used.
(35) In the spectrum of isomer OR-2, the ^{15}N resonance could be seen from the minor isotopic isomer in which the 6-cystyl residue contained an α proton. The two-bond deuterium substitution effect was found to be 0.13 ppm upfield by comparison of the frequencies of the minor and major peaks.
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Intramolecular Water Bridge between the 2'-OH and Phosphate Groups of RNA. Cyclic Nucleotides as a Model System

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Abstract: The investigation of the ^1H NMR spectra of cNMPs in aqueous and mixed solvents shows that the 2'-OH proton is protected from exchange with bulk water. In the presence of low salt, 0.05 M, the free energy of stabilization of the 2'-OH is about 1.5 kcal and the activation energy for exchange is about 7 kcal. The protection of the 2'-OH proton against exchange cannot be attributed to an intermolecular association. The ^1H NMR results are consistent with there being an intramolecular water bridge between the 2'-OH and the phosphate group. A similar water bridge has been proposed for RNA to explain the ^1H NMR results obtained for a variety of RNA samples. The energies determined for the cNMP intramolecular water bridge can be cautiously extended to RNA.

Introduction

The backbones of RNA and DNA differ only in the substituent at the 2' position of the ribose and yet the conformational properties of the two polymers are quite different.[1,2] DNA double helices are normally found in the B form with a 2'-endo ribose conformation, but can adopt a number of other conformations in the appropriate experimental conditions. In contrast to the variety of conformations found for DNA, RNA is only found to exhibit ordered, helical conformations of the A family of helices in which the ribose is in the 3'-endo conformation.[1,2] While it has been known for some time that the 2'-OH group of RNA is responsible for these differences in the properties of RNA and DNA, the role of the 2'-OH has remained unclear. Recently, we proposed that the 2'-OH of RNA forms an *intra*molecular water bridge with the adjacent 3'-phosphate, as shown in Figure 1.[3] This proposed water bridge accounts for ^1H NMR results which showed that the exchange rate of the 2'-OH of RNA samples in aqueous solution is anomalously slow and that the resonance position of the 2'-OH proton in polymers is shifted about 1.5 ppm to lower field than that observed for mononucleosides. This hydrogen-bonding scheme involving a "bound" water molecule may also explain, at least in part, the differences between RNA and DNA.

Attempts to test the proposed hydrogen bonding scheme and to gain information about the strength of the hydrogen bonding involved have been hampered by the limited range of conditions in which the 2'-OH resonance of RNA samples can be observed.[3,4] For example, the 2'-OH resonance of denatured RNA cannot be observed, as disruption of the helical structure results in rapid exchange of the 2'-OH proton with water.[3] To overcome some of these limitations, we searched for other molecules which might exhibit a water-2'-OH-phosphate interaction similar to that proposed for RNA. Specifically, we looked for molecules with a stereochemical arrangement of the ribose hydroxyl group and an oxygen atom of a neighboring phosphate group that might mimic that of the A form RNA helix.

The 3',5' cyclic nucleotides have a rigid ribose conformation which is similar to that of RNA[5] and appear to be suitable for our purpose. The ribose conformation is a modification (3'-endo, 4'-exo) of the 3'-endo form found for RNA and the distance between the 2'-OH oxygen atom and the nearest phosphodiester oxygen atoms is about 0.36 nm, compared with 0.48 nm in the A form of RNA.[6] The ^1H NMR data on cyclic nucleotides presented here support the notion that 3',5'-cNMPs do form an intramolecular water bridge similar to that proposed for RNA. The unique properties of the cNMPs allow the further characterization of the nature of the hydrogen-bonding interactions responsible for the slow exchange of, and unexpectedly large downfield chemical shift of, the 2'-OH proton in aqueous solution.

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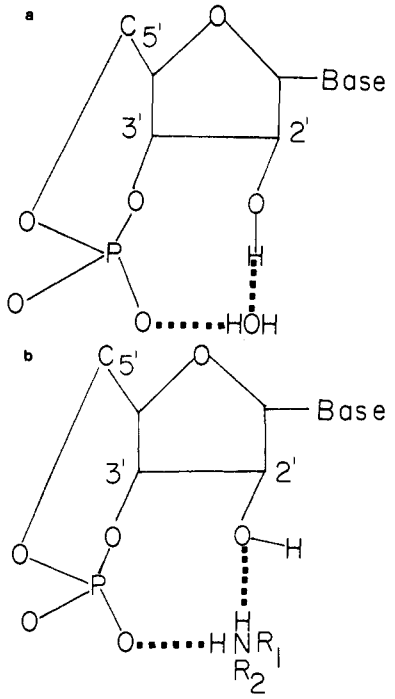

Figure 1. (a) Schematic drawing of intramolecular water bridge between 2′-OH and phosphate group. (b) Schematic drawing of interaction of ammonium group with 2′-OH and phosphate groups.

