 ^{13}C NMR relaxation and conformational flexibility of the deoxyribose ring

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ABSTRACT

^{13}C T_1 's and NOE's have been measured for all protonated carbons of 2'-deoxy-D-ribose (2'-d-ribose), 2'-deoxyadenosine-5'-monophosphate (5'-dAMP), thymidine-3'-monophosphate (3'-TMP) and thymidine-5'-monophosphate (5'-TMP) in D_2O solutions. In all of the deoxy sugars examined, NT_1 values for C-2' are significantly larger than the values for the remaining carbons. This result is interpreted in terms of rapid puckering motion of C-2'. By contrast, NT_1 values measured in ribose are found to be equal, within experimental error. The results are compared with analogous data obtained for the five membered pyrrolidine ring of proline and with results for DNA itself.

INTRODUCTION

Recent developments in instrumentation and sample preparation methods have made it possible to obtain high quality nuclear magnetic resonance (NMR) spectral data for large biopolymers such as DNA. On the basis of ^1H , ^{13}C and ^{31}P NMR spin relaxation data, a number of groups²⁻⁸ have suggested the presence of rapid internal motions in DNA, with correlation times of nanosecond order. Because of possible complications⁹ that can occur in the interpretation of ^1H and ^{31}P NMR relaxation data, our group^{4,5} has stressed the importance of ^{13}C NMR measurements. The relaxation mechanisms of this nucleus are well defined, and it is possible to derive detailed information about molecular dynamics from T_1 's, T_2 's (in this case, derived from shielding-corrected linewidths) and nuclear Overhauser enhancements, NOE's, under conditions when dipolar relaxation predominates, as it does for protonated carbons in large molecules such as DNA. We have stressed that, for systems undergoing complex molecular dynamics, the measurement of spin relaxation data at multiple and dispersed magnetic fields is critical to an unambiguous

determination of a molecular dynamics model.^{4,5}

In our theoretical analyses⁵ of ^{13}C NMR relaxation parameters⁴ for double and single-stranded DNA molecules (sized specifically to less than 100 base pairs (bp), or to 120-160 bp, and to several hundred bp in length) we have investigated possible models for internal motion of the deoxyribose methine carbons. These models incorporate restricted amplitude (e.g., conic boundary condition) diffusion of the individual C-H vectors, superimposed on either isotropic overall motion¹⁰ or rod like anisotropic overall motion of the DNA helix.¹¹ We have shown⁵ that overall tumbling of DNA molecules is not as much affected by denaturation as is the internal "wobbling" motion, which increases both in rate and especially, amplitude upon denaturation. These theoretical analyses have so far been applied only to ^{13}C relaxation data of the deoxyribose methine carbons. A number of experimental observations suggest that the internal motion of C2' may be somewhat different (increased). Thus, it is found⁴ that NT_1 (N is the number of attached hydrogens) for the methylene carbon, C-2', is slightly larger than T_1 for the deoxyribose methine carbons. Combined with the fact that NOE's for C2' in native DNA samples are significantly greater than those for the other carbons, this suggests that there is greater motional freedom associated with C2'. Furthermore, under conditions that restrict DNA dynamics, such as when studies are carried out at high solution concentrations or using larger sized molecules (>400 bp), the C-2' carbon resonance is not affected to the degree observed for the remaining DNA carbons, which show a significant loss in signal intensity from broadening due to motional restriction.

In order to understand the reason for the apparently higher mobility of the C2' carbon in DNA, we decided to investigate whether parallel behavior is present in the individual structural units which make up DNA. An examination of literature data reveals that the effect may be specifically linked to the deoxyribose structural unit. Spin-lattice relaxation times of the ribose moiety in AMP¹² show no evidence of additional internal motion of the C2' carbon compared with the other ring carbons. This also occurs in a number of nucleosides¹³. Although there have been many theoretical or structural studies¹⁵⁻²⁹ of conformations of ribose and deoxyribose

derivatives, and some experimental NMR relaxation studies of derivatives containing ribose moieties,³⁰⁻³² motional dynamics studies of deoxyribose derivatives are lacking in the literature.

In this paper we report ^{13}C relaxation parameters (T_1 's and NOE's) for all protonated carbons of 2'-deoxy-D-ribose (2'-d-ribose), 2'-deoxyadenosine-5'-monophosphate (5'-dAMP), thymidine-3'-monophosphate (3'-TMP) and thymidine-5'-monophosphate (5'-TMP) in D_2O solutions. We have also investigated the dependence of these relaxation data on solution concentration. In addition, since accurate T_1 data for ribose itself are not available in the literature, ^{13}C T_1 's and NOE's have been measured and are reported herein.

