bearing three Si-C bonds are found. Data[8] illustrating the shift are listed:

Compound	ν(SiH)
$HSi(OCH_3)_3$	2203 (CCl_4)
	2201 (Piperidine)
	2202 (Pyridine)
$HSi(OCH_2CH_3)_3$	2196 (CCl_4)
$HSi[OCH(CH_3)_2]_3$	2191 (CCl_4)
$HSi(OCH_2CH_2)_3N$	2137 ($HCCl_3$)
	2117 (CH_3OH)
$HSi(C_6H_5)_3$	2126 (CCl_4)
$HSi(CH_2CH_3)_3$	2097 (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[9] 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.[10] Such associative propensities could result from the dipolar nature implied by the intramolecular dative bond.

The hybridization of the silicon in the triptychsiloxazolidines is probably of the sp^3d type, wherein the oxygens are coplanar with the silicon and situated at the three equatorial positions ($\angle OSiO = 120°$), 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 pentacoördinate 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 Swietoslawski 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 $CH_3CH_2OSi(OCH_2CH_2)_3N$ (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 triptychsiloxazolidines 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[2-5] that Mg^{++} interacts with the purine or pyrimidine rings of NTP,[1] 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 Coördination 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).

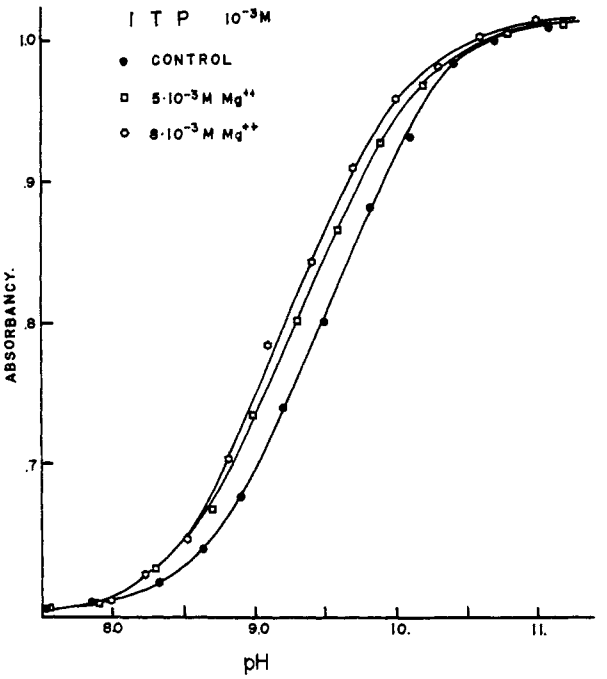

Fig. 1.—Spectrophotometric titration of OH-group in ITP in 0.05 *M* $(CH_3)_4NCl$ at 263 mμ.

Addition of Mg^{++} or Ca^{++} to the un-ionized ring causes the same spectral shift as neutralization with OH^-[6]; 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 mμ for the 6-OH group of inosine nucleotides, 223 mμ for the 6-NH_2 group in adenosine nucleotides, and 245 mμ for the 4-NH_2 group of cytidine nucleotides.

If ΔpK 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.[7]

Table I shows that K_m of Mg^{++} for a ring containing an OH group is greater than for a ring containing an NH_2 group. Also, Ca^{++} and 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[2,3] with Mg^{++} chelated between pyrophosphate structure and base. Apparent K_m depends strongly on both Mg^{++} and nucleotide concentration, suggesting that more than one Mg^{++} per nucleotide is bound.[8-10]

(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

$$N + H \underset{}{\overset{K_m}{\rightleftharpoons}} NH \text{ and } N + M \overset{K_m}{\rightleftharpoons} NM,$$

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. Alberty, *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).

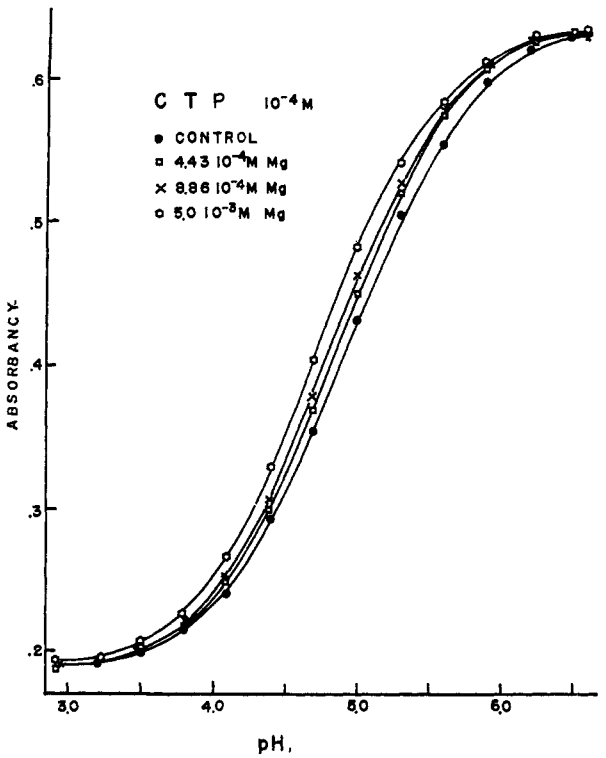

Fig. 2.—Spectrophotometric titration of NH_2-group in CTP in 0.05 M $(CH_3)_4NCl$ at 245 mμ.

