

We thank Dr. George A. Wiley for preparing the crystals which we used. Further refinement of this structure is in progress.

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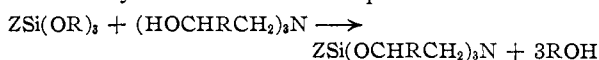
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**TRIPTYCH-SILOXAZOLIDINES:  
PENTACOORDINATE BRIDGEHEAD SILANES  
RESULTING FROM TRANSANNULAR INTERACTION  
OF NITROGEN AND SILICON**

Sir:

We have found the alcoholysis of trialkoxysilanes by trialkanolamines to lead to the exclusive formation of crystalline monomeric products.<sup>1</sup>



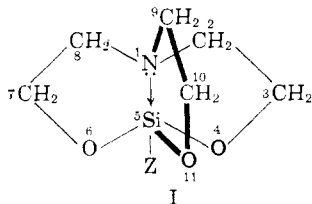
This is in striking contrast to the polymeric products one might reasonably have anticipated from the condensation of such highly functional reactants. A series of such derivatives has been prepared and representative members are shown in Table I.

TABLE I  
TRIPTYCH-SILOXAZOLIDINES

Substituents	M.p., <sup>a</sup> °C.	Molecular formula	Silicon, %		Neut. equiv.	
			Calcd.	Found	Calcd.	Found
None	253-256	C <sub>8</sub> H <sub>14</sub> O <sub>3</sub> SiN	16.02	16.23	175	177
5-Methyl <sup>b</sup>	123-125	C <sub>7</sub> H <sub>16</sub> O <sub>3</sub> SiN	14.84	14.66	189	189
	151-153 <sup>c</sup>					
3,5-Dimethyl	95-97	C <sub>8</sub> H <sub>17</sub> O <sub>3</sub> SiN	13.82	13.60	203	203
5-Octadecyl	85-86	C <sub>24</sub> H <sub>49</sub> O <sub>3</sub> SiN	6.57	6.73	428	428
5- $\alpha$ -Phenethyl	192-194	C <sub>14</sub> H <sub>21</sub> O <sub>3</sub> SiN	10.05	10.16	279	282
5-Vinyl	163-165	C <sub>8</sub> H <sub>15</sub> O <sub>3</sub> SiN	13.96	14.14	201	202
5-Phenyl	208-209	C <sub>12</sub> H <sub>17</sub> O <sub>3</sub> SiN	11.18	11.24	251	250
3-Methyl-5-phenyl	85-87	C <sub>13</sub> H <sub>19</sub> O <sub>3</sub> SiN	10.58	10.48	265	267
5-Ethoxy <sup>d</sup>	100-102	C <sub>8</sub> H <sub>17</sub> O <sub>4</sub> SiN	12.81	12.72	219	218
5(-)-Menthoxy	152-154	C <sub>16</sub> H <sub>31</sub> O <sub>4</sub> SiN	8.52	8.32	330	333

<sup>a</sup> Uncorrected. <sup>b</sup> B.p. 174° (31 mm.). <sup>c</sup> Apparent polymorphism; the lower-melting form was obtained by crystallizing the melt at about 100°. <sup>d</sup> B.p. 180° (0.6 mm.).

That even a fourth substituent on the silicon may be functional is illustrated by the monomeric products derived from such silanes as trimethoxysilane and ethyl orthosilicate. For reasons cited below, these silanes are believed to be pentacoordinate as a result of transannular dative bonding between the nitrogen and silicon atoms (I). They have been



designated as triptych-siloxazolidines<sup>2,3</sup> by analogy

(1) Subsequent to completion of this work, an account of the independent preparation of C<sub>8</sub>H<sub>14</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N and CH<sub>3</sub>CH<sub>2</sub>OSi(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N appeared in U. S. Patent 2,953,545 granted to Arnold B. Finestone, Sept. 20, 1960. The melting point of the latter compound (35-37°) differs significantly from our value (100-102°).

(2) This nomenclature is best illustrated by a specific example such as the naming of C<sub>2</sub>H<sub>5</sub>OSi(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N. Using the numbering scheme shown (I), one obtains the name 5-ethoxytriptych-siloxazolidine. This compares favorably with the precise but unwieldy

with the structurally related borates.<sup>4,5</sup> While pentacoordinate complexes of various halosilanes have been reported,<sup>6</sup> the triptych-siloxazolidines herein described are believed to be the first examples of pentacoordinate alkoxy silanes. Their marked stability despite the weakly basic nature of trialkanolamines<sup>7</sup> and the apparent failure of trimethoxysilane to complex with an amine as nucleophilic as piperidine (*vide infra*) underscores the importance of steric factors in such interactions.

Brown<sup>4c</sup> based his assignment of a triptych structure to triethanolamine borate upon the inertness of the nitrogen atom toward methyl chloride and its sluggish neutralization by methanesulfonic acid in nitrobenzene solution. Similarly, we have found that triptych-siloxazolidines are not neutralized immediately by perchloric acid in a glacial acetic acid medium, thereby supporting a structure wherein the nitrogen's basic pair of electrons is not available for immediate protonation.

