{25}$ 1·4351; for $SiC_4H_9Cl_3O$ (207·6) calculated: 13·53% Si, 51·24% Cl; found: 13·51% Si, 51·16% Cl. Diethoxychlorosilylethyl chloride, b.p. 83—85°C/14 Torr, $d_{25}^{25}$ 1·1059, $n_D^{25}$ 1·4207; for $SiC_6H_{14}Cl_2O_2$ (217·2) calculated: 12·93% Si, 33·18% C, 6·50% H, 32·65% Cl; found: 12·99% Si, 33·10% C, 6·44% H, 32·51% Cl. Reaction of triethoxysilylethyl chloride with ammonia in autoclave (120°C, 80 atm, 20 fold excess of liquid ammonia) gave triethoxysilylethylamine in 42% yield as fraction boiling 97·6—98°C/15 Torr, $d_{25}^{25}$ 0·9503, $n_D^{25}$ 1·4149. For $SiC_8H_{21}NO_3$ (207·4) calculated: 13·55% Si, 46·34% C, 10·21% H, 6·76% N; found: 13·61% Si, 46·59% C, 10·18% H, 6·62% N.

*Methyldiethoxysilylethylamine.* Methylethyldichlorosilane, prepared by reaction of methyltrichlorosilane with ethylmagnesium bromide[22], was chlorinated by sulfuryl chloride[23]. The obtained 2-chloroethylmethyldichlorosilane (78·8 g) was reacted with ethanol (52 g), to give 2-chloroethylmethyldiethoxysilane in 72% yield; b.p. 104°C/28 Torr, $d_{25}^{25}$ 0·9981, $n_D^{25}$ 1·4207; for $SiC_7H_{17}ClO_2$ (196·8) calculated: 42·73% C, 8·71% H; found 42·93% C, 9·20% H. Reaction of 2-chloroethylmethyldiethoxysilane with ammonia in rocking autoclave, carried out under the conditions described in the preceding paragraph, afforded methyldiethoxysilylethylamine in 33% yield. B.p. 88—89°C/25 Torr, $d_{25}^{25}$ 0·9130, $n_D^{25}$ 1·4161. For $SiC_7H_{19}NO_2$ (177·3) calculated: 15·84% Si, 47·41% C, 10·80% H, 7·90% N; found: 15·69% Si, 47·36% C, 10·72% H, 7·85% N.

*Trimethylsilylethylamine.* 2-Chloroethyltrichlorosilane, dissolved in dry ether, was methylated with equimolar amount of methylmagnesium chloride while cooling the reaction mixture with ice.

After three days the reaction mixture was hydrolysed at ice-bath temperature with the water acidified by hydrochloric acid. Fractional distillation of the separated and dried ether portion afforded 2-chloroethyltrimethylsilane in 42% yield: b.p. $50-52°C/35$ Torr, $d_{25}^{25}$ 0·8755, $n_D^{25}$ 1·4258. For $SiC_5H_{13}Cl$ (136·7) calculated: 20·55% Si, 43·93% C, 9·59% H, 25·94% Cl; found: 20·18% Si, 42·82% C, 9·33% H, 24·70% Cl. After amination of this compounds (under milder conditions than were used in preparing the other silylalkylamines, $-40°C$, $25-28$ atm) only hexamethyldisilazane was isolated and identified as the main reaction product. Trimethylsilyl-ethylamine was therefore prepared both after Sommer[15] (b.p. 54°C/60 Torr, ref.[15] 121°C/734 Torr), and by the reduction of cyanomethyltrimethylsilane[24] with lithiumaluminiumhydride: b.p. 122°C/740 Torr, $d_{25}^{25}$ 0·7791 ($d_4^{25}$ 0·7807) (ref.[15]), $n_D^{25}$ 1·4231 (ref.[15] 1·4244).

