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Preliminary communication

FIRST QUANTITATIVE MEASUREMENT OF THE BASICITY OF A SILYLAMINE IN AN AQUEOUS MEDIUM

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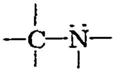
Summary

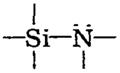
The first quantitative measurement of the basicity of a silylamine in an aqueous medium was accomplished by determining the pK_B of 1-diethylamino-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (IIIa) in 40% H_2O/60% THF solution. The pK_B showed that IIIa is a substantially weaker base than analogous carbon amines. The results are accomodated by d_π—p_π bonding in the ground state, although an additional factor, the "adjacent charge rule" may also be involved.

We wish to report the first quantitative measurement of the basicity of a silylamine in an aqueous medium using the standard half-neutralization method. Use of the latter has the great advantage that a large number of organic amines have been studied by this method, and thus the present work makes possible, for the first time, a precise and meaningful comparison between the basicities of systems I and II.



$-\overset{|}{\underset{|}{C}}-\overset{..}{\underset{|}{N}}-$

(I)

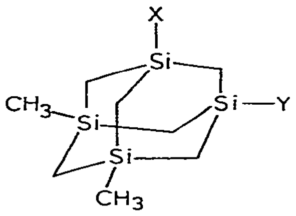


$-\overset{|}{\underset{|}{Si}}-\overset{..}{\underset{|}{N}}-$

(II)

We have accomplished our objective of precise determination of the basicity of II by taking advantage of the recent observation by Frye [1] that silylamines derived from the 1,3,5,7-tetrasilaadamantane system (III) are stable to aqueous HCl for long periods of time, in sharp contrast to other silylamines which give extremely rapid silicon—nitrogen cleavage under such conditions.

In Table 1 are summarized the results of our basicity measurements on five amines, all under identical conditions.



(III)

a, X = CH_3; Y = $N(C_2H_5)_2$
b, X = CH_3; Y = C_6H_5
c, X = Y = C_6H_5

TABLE 1

pK_B DETERMINATIONS IN 40% H_2O/60% THF AT 26° C

Compound	pK_B
Silylamine IIIa	8.32 ± 0.02
Triethylamine	4.72 ± 0.02
N,N-Diethylaniline	9.82 ± 0.02
1-Aminoadamantane	4.56 ± 0.02
t-Butylamine	4.08 ± 0.02

The work was carried out with 1-diethylamino-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (IIIa) which was prepared by the method of Frye [1]. This compound gave satisfactory IR, NMR, mass spectral, and elemental analyses. The carbon amines used for comparison were obtained from the usual suppliers and were purified by standard methods prior to use.

The basicities of the amines were determined by the half-neutralization technique using a Beckman Expandomatic pH Meter fitted with glass and calomel electrodes and calibrated with the appropriate standard buffer solutions. The temperature was maintained at 26.0 ± 0.5° C. A 40% H_2O/60% THF (v/v) solvent system was required in order to maintain completely homogeneous conditions during the experiments. This solvent system gives higher pK_B values than those obtained in 100% H_2O. The measured pK_B's were found to increase in a continuous manner with increasing THF concentration. When solubility allowed (triethylamine), extrapolation to 100% H_2O gave the accepted pK_B value with an error of ±2%.

No decomposition of silylamine IIIa was detected and IIIa was recovered from the test solutions in 88% yield. GLPC, IR, and NMR showed the recovered IIIa to be pure.

The results from Table 1 show a reduction in basicity of 3.60 pK_B units in going from triethylamine to silylamine IIIa. This effect, though large, is not as great as the reduction in basicity in going from triethylamine to *N,N*-diethylaniline (5.10 pK_B units). The rigid adamantane cage structure of IIIa does not appear to exert any "special effect" since 1-aminoadamantane, the analogous carbon amine, does not show an unusually low basicity in comparison to t-butylamine.

Since it was possible that the large reduction in basicity of silylamine IIIa was due to some collective effect of all four silicon atoms through a

1,3-(*d*—*d*) interaction[*], an attempt to detect the existence of such an interaction in the 1,3,5,7-tetrasilaadamantane system was made by determining the UV absorption spectra of IIIb and IIIc. The data from Table 2 does not support the existence of a 1,3-(*d*—*d*) interaction since the two phenyl groups in IIIc are shown to be electronically isolated.

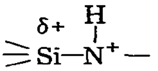
TABLE 2

ULTRAVIOLET SPECTRAL DATA [a]

Compound	λ_{max}(mμ)	ϵ
Phenyltrimethylsilane	259.0	270
IIIb [b]	260.5	259
IIIc [b]	260.4	513

[a] The spectra were recorded in purified isooctane on a Cary 14 Recording Spectrophotometer. [b] These phenylated 1,3,5,7-tetrasilaadamantanes were prepared from the corresponding chlorosilanes and phenyllithium and were purified by preparative GLPC. They both gave satisfactory IR, NMR, mass spectral, and elemental analysis.

Prior studies [3—6] as well as the present one indicate that silylamines are weaker donors than carbon amines of analogous structure. Since inductive electron release from silicon should give the reverse basicity effect, and since trisilylamine is planar [6], other workers have concluded that ground state d_π—p_π bonding is responsible for the base-weakening effect in silylamines compared to analogous carbon amines. We are inclined to agree, but would like to point out that, to an unknown extent, operation of Pauling's adjacent charge rule [7], may also be responsible for the decrease basicity of silylamines. To the extent that the *net* charge on Si, due to electron release from silicon to the attached organic groups is *positive*, protonation of nitrogen could lead to energetically unfavorable charge distribution as shown in IV.



$\geqslant\overset{\delta+}{\mathrm{Si}}-\overset{\overset{\textstyle\mathrm{H}}{|}}{\mathrm{N}}{}^{+}-$ (IV)

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[*] The possibility of a 1,3-(*d*—*d*) interaction in the excited state for other Si—CH_2—Si compounds was investigated. The authors concluded that this effect was not significant for the compounds studied (see ref. 2 for detailed discussion).