The silicon system provides the means for a unique test of the triptych model. Smith and Angelotti<sup>8</sup> studied the effect of molecular structure upon the Si-H stretching frequency, showing clearly that

increased electron supply at the silicon displaces the absorption to lower energy regions. Although showing some solvent dependency, the position of  $\nu(\text{SiH})$  for HSi(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N was displaced from the region characteristic of silanes bearing three Si-O bonds to a lower energy region wherein silanes

systematic<sup>8</sup> name 4,6,11,1,5-trioxazasil-5-ethoxytricyclo[3.3.3.0<sup>1,5</sup>]-undecane.

(3) IUPAC 1957 Rules, *J. Am. Chem. Soc.*, **82**, 5573 (1960).

(4) (a) A. A. Schleppek and C. D. Gutsche, *J. Org. Chem.*, **25**, 1378 (1960); (b) H. Steinberg and D. L. Hunter, *J. Am. Chem. Soc.*, **82**, 853 (1960); (c) H. C. Brown and E. A. Fletcher, *ibid.*, **73**, 2808 (1951); (d) C. A. Rojahn, German Patent 582,149 (*Chem. Zentr.*, **104**, II, 2704 (1933)).

(5) It seems likely that similar compounds containing such elements as Al, Fe, Ti, Sn, Ge, P, etc., might be feasible. In this connection, preliminary studies have shown sublimable material of the anticipated composition to result from the reaction of triisopropanolamine and aluminum isopropylate. The importance of atomic size and/or the presence of relatively low-lying vacant orbitals was demonstrated by the condensation of ethyl orthoformate and triethanolamine to form a cross-linked polymer rather than a monomeric species.

(6) (a) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, 1960, p. 92; (b) F. G. A. Stone and D. Seyferth, *J. Inorg. and Nucl. Chem.*, **1**, 112 (1955).

(7) H. K. Hall, *J. Am. Chem. Soc.*, **79**, 5441 (1957).

(8) A. L. Smith and N. C. Angelotti, *Spectrochim. Acta*, **15**, 412 (1959).

bearing three Si-C bonds are found. Data<sup>8</sup> illustrating the shift are listed:

Compound	$\nu(\text{SiH})$	
$\text{HSi}(\text{OCH}_3)_3$	2203 ( $\text{CCl}_4$ )	
	2201 (Piperidine)	
	2202 (Pyridine)	
$\text{HSi}(\text{OCH}_2\text{CH}_3)_3$	2196 ( $\text{CCl}_4$ )	
	$\text{HSi}[\text{OCH}(\text{CH}_3)_2]_3$	2191 ( $\text{CCl}_4$ )
	$\text{HSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$	2137 ( $\text{HCCl}_3$ )
	2117 ( $\text{CH}_3\text{OH}$ )	
$\text{HSi}(\text{C}_6\text{H}_5)_3$	2126 ( $\text{CCl}_4$ )	
$\text{HSi}(\text{CH}_2\text{CH}_3)_3$	2097 ( $\text{CCl}_4$ )	

This shift is consistent with the triptych model which would certainly appear to involve increased electron supply at the silicon atom.

Observations of solute association made in the course of our molecular weight determinations<sup>9</sup> are not inconsistent with the triptych structure. Whereas a polar solvent such as acetonitrile yielded ideal solutions over a wide concentration range, the relatively non-polar toluene did not.<sup>10</sup> Such associative propensities could result from the dipolar nature implied by the intramolecular dative bond.

The hybridization of the silicon in the triptych-siloxazolidines is probably of the  $sp^3d$  type, wherein the oxygens are coplanar with the silicon and situated at the three equatorial positions ( $\angle \text{OSiO} = 120^\circ$ ), while the nitrogen and Z, the remaining substituent, occupy the axial positions. X-Ray studies now in progress should permit a more precise description of the actual disposition of atoms. Since the silicon atom in such a structure (I) is at once pentacoordinate and a bridgehead site, its reactivity as well as that of Z, the "fifth" substituent, may be altered considerably. Studies dealing with these aspects will be reported at a later date.

(9) We used a modified Swietoslowski differential ebulliometer as described by W. E. Barr and V. J. Anhorn in *Instr. and Automation*, **20**, 822 (1947).

(10) These apparent molecular weight values for  $\text{CH}_3\text{CH}_2\text{OSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$  (calcd. mol. wt., 219) were obtained with toluene as solvent and illustrate the increasing degree of association with increasing molality: 257 (0.1 m); 306 (0.3 m); 342 (0.5 m); 379 (0.7 m). The other triptych-siloxazolidines displayed very similar associative tendencies.

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#### EVIDENCE FOR INTERACTION BETWEEN MAGNESIUM AND PURINE OR PYRIMIDINE RINGS OF 5'-RIBONUCLEOTIDES

Sir:

The evidence from ultraviolet spectra given here supports suggestions<sup>2-5</sup> that  $\text{Mg}^{++}$  interacts with the purine or pyrimidine rings of NTP,<sup>1</sup> possibly in enzymatic process.