3-*Chloropropyltrichlorosilane* was prepared[25] in 59% yield by the addition of trichlorosilane to allyl chloride. B.p. $180-181°C/740$ Torr (ref.[26] 181·5°C/750 Torr), $d_{25}^{25}$ 1·3508 ($d_4^{25}$ 1·354) (ref.[26]), $n_D^{25}$ 1·4641 (ref.[26] 1·4638).

3-*Trimethylsilylpropylamine*. Methylation of 3-chloropropyltrichlorosilane by 10% excess of methylmagnesium chloride[27] gave 3-trimethylsilylpropyl chloride (74%), b.p. $149-150°C/740$ Torr (ref.[28] 150·5°C/744 Torr, $d_{25}^{25}$ 0·8752 ($d^{20}$ 0·8789) (ref.[28]), $n_D^{25}$ 1·4280 ($n_D^{20}$ 1·4319) (ref.[28]). Its subsequent amination under pressure (90°C, $55-65$ atm, 18 h) yielded 3-trimethylsilylpropyl-amine[29] (63%), b.p. 57°C/30 Torr (ref.[15] 145·5°C/732 Torr), $d_{25}^{25}$ 0·7818 ($d_4^{20}$ 0·7866) (ref.[15]), $n_D^{25}$ 1·4280 ($n_D^{20}$ 1·4295) (ref.[15]).

3-*Methyldiethoxysilylpropylamine*. 3-Chloropropylmethyldichlorosilane, prepared by the addition of methyldichlorosilane to allyl chloride, was esterified, giving trichloropropylmethyl-diethoxysilane in 72% yield: b.p. 90·8°C/13 Torr (ref.[26] 109°C/30 Torr), $d_{25}^{25}$ 0·9739 ($d_4^{20}$ 0·973) (ref.[26]), $n_D^{25}$ 1·4229 (ref.[26] 1·4232); its amination under the conditions described above afforded 3-methyldiethoxysilylpropylamine (58%), b.p. 94°C/14 Torr (ref.[30] $85-88°C/8$ Torr), $d_{25}^{25}$ 0·9163 ($d_4^{20}$ 0·9162) (ref.[30]), $n_D^{25}$ 1·4244 (ref.[30] 1·4260).

3-*Dimethylethoxysilylpropylamine*. Partial methylation of 3-chloropropylmethyldichlorosilane by equimolar amount of methylmagnesium chloride and subsequent extraction of formed magnesium salts afforded 3-chloropropyldimethylchlorosilane (48%), b.p. $177-177·5°C/740$ Torr (ref.[26] 179°C/750 Torr), $d_{25}^{25}$ 1·0500 (ref.[26] 1·043), $n_D^{25}$ 1·4480 (ref.[26] 1·4488); its reaction with absolute ethanol gave 3-dimethylethoxysilylpropyl chloride in 61% yield: b.p. 81·5°C/23 Torr (ref.[29] 87°C/30 Torr), $d_{25}^{25}$ 0·9330 (ref.[29] 0·9319), $n_D^{25}$ 1·4270 (ref.[29] 1·4270). The usual pressure amination of this product yielded 3-dimethylethoxysilylpropylamine (64%), b.p. 85°C/28 Torr (ref.[29] $78-79°C/24$ Torr), $d_{25}^{25}$ 0·8603 (ref.[29] 0·8570), $n_D^{25}$ 1·4270 (ref.[29] 1·4276).

3-*Triethoxysilylpropylamine*. Reaction of 3-chloropropyltrichlorosilane with anhydrous ethanol afforded triethoxysilylpropyl chloride (52%), b.p. 106°3/12 Torr (ref.[26] 124°C/30 Torr), $d_{25}^{25}$ 0·9993 (ref.[26] 1·0002), $n_D^{25}$ 1·4173 (ref.[26] 1·4178); its pressure amination gave 3-triethoxysilyl-propylamine (48%), b.p. 121·5°C/28 Torr (ref.[30] $122-123°C/31$ Torr, $d_{25}^{25}$ 0·9481 (ref.[30] 0·9463), $n_D^{25}$ 1·4208 (ref.[30] 1·4220).