Experimental Section

Chemicals. Cyclic UMP and AMP were obtained from both Calbiochem and P-L Biochemicals. All other nucleotides and polynucleotides were obtained from P-L Biochemicals. Spermine was obtained from Calbiochem, lysine from Sigma, and the other reagents were of the highest purity commercially available. The poly(U) sample for the ^{1}H NMR studies was prepared as described elsewhere.[4] Concentrations were determined using the extinction coefficients given in the P-L Biochemicals Catalog 105 (1977).

pH and Salt Studies. The samples were dissolved in doubly distilled water and the pH was adjusted to the appropriate value with dilute (0.05 M) HCl or NaOH. The pH was measured using a Beckman Model 3500 pH meter and Beckman Futura 39013 combination electrode. In the experiments on the pH dependence of the line width of the 2′-OH proton resonance, the pH was measured before and after the NMR measurements. The pH varied less than 0.1 pH unit during the course of measuring the ^{1}H NMR spectra. For the measurements of the salt effect, the cNMPs were dissolved in the appropriate salt solution and the pH adjustments performed as described above.

Catalysis of Exchange. Samples of the catalyst of interest were dissolved in doubly distilled water and the pH was adjusted to 6 with dilute HCl or NaOH. Aliquots of the catalyst were then added to a sample of cNMP at pH 6 and the ^{1}H NMR spectrum of the sample was obtained. The pH of the sample was checked after the spectrum was obtained.

Mixed Solvent and Concentration Dependence Experiments. The experiments on the samples of cNMPs in mixed solvent were performed by preparing a very concentrated solution of cNMP at pH 5.9. This solution was then diluted with known amounts of water and/or Me_2SO. Samples of cNMPs in Me_2SO were obtained by drying aqueous samples (pH 5.9) of the cNMPs and then dissolving them in spectroscopic grade Me_2SO. The Me_2SO solutions contained about 50 mM cNMP and about five to ten water molecules per nucleotide, judging from the intensity of the water peak in the ^{1}H NMR spectrum. The spectra of dry Me_2SO samples were obtained at 20 °C and the spectra of the mixed solvent samples at 12 °C.

NMR Spectra. All of the ^{1}H NMR spectra were obtained with a Varian HR-300 spectrometer interfaced to a Nicolet 1020A, which in turn was interfaced to the UCSD Chemistry Department computing facility. All of the spectra shown in this paper were obtained by use of correlation spectroscopy.[7] The natural line widths of the nonexchangeable proton resonances are much less than those of the 2′-OH. Therefore, for presentation purposes some spectra were line broadened by 5 Hz in the correlation procedure such that all peaks of equal intensity would have similar heights. Temperatures were controlled using the Varian temperature unit and are accurate to within 1 °C. Line widths were determined by direct reading of the full width at half height of the digitized spectrum. The accuracy of the line-width determinations is about 10% except for the very broad lines (>160 Hz), for which the accuracy is probably only about 15%. Chemical shifts of samples in aqueous solution were measured by sideband modulation of the water peak which was in turn referenced to the usual standard DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid). In the mixed solvent experiments the chemical shifts were measured relative to TSP (sodium 3-trimethylsilylproprionate-*2,2,3,3-d*$_4$).