(1) The abbreviations used are: NTP, nucleosides triphosphates; ATP, adenosine triphosphate; ITP, inosine triphosphate; CTP, cytidine triphosphate.

(2) A. Szent-Györgyi in "Enzymes, Units of Biological Structure and Function," Ed. O. H. Gaebler, Academic Press, Inc., New York, N. Y., 1956, p. 393.

(3) G. L. Eichhorn in "The Chemistry of the Coordination Compounds," Ed. J. C. Bailar, Jr., Reinhold Publ. Co., New York, N. Y., 1956, p. 698.

(4) W. G. McCormick and B. H. Levedahl, *Biochem. et Biophys. Acta*, **34**, 303 (1959).

(5) J. J. Blum, *Arch. Biochem. Biophys.*, **55**, 486 (1955); **87**, 104 (1960).

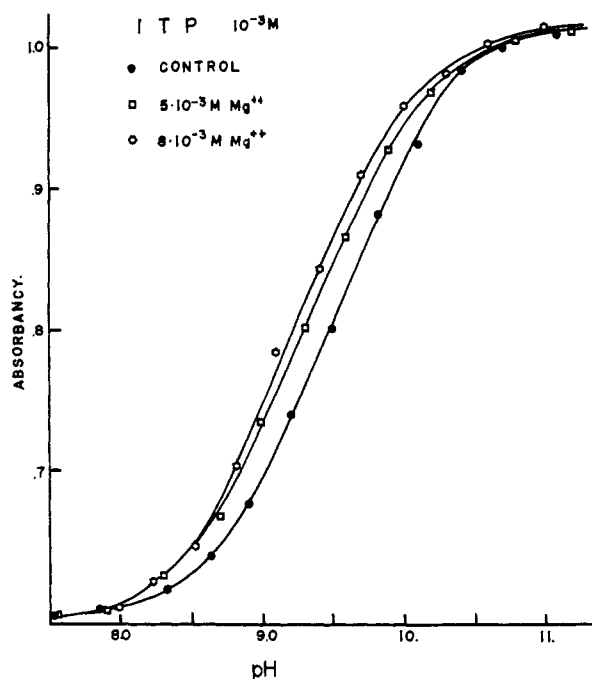


Fig. 1.—Spectrophotometric titration of OH-group in ITP in 0.05 M  $(\text{CH}_3)_4\text{NCl}$  at 263  $m\mu$ .

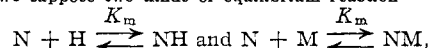
Addition of  $\text{Mg}^{++}$  or  $\text{Ca}^{++}$  to the un-ionized ring causes the same spectral shift as neutralization with  $\text{OH}^-$ ; presumably in both cases protons are displaced from the ring. Spectral titration curves, enabling the determination of ring apparent  $pK$  as the pH of half ionization, were carried out at the wave length of maximum shift: 263  $m\mu$  for the 6-OH group of inosine nucleotides, 223  $m\mu$  for the 6-NH<sub>2</sub> group in adenosine nucleotides, and 245  $m\mu$  for the 4-NH<sub>2</sub> group of cytidine nucleotides.

If  $\Delta pK$  is the difference in  $pK$ 's of half titration without and with metal, then, assuming one metal ion bound per molecule of nucleotide, the metal-nucleotide affinity constant is  $K_m = 2A(A-1)/\{N_0 + A(2M_0 - N_0)\}$  where  $A = 10^{\Delta pK}$ ,  $M_0$  is the total concentration of metal ion and  $N_0$  is the total concentration of nucleotide.<sup>7</sup>

Table I shows that  $K_m$  of  $\text{Mg}^{++}$  for a ring containing an OH group is greater than for a ring containing an NH<sub>2</sub> group. Also,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  do not shift the spectral titration curves of the corresponding bases or nucleosides, indicating that for interaction, phosphate as well as ring is necessary, and suggesting that in solution NTP is partly in a curled configuration<sup>2,3</sup> with  $\text{Mg}^{++}$  chelated between pyrophosphate structure and base. Apparent  $K_m$  depends strongly on both  $\text{Mg}^{++}$  and nucleotide concentration, suggesting that more than one  $\text{Mg}^{++}$  per nucleotide is bound.<sup>8-10</sup>

(6) R. M. Bock, Nan-Sing Ling, S. A. Morrell and S. H. Lipton, *ibid.*, **62**, 253 (1956).

(7) If we suppose two kinds of equilibrium reaction



with the mass law equations, the equation for the conservation of mass and the condition  $N = N_0/2$  at half titration points, the equation  $K_m$  in the text is obtained.

(8) R. Smith and R. Albery, *J. Am. Chem. Soc.*, **78**, 2376 (1956).

(9) C. Liebecq and M. Jacquemotte-Louis, *Bull. Soc. Chim. Biol.*, **40**, 67 (1958).

(10) J. M. Lowenstein, *Biochem. Z.*, **70**, 222 (1958).