3-*Cyanopropyltrichlorosilane* was prepared by the $H_2PtCl_6$-catalysed addition of trichlorosilane[31] to allyl cyanide: the product isolated by fractional distillation in 69% yield had b.p. 121·5°C/18·5 Torr (ref.[32] $93-94°C/8$ Torr), $d_{25}^{25}$ 1·2620 ($d_4^{25}$ 1·2894) (ref.[33]), $n_D^{25}$ 1·4612 (ref.[33] 1·4620). Its careful reaction with 10% excess of methylmagnesium chloride at ice-bath temperature afforded 2-cyanopropyltrimethylsilane (70%), b.p. $82-83·5°C/14$ Torr (ref.[34] $79-80°C/16$ Torr), $d_{25}^{25}$ 0·8231 ($d_4^{25}$ 0·8244) (ref.[34]), $n_D^{25}$ 1·4246 (ref.[35] 1·4258). If, on contrary, 3-cyanopropyltrichlorosilane was added dropwise to the ether solution of ethylmagnesium chloride, the main product after hydrolysis of the reaction mixture by dilute hydrochloric acid was 5-trimethylsilyl-2-pentanone (34%), b.p. $71-71·5°C/14$ Torr (71°C/13 Torr), $d_{25}^{25}$ 0·8282, $n_D^{25}$ 1·4231.

*4-Trimethylsilylbutylamine* was prepared by hydrogenation of 3-cyanopropyltrimethylsilane in a 250 ml-horizontal rocking autoclave under catalysis of Raney cobalt[37]. The autoclave was charged with 40 ml of the cyano derivative and then the catalyst was added as its solution in 40 ml of dry ether; the autoclave was flushed out twice with hydrogen, pressured to 100 atm and heated to 85—95°C. After the consumption of hydrogen had ceased (max. 8—10 g) the product was separated from the catalyst by decantation and purified by fractional distillation: b.p. 75—76°C/29 Torr (74—75°C/29 Torr[37]), $d_{25}^{2}$ 0·7968 ($d_{4}^{20}$ 0·7941) (ref.[37]), $n_{D}^{25}$ 1·4311 ($n_{D}^{20}$ 1·4345) (ref.[30]).

*4-Triethoxysilylbutylamine.* Reaction of 3-cyanopropyltrichlorosilane with ethanol gave 3-cyanopropyltriethoxysilane (60%), b.p. 130—131°C/14 Torr (ref.[31] 108°C/4 Torr), $d_{25}^{2}$ 0·9658 ($d_{4}^{20}$ 0·9673) (ref.[31]), $n_{D}^{25}$ 1·4149 ($n_{D}^{20}$ 1·4158) (ref.[31]). Its catalytic hydrogenation carried out in the way described above afforded 4-triethoxysilylbutylamine in 44% yield, b.p. 114—116°C/14 Torr (ref.[38] 123—124°C/15 Torr), $d_{25}^{2}$ 0·9408 (ref.[38] 0·934), $n_{D}^{25}$ 1·4270 (ref.[38] 1·4222).

*4-Methyldiethoxysilylbutylamine.* 3-Cyanopropylmethyldiethoxysilane, prepared in 88% yield similarly as 3-cyanopropyltrichlorosilane, by the addition of methyldichlorosilane to allyl cyanide (b.p. of the product was 121°C/16 Torr, ref.[39] 122°C/17 Torr; $d_{25}^{2}$ 1·1459, ref.[40] 1·145; $n_{D}^{25}$ 1·4553, ref.[40] 1·4551), was esterified by absolute ethanol to give 3-cyanopropylmethyldiethoxysilane (55%), b.p. 131°C/15 Torr (ref.[30] 119—130°C/13—14 Torr), $d_{25}^{2}$ 0·9406 ($d_{4}^{20}$ 0·9359) (ref.[30]), $n_{D}^{25}$ 1·4202 ($n_{D}^{20}$ 1·4237) (ref.[30]). Its catalytic hydrogenation gave 4-methyldiethoxysilylbutylamine (51%), b.p. 103—105°C/14 Torr (ref.[30] 115—116°C/29 Torr), $d_{25}^{2}$ 0·9106 (ref.[30] 0·9125), $n_{D}^{25}$ 1·4283 (ref.[30] 1·4308).