Results and Discussion

Assignment of ^{1}H NMR Spectra of cNMPs. The resonances of the nonexchangeable protons of cNMPs have been previously assigned and these are indicated in Figure 2.[8] The assignment of resonances of the exchangeable protons in water is straightforward. These resonances are first assigned for the samples in aprotic solvent and then tracked as the solution is made progressively richer in water. For example, the spectra for cAMP in Figure 2a shows that in Me_2SO–water there are two peaks from exchangeable protons. The peak at 7.2 ppm with intensity corresponding to two protons is assigned to the amino protons of cAMP. The resonance position of the amino protons is about the same as for other adenosine derivatives in similar conditions. The peak at 6.2 ppm in Me_2SO is also from an exchangeable proton, and therefore must be assigned to the 2′-OH proton, as this is the only other exchangeable proton of the molecule. For cUMP there is a single peak from an exchangeable proton between 6 and 9 ppm, as shown in Figure 2. This resonance is assigned to the 2′-OH proton since the only other exchangeable proton of cUMP, the imino proton, has a resonance position of about 11.5 ppm (in the presence of small amounts of water, greater than about 0.5 M, this resonance is very broad and the imino proton of cUMP was only observed in very dry Me_2SO samples). The spectra of cUMP in solutions of different mole percent water (Figure 3) show that the resonance of the 2′-OH proton shifts downfield linearly with increasing mole percent water from about 6.2 ppm in Me_2SO solution to about 7.2 ppm in water. According to this assignment of the cAMP and cUMP spectra, the cyclic deoxyribonucleotides should not exhibit any resonance corresponding to the 2′-OH proton. The spectra of cdAMP in Figure 2b shows that the only peak from exchangeable protons is from the amino protons and that, as expected, the resonance from the 2′-OH proton is absent.

These results confirm the assignment of the 2′-OH proton of cUMP and cAMP in *aqueous* solution to the resonance at ~7.2 ppm. They also show that the 2′-OH proton is hydrogen bonded to water since the structures of cNMPs rule out any direct *intra*molecular interaction with other hydrogen-bonding groups in the molecule. We have previously shown that hydrogen bonding of a 2′-OH proton of nucleosides and polynucleotides to water results in a downfield shift of about 1 ppm relative to the position observed in Me_2SO.[4]

Exchange Rate of the 2′-OH Proton. The spectra in Figure 4 show that the resonance of the 2′-OH of cUMP can be observed in aqueous solution at temperatures as high as 40 °C. This is in contrast with the results obtained for mononucleosides, mononucleotides, and 2′,3′-cyclic mononucleotides in water. For these compounds the hydroxyl resonances are not observable at 0 °C in aqueous solution. Thus the observation of the 2′-OH proton resonance in aqueous solution at temperatures as high as 40 °C clearly indicates that the 2′-OH proton is protected from exchange.

The possibility that the protection arises from an intermolecular association can be ruled out by an examination of the effect of the cyclic nucleotide concentration on the 2′-OH