Finally, we undertook treatment of the observed relaxation data in terms of motional dynamics models. In a recent study by Keepers and James,³³ which examined 2 models for internal motion of the sugar carbons of DNA, NT_1 for $\text{C}2'$ was not predicted to be larger than for the other carbons. This stands in contrast to our experimental results in free deoxyribose, in nucleotides containing this structural unit, and in DNA.⁴ Factors contributing to this dichotomy are discussed.

RESULTS AND DISCUSSION

2'-Deoxyribose exists in aqueous solution as an equilibrium mixture of α - and β - pyranoses and α - and β - furanoses. Our ^{13}C spectra indicate that significantly different amounts of furanose and pyranose forms are present in D_2O solution, although within each form approximately equal amounts of α and β anomers are present. From the intensities derived from a spectrum obtained using long delays ($>10 T_1^{\text{max}}$) between rf pulses and suppression of NOE, we estimate a furanose to pyranose ratio of 17:83. This is similar to the ratio found³⁴ for ribose in $1\text{M } \text{D}_2\text{O}$, and indicates that the replacement of OH by H on the C-2' carbon has little impact upon furanose/pyranose isomer populations for this sugar. There are, however, significant differences in the relative proportions of α and β anomers in the ribose and deoxyribose derivatives. Peak assignments for the various species present in a D_2O solution of deoxyribose were based on those of Breitmaier and Jung.³⁵ In the following discussion we use the established³⁴ nomenclature of denoting

the furanose and pyranose forms by the letters F and P respectively. Roman numerals denote the carbon site, and greek letters the anomer. For example, the symbol F4 β refers to C4 in the β anomer of deoxy-ribofuranose. A number of peaks overlap (F5 $_{\alpha}$, F5 $_{\beta}$; P1 $_{\alpha}$, P1 $_{\beta}$ and F2 $_{\alpha}$, F2 $_{\beta}$) and there are also a number of closely spaced peaks which could not be unambiguously assigned. These involved the α and β anomers of F4, F3 and P4. In each case, the downfield peak of the two closely spaced resonances had a slightly smaller intensity and was arbitrarily assigned as being from the α anomer, by analogy with trends in ribose.³⁴

Spin lattice relaxation times (T_1 's) and nuclear Overhauser enhancements (NOE's) of all protonated carbons in 0.12M and 0.36M solutions of deoxyribose are given in Table 1. Within experimental

Table 1
¹³C NMR Relaxation Parameters of 0.12 M and 0.36 M Solutions
of Deoxyribose in D₂O at 31°C

Carbon	Furanose Forms			Pyranose Forms		
	NT ₁		NOE	NT ₁		NOE
	0.12 M	0.36 M	0.36 M	0.12 M	0.36 M	0.36 M
C1	2.1 ^b	2.2	2.9 ₅	2.1 ^b	2.2	2.9 ₅
C2	2.9 ^c	2.9	3.1 ₅	2.5	2.4	2.9 ₅
C3	1.9 ^d	2.2	2.9 ₅	2.2	2.1	3.0 ₅
C4	1.6 ^e	2.0	2.3 ^h	2.2 ^g	2.2	3.0
C5	2.4 ^f	2.2	2.4 ^h	2.2	2.2	3.0
C1	2.0	2.1	2.9 ₅	2.3	2.3	2.9 ₅
C2	2.9 ^c	2.9	2.9 ₅	2.4	2.3	3.1 ₅
C3	2.3 ^d	2.2	3.0 ₅	2.0	1.9	3.1
C4	2.0 ^e	2.0	2.3 ^h	2.2 ^g	2.2	3.0
C5	2.4 ^f	2.2	2.4 ^h	2.4	2.4	3.0

a) T_1 's are average values from 2 experiments. b) F1 $_{\alpha}$ and P1 $_{\alpha}$ overlap: composite T_1 . c) F2 $_{\alpha}$, F2 $_{\beta}$ overlap: composite T_1 . d) Assignments for F3 $_{\alpha}$, F3 $_{\beta}$ could be reversed. e) Assignments for F4 $_{\alpha}$, F4 $_{\beta}$ could be reversed. f) F5 $_{\alpha}$, F5 $_{\beta}$ overlap: composite T_1 . g) Assignments for P4 $_{\alpha}$, P4 $_{\beta}$ could be reversed. h) These NOE values have a large uncertainty because of the small signal-to-noise ratios for these peaks. It has been assumed that NOE's for these carbons are actually full, as for other carbons.

error, the NOE value of each protonated carbon is equal to the theoretical maximum (2.99). This shows that the observed T_1 's reflect purely dipolar relaxation, and that the overall motion is fast enough to fall inside the extreme motional narrowing limit. In addition, T_1 's in Table 1 are essentially independent of concentration, indicating that sugar aggregation is similar over the range examined.