*4-Dimethylethoxysilylbutylamine.* Partial methylation of 3-cyanopropylmethyldichlorosilane by equimolar amount of methylmagnesium chloride[41] at —40 to —60°C afforded 3-cyanopropyl-dimethylchlorosilane, b.p. 107°C/14 Torr (ref.[42] 109°C/15 Torr). Its reaction with absolute ethanol gave 3-cyanopropyldimethylethoxysilane (71%), b.p. 101°C/14 Torr (ref.[43] 85—90°C/12 Torr), $d_{25}^{2}$ 0·8772, $n_{D}^{25}$ 1·4234. Catalytic hydrogenation of this product yielded 4-dimethylethoxy-silylbutylamine (63%), b.p. 87—88°C/14 Torr (ref.[38] 80—82°C/10 Torr), $d_{25}^{2}$ 0·8596, $n_{D}^{25}$ 1·4308.

*The structure* of prepared compounds was verified by their NMR spectra measured on a modified Tesla BS-477 spectrometer (60 MHz), using the signal of chloroform as a reference signal.

*Relative basicity* of studied carbofunctional compounds was determined from the spectra of hydrogen bonds measured in the region of LiF prism in a ternary mixture on a double-beam Zeiss, Model UR-20, spectrophotometer. The spectrograde $CCl_4$ was used as solvent. The concentration of deuteriochloroform, which in most measurements was employed as proton donor, was 2·5M; of other possible proton donors, phenol (0·02M), pyrrole (0·02M), and phenylacetylene (0·1M) were also tested. Proton acceptor concentration was 0·5M, cell thickness was 0·1 cm. The values of absorption maxima were the average of three successive measurements, with the reading accuracy of $\pm 2$ cm$^{-1}$.

## RESULTS

From synthetic point of view, in preparing model compounds we have obtained some interesting experience with β-elimination of carbofunctional silanes. While 2-chloro-ethyltrimethylsilane could be prepared in comparatively high yield (the so far reported 2-chloroethyltriethylsilane decomposes at ambient temperature to triethyl-chlorosilane and ethylene[22]), the attempt to convert this compound to 2-trimethyl-

silylethylamine has not met with success. The reaction with ammonia led under mild conditions only to hexamethyldisilazane, which is likely formed by condensation reaction of trimethylaminosilane, probably the product of the decomposition of transiently formed 2-trimethylsilylethylamine or amination of the trimethylchlorosilane formed by β-elimination from 2-chloroethyltrimethylsilane. The substitution of silicon by ethoxy groups suppresses the β-elimination to such a degree that not only are 2-chloroethyltriethoxysilane and methyl-2-chloroethyldiethoxysilane formed in good yields, but also their nucleophilic substitution by ammonia to 2-triethoxysilylethylamine and 2-methyldiethoxysilylethylamine, respectively, proceeds without difficulties.

The infrared spectra of all the silylalkylamines show absorption bands due to $v_{as}(N—H)$ at $3400 \text{ cm}^{-1}$, although absorption bands characterizing the amino group have not been found by Noll[16] in the spectra of silylmethylamines. The intensity of these bands, when compared to the other bands, is comparatively low. They can be, however, identified both in measurements in thin layers *in substantia*, and in measurements in tetrachloromethane. The wavenumbers of the N—H stretching vibration for all the model compounds were also estimated. The position of the maximum of this absorption band is constant within experimental errors.