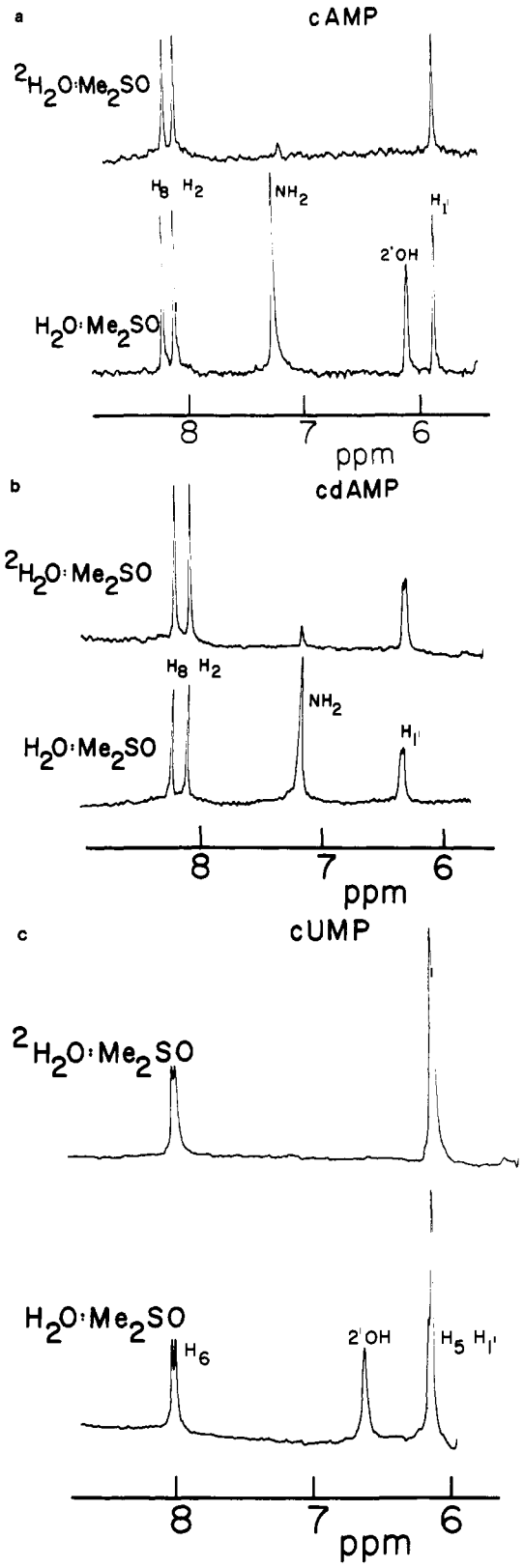

Figure 2. (a) 300-MHz ^1H NMR spectra of cAMP in Me_2SO-water (25 mol % H_2O) and in Me_2SO-^2H_2O (25 mol % ^2H_2O). (b) 300-MHz ^1H NMR spectra of cdAMP in Me_2SO-H_2O (25 mol % H_2O) and in Me_2SO-^2H_2O (25 mol % ^2H_2O). (c) 300-MHz ^1H NMR spectra of cUMP in Me_2SO-H_2O (50 mol % H_2O) and in Me_2SO-^2H_2O (50 mol % ^2H_2O).

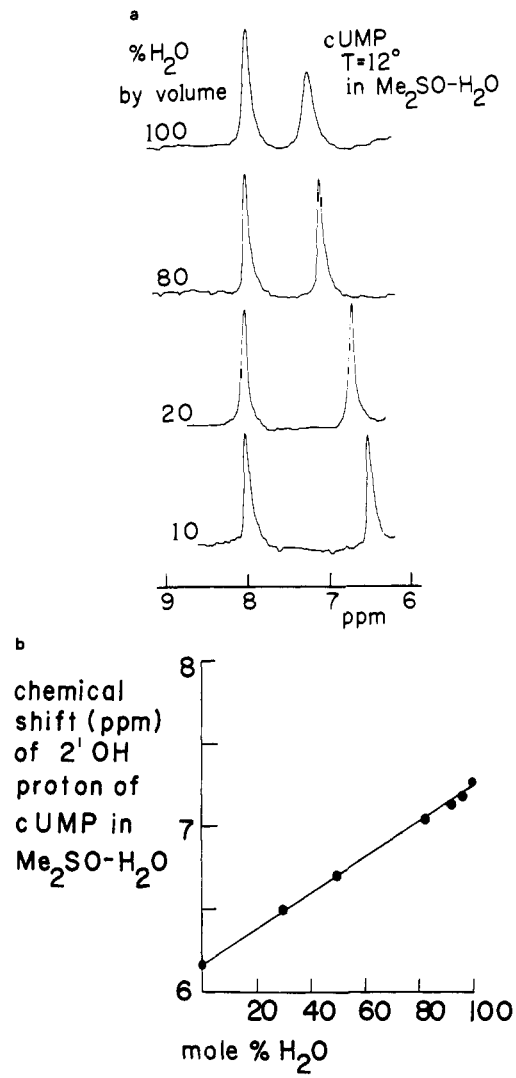

Figure 3. (a) 300-MHz ^1H NMR spectra of cUMP in Me_2SO-H_2O of composition indicated. (b) Plot of chemical shift of 2'-OH proton of cUMP in Me_2SO-H_2O as a function of the mole percent H_2O.

resonance. The spectrum of cUMP is shown in Figure 4a at concentrations ranging from 10 to 500 mM. It is seen that the resonance position and intensity of the 2'-OH proton are virtually unaffected by changes in concentration over this range. There is some decrease in the intensity of the 2'-OH resonance as the concentration is increased and this is attributed to the change in the salt concentration, as discussed below. Since derivatives of U are known to exhibit little or no self-association in aqueous solution, the ^1H NMR data eliminates the possibility that the protection of the 2'-OH proton is due to an intermolecular association.

Additional information about the protection of the 2'-OH proton can be obtained from the examination of the effect of pH on the exchange rate. The line width, $\Delta\nu_{1/2}$, of the 2'-OH proton was used to determine the exchange rate by use of the expression $k = \pi\Delta\nu_{1/2}$. The pH-dependent exchange rates were analyzed in terms of the equation

$$k = k_H[H^+] + k_{OH}[OH^-] \quad (1)$$

Use of this expression and the observed exchange rates gives rise to the rate constants listed in Table I for k_H and k_{OH}.