Although we are concerned mainly with the determination of internal motions in the furanose forms of deoxyribose, it is useful to first examine T_1 data for the pyranose forms, to investigate the effects of ring size on internal motions. In a rigid molecule undergoing isotropic motion in the extreme narrowing limit, NT_1 (where N is the number of hydrogens attached) is predicted to be equal for all protonated carbons.¹² Except for a slightly larger value of NT_1 for C2' in the α -anomer, this appears to be the case for all pyranose protonated carbons; thus the reorientational motion of the ring backbone is probably close to isotropic, with a correlation time of 2.1×10^{-11} sec, computed from the average value of NT_1 (2.2 sec). On the other hand, the T_1 data in Table 1 for the furanose forms show a significantly larger variation in NT_1 for the different carbons, suggesting that the overall motion of the sugar ring is not isotropic and/or that internal motions are characterized by a rate greater than or equal to the overall motion. The fact that NT_1 for C2' is larger (in both α and β anomers) than NT_1 for the remaining carbons, suggests that there is greater mobility at this site, presumably reflecting a dynamic conformational process in the five-membered ring.

Before discussing possible reasons for additional motion of C2', it is useful to examine T_1 data for ribose, where this carbon has an attached OH group. The ^{13}C spin-lattice relaxation times of the furanose form of ribose are shown in Table 2. Within the limits of experimental error, all carbons in the furanose ring in either α or β forms have identical NT_1 values, indicating that these molecules undergo essentially isotropic tumbling in D_2O solution. A correlation time for this motion of 1.9×10^{-11} sec was calculated from the average T_1 of 2.4 sec. NT_1 for C5' is longer than NT_1 of the carbons in the ring, indicating rotation about the C4'-C5' bond contributes significantly to dipolar relaxation of C5'.

Table 2
 ^{13}C NT₁'s for Ribofuranose in D₂O^a at 31°C

Anomer	C-1'	C-2'	C-3'	C-4'	C-5'
	2.45	2.4	2.4	2.4	2.7
	2.6	2.5	2.5	2.6	2.7

a) Concentration, 0.36 M.

Differences in the relaxation data of ribose and 2'-deoxyribose arising from the replacement of an OH group by hydrogen on the C2' site may arise from two effects: a) Removal of the OH group from C2' in ribose lowers inertial constraints at this site and eliminates attractive hydrogen-bonding forces with D₂O solvent. These factors change the effective diffusion axis of the sugar ring, which may result in changes in overall tumbling motion and the possible introduction of anisotropic motion; b) New internal motional modes preferentially affecting C2' may also occur since this site is no longer restricted by the OH group. We feel that it is this latter (internal motion) effect which is most important in accounting for the differential behavior of C2'. One argument that can be used to discount the former proposal is the fact that similar behavior for C2' relative to the other carbons is noted in such diverse systems as free deoxyribose, 5'-dAMP, and DNA.⁴ Since overall motions in these systems are decidedly different, an explanation for the observed relaxation behavior of C2' based solely on anisotropic motion seems inappropriate. Furthermore, it has recently been shown that analogous differential relaxation behavior for C-γ in proline cannot be accounted for by anisotropic motion.³⁶ Instead, an explanation based on a fast motional jump between two stable conformations was utilized.³⁶ A similar approach will be followed here in subsequent analyses. A qualitative discussion of the remainder of the experimental data will be given first however.

Spin-lattice relaxation times of 0.01M, 0.05M and 0.15M 5'-dAMP in D₂O are shown in Table 3, along with NOE data for the 0.15M solution. The NOE data indicate complete dipolar relaxation for all protonated carbons. ^{13}C NT₁'s for the sugar residue show

Table 3
 ^{13}C NT₁'s and NOE's for
 Protonated Carbons in 5'-dAMP in D₂O at 31°C

Concentration	C-2	C-8	C-1'	C-2'	C-3'	C-4'	C-5'
0.01 M ^a	0.66	0.55	0.65	0.92	0.69	0.60	0.70
0.05 M ^b	0.54	0.48	0.55	0.92	0.78	0.69	0.78
0.15 M ^c	0.56	0.54	0.57	1.02	0.72	0.68	0.70
0.15 M NOE	2.8	2.9	2.8	2.9	3.0	3.0 ₅	2.9

a) pH = 9.55. b) pH = 9.00. c) pH = 8.85.

similar values for C-3' and the exocyclic C-5', with a significantly longer NT₁ for C-2' and a somewhat shortened NT₁ for C-1', the carbon linking the sugar and base groups via the glycosidic bond. No appreciable concentration dependence is noted above 0.01M, where 5'-deoxy-AMP is probably already largely aggregated.