In order to determine relative basicities of the silylalkylamines we first sought for suitable proton donor. The interaction of the nitrogen of relatively strong nitrogen-containing bases with the acidic hydrogen of phenol was indicated in the spectra of all the compounds measured by the extinction of the absorption of the free phenol $(v(O—H)_{free}\ 3605 \text{ cm}^{-1})$ and by broad diffuse band from which only the higher wavenumber side of the band could be observed, while the absorption maximum of this band overlapped with the proper absorption of C—H bonds. As the use of phenol turned out to be unsuitable, also less acidic proton donors were tested. Already from the presence of proper absorption bands corresponding to $v(N—H)$ of the nitrogeneous bases at around $3400 \text{ cm}^{-1}$ it could be expected that the donors with N—H bonds would not be suited for basicity measurements. This was confirmed by preliminary experiments with pyrrole $v(N—H)\ 3500 \text{ cm}^{-1}$. In addition, the intensity of the band decreased with time. This decrease was observed both with *e.g.* 3-trimethylsilylpropylamine and n-butylamine, the latter compound being chosen as standard. Another unsuitable proton donor was phenylacetylene, though its hydrogen is weakly acidic; the intensity of the bands of the associated phenylacetylene was so low that the absorption maximum could not be even roughly estimated. The best proton donor for basicity measurements turned out to be deuteriochloroform $(v(C—D)\ 2257 \text{ cm}^{-1})$. Although it is only a weak acid, the associated component exhibits distinct absorption bands with well readable maxima. We also attempted at using studied compounds as proton donors in binary systems with tetrahydrofurane. The spectra of these mixtures showed, however, only absorption bands corresponding to $v(N—H)_{free}$, similarly as in tetrachloromethane.

The experimental wavenumbers of the stretching vibration $v(C—D)_{free}$ of deuterio-chloroform and of the bands belonging to the associated component, $v(C—D\cdots N)_{assoc}$ are summarized in Table I. The spectra of all the compounds containing in their molecule at least one Si—O—C bond showed in the region of hydrogen bonds also the band arising probably from the interaction of the proton of deuteriochloroform with the oxygen atom, $v(C—D\cdots O)_{assoc}$. This is indicated by decreasing intensity of the broad $v(C—D\cdots N)_{assoc}$ band at $2212-2228$ cm$^{-1}$ with increasing number of oxygen atoms in the molecule as well as by increasing intensity of a new band of small half-width occurring at about $2250$ cm$^{-1}$. In Table I are also listed the calculated values of frequency shifts which were taken as the measure of relative basicity, and that both of nitrogen $(v(C—O) - v(C—D\cdots N))$, and of oxygen $(v(C—D) - v(C—D\cdots O))$.

## DISCUSSION

From Table I it is evident that all the silylmethylamines are distinctly less basic than the higher silylalkylamines; the earlier measurements of the basicity of methyl-ethoxysilylmethylamines by potentiometrical titration in aqueous media revealed that these compounds are comparable in basicity $(pK_a)$ with simple primary alkyl-amines[15,16]. Under the above conditions fast hydrolysis of the ethoxy derivatives to silanols took place already on their dissolving. The silanols formed could further condensate. The so determined basicities relate thus rather to the formed amino-methylsiloxanes. In some cases, also formation of the products insoluble in water cannot be excluded.

The results obtained cannot be explained by solvation effects[44]. In the used solvent, tetrachloromethane, no significant interactions can be expected to take place. Neither coordination of the solvent to silicon, nor the more extensive for-mation of charge-transfer complexes between tetrachloromethane and the amino or ethoxy groups of studied compounds seems probable. The low basicity of the silylmethylamines can be most likely attributed to hyperconjugative effect, providing that it would be strong enough to prevail over relatively strong positive inductive effect of the trimethylsilyl group. The operation of this effect seems to be indicated by relatively high basicity of the silylethylamines. The values of $\Delta v$ for this series are distinctly higher than those for the silylpropylamines and the silylbutylamines, the latter ones being identical within experimental errors with the value for n-butyl-amine used as carbon standard. The value of $\Delta v$ $(42 \pm 2$ cm$^{-1})$ obtained for all the silylalkylamines which contain nitrogen in position 3 or 4 with respect to silicon, comports with the expected lowering of the +I effect of the silyl group due to its transfer through carbon chain.