According to Eigen,[9] the rate constant for encounter-controlled exchange of a proton between a donor and an acceptor is given by

$$k = 10^{10}C\frac{10^{\Delta pK}}{1 + 10^{\Delta pK}} \quad (2)$$

where C is the acceptor concentration and $\Delta pK = pK_{acceptor} - pK_{donor}$. Equation 2 assumes that the exchange of the proton of interest is governed solely by the rate of encounter between

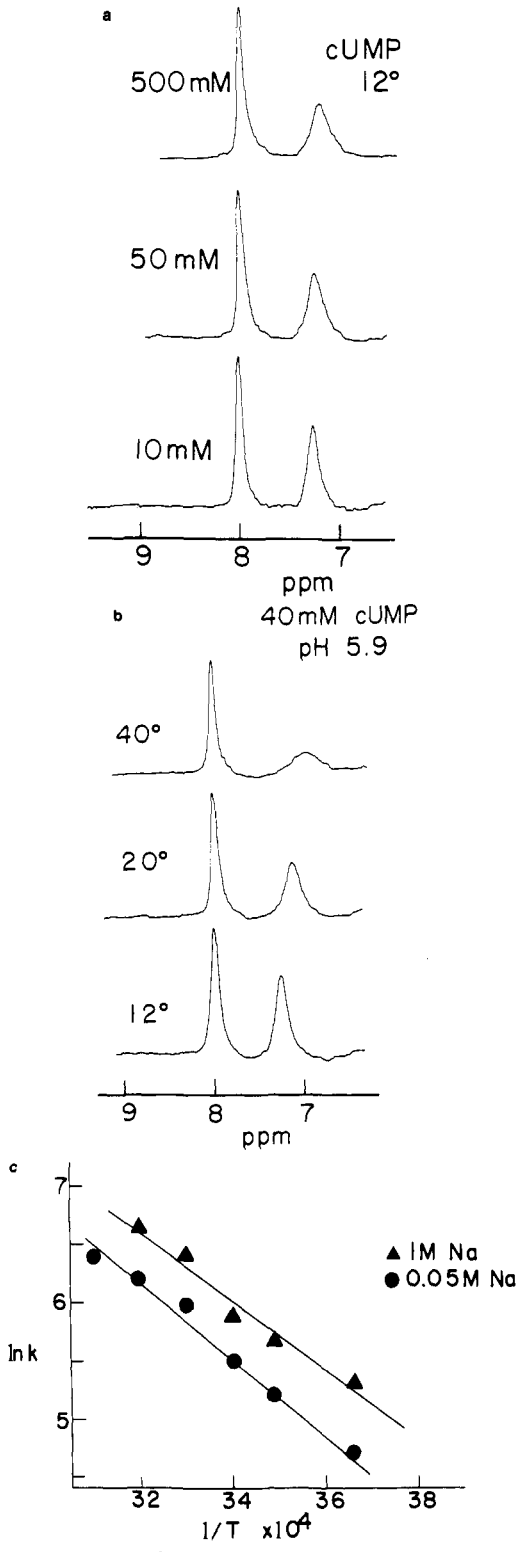

Figure 4. (a) 300-MHz ^{1}H NMR spectrum of cUMP at the indicated concentrations. (b) 300-MHz ^{1}H NMR spectrum of cUMP at the indicated temperatures. (c) Plot of the natural logarithm of the exchange rate of the 2′-OH proton of cUMP as a function of the inverse of the temperature. Shown are the plots for 0.05 M Na^+ and 1 M Na^+ as indicated.

the acceptor and donor and the difference in their pKs. In cases where a proton is protected from exchange, for example, by intramolecular hydrogen bonding as in salicylate, eq 2 does not apply and significant deviations may be observed. Deviations of the observed exchange rates from those predicted by eq 2 usually imply that the exchange rate of the proton is affected by structural factors which do not affect the pK. Rate constants

Table I. Rate Constants for the Catalyzed Exchange of the 2′-OH Proton of cUMP at 12 °C

	obsd exchange rates, k		calcd exchange rate[a]	R_1[b]
	0.05 M Na^+	1 M Na^+		
k_{OH^-}	5×10^8	10^{10}	10^{10}	0.05
$k_{phosphate}$[c]	4×10^3	10^4	7×10^3	0.5
$k_{spermine}$[c]	1×10^5	2×10^4	7×10^3	14
k_{lysine}[c]	2×10^4	10^4	7×10^3	3
k_{H^+}	5×10^6	10^4		

[a] Calculated using eq 2[8] and a pK for the 2′-OH proton of 12.5.[9] [b] $R_1 = k(0.05\ M\ Na^+)/k(\text{calcd})$. [c] Rate constants determined at pH 6.