Over-all values of $K_m(M^{-1})$ obtained not spectrally but with an titrimeter (and therefore sensitive to proton displacement from the whole molecule not just the ring) are[11]: ITP, 1.2×10^4; ATP, 8×10^3; IDP 5.7×10^3; ADP, 2.2×10^3 M^{-1}. These are in the range reported by others.[8,12-15] Variation among previous reports probably was due to concentration effects. For instance, the values of Smith and Alberty[8] who used rather high concentrations, are lower than those of others[12-14] who used lower concentrations. Except Burton's results[16] there is an inverse correlation between concentrations of nucleotide and Mg^{++} and apparent K_m.

TABLE I

AFFINITY CONSTANTS FOR Mg^{++} OF PURINE AND PYRIMIDINE RING IN 0.05 M $(CH_3)_4NCl$

Mg. concn. $M \times 10^3$	Apparent affinity constant $\times 10^{-3}$ M^{-1} ITP 10^{-4} M	ATP 10^{-4} M	CTP 10^{-4} M	IDP 10^{-4} M	ADP 10^{-4} M	CDP 10^{-4} M
0.044	15.6					
0.115	6.9					
0.44	2.0			1.3		
0.88			0.30	1.05		
1.0	1.4	0.42	.18	0.42		
2.5		.15				
5.0	0.26	.17	.09	.24		0.030
10.0		.09	.048	.063	0.026	.026
5.0	12.2[a]					
8.8	0.15[a]					
50.0	.22[a]					

[a] These values are for 10^{-3} M ITP concentration.

Comparing spectrally-obtained (ring) affinity constants with titrimeter-obtained (over-all) affinity constants we found ratios of the order of 1:100 with ITP and 1:50 with ATP. From these ratios can be estimated the fraction of nucleotide in "curled" and "linear" forms. Ring K_m (ITP) > Ring K_m (ATP), but at neutral pH due to the great difference in ring ionization constants of the two nucleotides, the fraction of ATP binding Mg^{++} will be about 100 times greater than the corresponding fraction for ITP. This may be particularly important for the model[5] of myosin NTPase which assumes interaction between the 6-position in the purine ring and Mg^{++} or Ca^{++} and myosin.

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(11) The concentration of nucleotides was 10^{-3} M and of $MgCl_2$ 10^{-3} M; solvent was 0.05 M tetramethylammonium chloride.

(12) L. B. Nanninga, *J. Phys. Chem.*, **61**, 1144 (1957).

(13) A. E. Martell and G. Schwarzenbach, *Helv. chim. acta*, **39**, 653 (1956).

(14) E. Walaas, *Acta chem. scand.*, **12**, 528 (1958).

(15) K. Burton, *Biochem. J.*, **71**, 388 (1959).

(16) At neutral pH, $[N_0] = 10^{-4}$ M, $[M_0] = 10^{-3}$ M, the approximate fraction of metal-ring complex can be calculated as: $K_m[M]/\{(1 + K_m[M] + K_h[H]\}$ substituting the values: K_m, 0.42×10^3, 1.4×10^3 M^{-1}; K_h, $10^{4.5}$, $10^{9.5}$ M^{-1} for ATP and ITP, respectively, and $[H] = 10^{-7}$, $[M] = 10^{-3}$ M, we get the fraction for ATP, 0.30; for ITP, 0.003.

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THE STEREOCHEMISTRY OF RIMUENE

Sir:

Rimuene has attracted attention in recent years in view of its possible central position in the biosynthesis of tetracarbocyclic diterpenic substances.[1] While physical and chemical evidence has pointed to I as its structure,[2] no rigorous stereochemical assignment of its asymmetric centers C-9 and 13 has been made. Contrastingly, the structurally related isopimaric, sandaracopimaric and pimaric acids (II) have been shown to possess configurations IIIa, b and c, respectively.[3] The non-identity of the hydrocarbons derived from these acids with rimuene[4] suggests that rimuene may

(1) (a) E. Wenkert, *Chemistry & Industry*, 282 (1955); (b) L. H. Briggs, B. F. Cain, B. R. Davis and J. K. Wilmhurst, *Tetrahedron Letters*, No. 8, 13 (1959).

(2) (a) L. H. Briggs, B. F. Cain and J. K. Wilmhurst, *Chemistry & Industry*, 599 (1958) and references contained therein; (b) L. H. Briggs, B. F. Cain and R. C. Cambie, *Tetrahedron Letters*, No. 8, 17 (1959).

(3) (a) E. Wenkert and J. W. Chamberlin, *J. Am. Chem. Soc.*, **81**, 688 (1959); (b) O. E. Edwards and R. Howe, *Can. J. Chem.*, **37**, 760 (1959); (c) B. Green, A. Harris and W. B. Whalley, *J. Chem. Soc.*, 4715 (1958); (d) O. E. Edwards, A. Nicholson and M. N. Roger, *Can. J. Chem.*, **38**, 663 (1960); (e) A. K. Bose, *Chemistry & Industry*, 1104 (1960).

(4) The conversions of pimaric and isopimaric acids to their hydrocarbons have been accomplished in These Laboratories (unpublished experiments by B. G. Jackson and J. W. Chamberlin) and in the laboratories of Professors L. H. Briggs (Auckland, New Zealand) (private communication) and R. E. Ireland (Michigan) (*cf.* R. E. Ireland and P. W. Schiess in Abstracts of Papers of the International Symposium on the Chemistry of Natural Products, Australia, August 15–25, 1960, p. 57). The Michigan workers also transformed Edwards' sandaracopimaric acid[3d] into a hydrocarbon and carried out a total synthesis of racemic pimaradiene of the pimaric and sandaraco-