From all the results obtained it follows that in no case was the basicity decreased in silylpropylamines and silylbutylamines, the compounds in which intramolecular

TABLE I

The Wavenumbers of $\nu$(-D) Vibration and the Frequency Shifts $\Delta\nu$ (in $cm^{-1}$) Due to Interaction of Deuteriochloroform with Silylalkylamines

| Proton acceptor | $\nu(C{-}D)_{free}$ | $\nu^{assoc.}$ (C—D$\cdots$N) | $\nu^{assoc.}$ (C—D$\cdots$O) | $\Delta\nu_N^a$ | $\Delta\nu_0^b$ |
|---|---|---|---|---|---|
| $(CH_3)_3SiCH_2NH_2$ | 2 259 | 2 223 | — | 36 | — |
| $(CH_3)_2(C_2H_5O)SiCH_2NH_2$ | 2 258 | 2 220 | 2 250 | 38 | 8 |
| $(CH_3)(C_2H_5O)_2SiCH_2NH_2$ | 2 258 | 2 223 | 2 252 | 35 | 6 |
| $(C_2H_5O)_3SiCH_2NH_2$ | 2 260 | 2 228 | $c$ | 32 | |
| $(CH_3)_3Si(CH_2)_2NH_2$ | 2 259 | 2 213 | — | 46 | — |
| $(CH_3)(C_2H_5O)_2Si(CH_2)_2NH_2$ | 2 258 | 2 213 | 2 252 | 45 | 6 |
| $(C_2H_5O)_3Si(CH_2)_2NH_2$ | 2 258 | 2 212 | $c$ | 46 | |
| $(CH_3)_3Si(CH_2)_3NH_2$ | 2 259 | 2 217 | — | 42 | — |
| $(CH_3)_2(C_2H_5O)Si(CH_2)_3NH_2$ | 2 258 | 2 215 | 2 248 | 43 | 10 |
| $(CH_3)(C_2H_5O)_2Si(CH_2)_3NH_2$ | 2 258 | 2 217 | 2 251 | 41 | 7 |
| $(C_2H_5O)_3Si(CH_2)_3NH_2$ | 2 258 | 2 219 | $c$ | 39 | |
| $(CH_3)_3Si(CH_2)_4NH_2$ | 2 259 | 2 216 | — | 43 | — |
| $(CH_3)_2(C_2H_5O)Si(CH_2)_4NH_2$ | 2 259 | 2 215 | 2 248 | 44 | 11 |
| $(CH_3)(C_2H_5O)_2Si(CH_2)_4NH_2$ | 2 259 | 2 217 | 2 251 | 42 | 8 |
| $(C_2H_5O)_3Si(CH_2)_4NH_2$ | 2 258 | 2 218 | $2\ 253^d$ | 40 | 5 |
| $CH_3CH_2CH_2CH_2NH_2$ | 2 259 | 2 216 | — | 43 | — |

$^a$ $\Delta\nu_N = \nu(C{-}D)_{free} - \nu^{assoc.}(C{-}D\cdots N)$; $^b$ $\Delta\nu_0 = \nu(C{-}D)_{free} - \nu^{assoc.}(C{-}D\cdots O)$; $^c$ the band of the free component was broadened; $^d$ shoulder.

coordination of nitrogen to the silicon could be expected to lead to formation of sterically favoured five- or six-membered rings. This circumstance indicates that still more suitable structure is needed for such a coordination. This is *e.g.* the case of silatranes, the nitrogen of which is fixed by tricyclic structure to the position close to the silicon. The fact that even in sterically optimum cases no intramolecular coordination is taking place indicates that the more important coordination cannot be expected to occur also in silylmethyl- amines. Such an interaction, which could otherwise provide an alternative explanation of the reduced basicity of silylmethyl-amines, would be much less probable.

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