calculated using eq 2 and the known pKs of mononucleosides are given in Table I. The pK of mononucleosides was used to estimate the exchange rate of the 2′-OH proton in the absence of the interaction giving rise to the protection of the 2′-OH in cNMPs. It is assumed that the pK of the cNMPs is not substantially different from that of NMPs. It is seen that the "apparent pK" of the cNMPs, as determined from the ^{1}H NMR line width data, is much greater than that of the mononucleosides. The protection of the 2′-OH of cNMPs can be quantitated by comparing the observed exchange rate with that predicted on the basis of the pK. As discussed by Eigen,[9] the stability constant of protection of a proton from exchange can be determined from the ratio of k_{OH} calculated from eq 2 with the observed k_{OH}. The rate constants in Table I show that the stability constant for the protection of the 2′-OH proton of cNMPs is about 20 in low salt. The free energy of stabilization can be determined in the usual manner from the expression $K = \exp(-\Delta G/kT)$. This gives a value for the free energy of stabilization of the 2′-OH proton from exchange of about 1.5 kcal in low salt.

The activation energy of exchange can be determined from Arrhenius plots of ln ($k_{exchange}$) against $1/T$ and such plots are shown in Figure 4c. The activation energy is found to be about 7 kcal at pH 6 in the presence of low salt. It is interesting to note that the activation energy is much larger than the free energy of stabilization.

The effect of salt concentration on the rate of exchange of the 2′-OH proton was also investigated. The results (Table I and Figure 4) showed that an increase in sodium concentration increases the rate of exchange. Analysis of the effect of salt at different temperatures showed that the activation energy and stabilization energy of the 2′-OH proton decrease in the presence of 1 M sodium relative to 0.05 M sodium; see Table I and Figure 4. Tetramethylammonium chloride and tetraethylammonium chloride give rise to effects similar to that of sodium chloride.

According to Eigen's encounter model of proton exchange,[9] all of the catalysts examined here are predicted (eq 2) to have about the same activity per mole in increasing the exchange rate of the 2′-OH proton near neutral pH. However, the results in Table I show that the different catalysts have widely varying activities in catalyzing the exchange of the 2′-OH proton. This is not surprising since the evidence presented above shows that the 2′-OH proton is protected from exchange, and hence eq 2, which is derived for encounter-controlled proton transfer, is *not* a reasonable representation of the exchange of the 2′-OH proton. Spermine and lysine are of special interest in that the observed exchange rates are greater than those predicted by eq 2 for cNMPs using the pK, 12.5,[10] experimentally determined for nucleosides. For the other catalysts the rate is much slower than predicted.

Taken together, the ^{1}H NMR results show that the 2′-OH proton of cNMPs is hydrogen bonded to water and is protected from exchange with bulk water. The exchange of the 2′-OH

proton is catalyzed by different catalysts to different extents, the activation and free energies of the protection of the 2′-OH proton decrease as the salt concentration increases, the activation energy for exchange of the 2′-OH is considerably greater than the free energy of the protection, and in 0.05 M salt the activation and free energies are respectively 7 and 1.5 kcal. We now consider some models which may be consistent with these results, since the encounter-controlled model is inadequate.

Models of the Protection of the 2′-OH of cNMPs. It might be assumed that electrostatic effects due to the proximity of the 2′-OH to the negatively charged phosphate group are responsible for the anomalously slow exchange of the 2′-OH of cNMPs. This proposal is attractive in that it predicts that the apparent pK of the 2′-OH will be greater than that of the mononucleosides, as is observed, since the presence of a nearby phosphate group is expected to hinder the abstraction of a proton. This proposal is also consistent with the observation that an increase in salt concentration increases the exchange rate of the 2′-OH since neutralization of the phosphate would reduce the electrostatic effect. Several points argue against attributing all of the anomalous properties of the 2′-OH to an electrostatic effect. It is difficult to rationalize a change in the apparent pK of the 2′-OH from 12.5 in mononucleosides[10] to about 16 (based on eq 2 and the observed k_{OH} in 0.05 M salt) in cNMPs on the basis of a negatively charged phosphate group located about 0.36 nm away. Also, no protection of the 2′-OH is observed in 3′-mononucleotides. The electrostatic model predicts that the apparent pK of the cNMPs should be the same for all catalysts, but this is not observed for the cNMPs, as the results in Table I demonstrate. The data given is for cUMP and entirely analogous results were obtained for cAMP. The electrostatic model is also inconsistent with the observation that the activation and free energies of the exchange are very different. The observation that the activation energy is much larger than the free energy of protection argues that the exchange processes involve some reorientation of the solvent molecules since the cNMPs are rigid. Furthermore, electrostatic effects have been shown to have little influence on proton transfer rates, including the series of compounds from phosphate to polyphosphate.[9] Collectively, these points show that the electrostatic model is inadequate to account for all of the exchange properties of the 2′-OH, though there may be some contribution from the electrostatic effect in determining the exchange properties.

The model we previously proposed to account for our ^{1}H NMR data on the 2′-OH of RNA is consistent with the ^{1}H NMR data on the cyclic mononucleotides. In this model, shown schematically in Figure 1, the 2′-OH proton is protected from exchange by hydrogen bonding to the "bound" water molecule which is simultaneously hydrogen bonded to a phosphate oxygen. According to this model, the exchange of the 2′-OH will be primarily governed by factors which destabilize the water bridge. The observation that the activation energy for exchange is much larger than the free energy of protection is now easily explained by this model. The activation energy is associated with the breaking of the water bridge and rehydration of the phosphate and 2′-OH groups. An activation energy of 5–7 kcal for this process is reasonable. The free energy of protection corresponds to the difference between the free energy of a state in which the 2′-OH is hydrogen bonded via a water bridge, as compared with the state where it is hydrogen bonded to other bulk water molecules. The free energy expected for this sort of water bridge was calculated by L. Allen (personal communication), who found a value of 1–2 kcal, in agreement with the experimentally determined value of 1.5 kcal in 0.05 M salt.

The effect of salt on the 2′-OH exchange rate is attributed to partial neutralization of the phosphate group which will tend to make the phosphate group a poorer acceptor of hydrogen bonding from the bridging water molecule. This will decrease both the activation and free energies of exchange as is observed. The differences in the activities of the different catalysts are also consistent with this model. The high activity of lysine and spermine is attributed to their special ability to displace the bridging water molecule, as shown schematically in Figure 1. In this state the 2′-OH is not protected from exchange with bulk water, and in fact might be accelerated by the presence of the positively charged amine. Thus, the activity of lysine and spermine in catalyzing the exchange as interpreted by this model is not due to their activity as proton acceptors, but rather through exposing the 2′-OH proton to exchange. Therefore, the water bridge model accounts for the anomalous exchange properties of the cNMPs in a reasonable fashion.

The investigation of the crystal structure of an analogue of cAMP has shown that in the crystal there is an *inter*molecular water bridge between the 2′-OH of one cNMP and the phosphate group of another cNMP.[6a] There is no crystallographic evidence for an *intra*molecular 2′-OH–water–phosphate interaction.[6a-d]

The results of ^{31}P NMR studies show that the phosphorus resonance of cNMPs is about 0.5 ppm to lower field than the resonance of cdNMPs. The 2′-OH has a similar effect on 3′-, but not 5′-, nucleotides. These results indicate that the 2′-OH influences the chemical shift of the adjacent 3′-phosphate. The ^{31}P chemical shift is sensitive to the O–P–O bond angle, but not to the hydrogen bonding of the phosphate.[12] This observation makes it unlikely that the observed effect of the 2′-OH on the chemical shift of the phosphate is due to hydrogen bonding (hydration) effects. The analysis of the coupling constants of cNMPs and cdNMPs indicates that the conformation of cdNMPs may be different than that of cNMPs, though the analysis is ambiguous in some cases.[13] A possible source of the chemical shift effect of the 2′-OH in both the 3′-nucleotides and cNMPs is the anisotropy of the 2′-OH. In this regard we note that the chemical shift of the 2′-OH proton of cNMPs is about 0.7 ppm to lower field than is observed for nucleosides, presumably owing to contributions from the anisotropy of the phosphate group.

Implications Regarding RNA Conformation. There is a close parallel between the above results and those obtained earlier with RNA. In both cases we observe that the 2′-OH proton is protected from exchange with bulk water (see Figure 5), even though the chemical shift data indicate that the proton is hydrogen bonded to water, and ammonium ions such as spermine and lysine are especially active in catalyzing the exchange rate. It therefore seems reasonable to extrapolate the results obtained with the cNMPs to RNA, even though the cNMPs have a rigid ribose conformation which is somewhat different from that of A form RNA. The fact that the chemical shifts of the 2′-OH resonance of cUMP and poly U (Figure 5) differ in water by about 0.7 ppm is simply due to the fact that positions in Me_2SO also differ by 0.7 ppm. The spectrum of poly(U) was obtained in conditions in which poly(U) is known to exhibit an ordered, helical conformation.[14]

One of the points about which our ^{1}H NMR studies of RNA offered little information is the energetics of the water bridge between the 2′-OH and phosphate group. It is known that the T_m of RNA is higher than the T_m of DNA of the same base composition.[12] How much, if any, of this extra stability is contributed by the 2′-OH–water–phosphate interaction is of interest. Assuming that the energetics for the proposed hydrogen bonding of the 2′-OH in cNMPs and RNA are about the same, we can say that the maximum free energy associated with the water bridge is about 1.5 kcal. This energy, while small, is significant on the scale of the energies which govern nucleic acid conformations. This energy, which can be attributed to the water bridge, may be partially responsible for the observation that the T_m of RNA is higher than that of

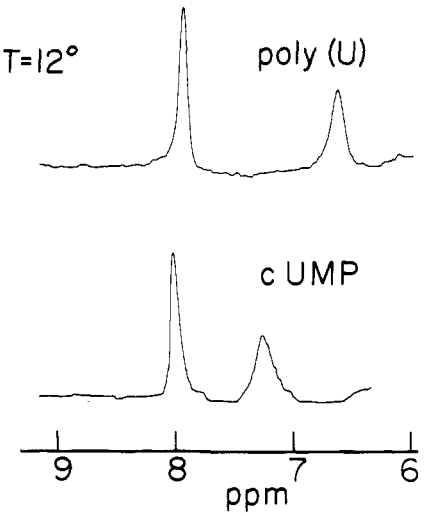

Figure 5. 300-MHz ^{1}H NMR spectra of cUMP and poly(U) in H_2O. The poly(U) sample was dialyzed against 0.1 M NaCl, 10 mM cacodylate buffer at pH 7.0. The pH of the cUMP sample was 5.9.

DNA even though the stacking interactions of DNA are thought to be more energetically favorable.[1,2] The T_m is determined by the relative stabilities of the helical and single-stranded (disordered) states of the nucleic acid. The 2′-OH-phosphate-water bridge is thought to only be present in helical RNA and hence would tend to stabilize the helical state relative to the single-stranded (disordered) state. At this time we tentatively propose that the 2′-OH-water-phosphate bridge is an important, though not the only, factor in the stabilization of the A form of RNA as well as contributing to the greater stability of helical RNA relative to helical DNA.

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Communications to the Editor

Satellite Structures in the ESCA Spectra of (Diphthalocyaninato)lanthanides(III) and -actinides(IV)

Sir:

Recently, X-ray photoelectron spectroscopy (ESCA) has been successfully applied to the study on the electronic structure of f transition metal complexes.[1,2] Special attention has been directed toward the satellites observed in the Ln 3d and An 4f photoelectron lines, since they are a potential source of information on the nature of bonding.[3-10] Some attempts have been made to understand these particular satellites, though most of the suggested mechanisms are unsatisfactory by themselves to explain the sharp variation in intensity throughout the Ln and An series. Coherent explanation for the satellite origin is now essential to the proper understanding of the electronic structure of f elements. In view of the interest in satellite structure, we have investigated ESCA spectra of a series of (diphthalocyaninato)lanthanides (H[LnPc$_2$] (Ln = La, Ce, Pr, Nd, and Gd) and -actinides AnPc$_2$ (An = Th and U)). In particular, the satellites accompanying lanthanide $3d_{5/2}$ and actinide $4d_{5/2}$ signals have been examined.

We report here findings of our satellite measurements and a new approach to interpret the satellite structure. This approach is based on a hypothesis that half-occupied f orbitals play an important role in the striking change of the satellite intensity throughout the f transition metal series.

All spectra reported here were measured on a Hewlett-Packard 5950 Å ESCA spectrometer using monochromatized Al Kα radiation. The charging effects were neutralized by an electron flood gun. Of the compounds we studied, ThPc$_2$ and UPc$_2$ had been prepared by Franz Lux, and lanthanide phthalocyanine compounds[11] were synthesized and purified as described in a previous paper.[11b] The powdered samples were stuck on double-stick scotch tape. Each of the samples was internally calibrated to the intense C 1s peak observed in the lowest energy side.[12] The binding energy of the standard peak is assumed to be 284.8 eV. The metal phthalocyanine complexes are extremely stable and we did not observe any visible evidence of decomposition and/or oxidation of the sample.

Figure 1 shows the observed lanthanide $3d_{5/2}$ and actinide $4d_{5/2}$ spectra of the diphthalocyaninato complexes. Each of the spectra reveals additional structure adjacent to the normal

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