To interpret these trends, it is necessary to consider the nature of internal and overall motions. The mobility of nucleotides and nucleosides is usually described by three modes of internal motions (Figure 1): a) Rotation of the base around the glycosidic bond (*syn:anti* equilibrium)³⁷, b) Ribose puckering (pseudorotation or other dynamic processes) characterized by the equilibrium between the conformational ranges S and N shown in Figure 1b.³⁸ c) Conformational changes of the C5' hydroxymethyl group, described by an equilibrium among *Gauche+*, *Trans* and *Gauche-* forms³⁹. Since the activation energy for the *syn/anti* transition in 5'-dAMP is expected to be similar to that in adenosine this conformational process will not contribute significantly to ^{13}C relaxation rates. This has been confirmed by Roder and coworkers¹³ in a study of ^{13}C relaxation rates of adenosine (Ado) and 2':3'isopropylidene adenosine (iAdo). In the latter compound, the mobility of the furanose ring is blocked by an isopropylidene group which bridges the C2' and C3' atoms, and only rotation of the base around the glycosidic bond and motions of the 5'-hydroxymethyl group are possible. It was found that the two base carbons and the four carbons of the furanose ring yield identical relaxation rates over a range of temperatures, showing that transitions between the *syn* and *anti* states are too infrequent to contribute to relaxation.

Figure 1. Conformational Equilibria In Deoxynucleosides and nucleotides.

Extending this conclusion to 5'-dAMP, it can be seen that of the three possible modes of motion mentioned above, only the latter two are likely to affect T_1 values in this system. In either of the *syn* or *anti* conformations, T_1 values for C1' and C4' are expected to be shorter than C2' and C3' because of greater motional restriction at the former carbons due to their attachment to other groups. Inertial and hydrogen-bonding properties of the OH group at C3' make this carbon more restricted than C2' and this is reflected in the experimental observation that C2' has the larger NT_1 value.

Internal rotations of side-chain carbons have been shown to significantly affect NT_1 values.⁴¹ Rapid internal rotation about the C4'-C5' bond would be expected to increase the effective motion for C5' and hence increase its NT_1 . The experimental data show that the NT_1 of C5' is shorter than NT_1 for C2'. Internal rotational motion in 5'-AMP thus has less effect on NT_1 of C5' than does puckering motion on NT_1 of C2'.

¹³C T_1 's and NOE values for the sugar carbons in 5'-TMP are given in Table 4. Again, NOE data indicate that dipole-dipole

Table 4
 ^{13}C T_1 's and NOE's for 0.15 M^a Deoxythymidine-5'-monophosphate (5'-dTMP) in D₂O at 31°C

	C-1'	C-2'	C-3'	C-4'	C-5'
T_1	0.52	0.37	0.68	0.57	0.30
NOE	2.9	3.05	3.08	2.92	3.05

a) pH = 7.25.

relaxation is dominant; NT_1 of C1' remains the shortest for all the carbons. Puckering motions still make the NT_1 of C2' and C3' longest compared with other carbons, however the difference between the relaxation rates of C2' and C3' is not as large in 5'-dAMP.

Spin-lattice relaxation times and NOE's for 3'-dTMP are presented in Table 5. NT_1 values for C-3', C-4' and C-5' are essentially equivalent, indicating that the effective motion of each of these carbons is similar. This shows that the phosphate linkage at C-3' brings about a decrease in the additional motion noted earlier for C-2' in 5'-TMP. The ratio $NT_1(\text{C-2}')/NT_1(\text{C-3}')$ of 3'-dTMP approaches unity and is significantly smaller than the analogous ratio for deoxyribose and deoxy-AMP. Decreased motion for C2' can be explained by changes in the rates of internal puckering motions.

A comparison of T_1 values in all of the species examined here is shown in Figure 2. This conveniently summarizes the trends and allows the following conclusions to be derived. a) In all cases, except for ribose, NT_1 for C2' is larger than for any other carbon. b) NT_1 for C4' is smallest in the free sugars, whereas C1' has a

Table 5
 ^{13}C T_1 's and NOE's for 0.10M^a Deoxythymidine-3'-monophosphate (3'-dTMP) in D₂O at 31°C.

	CH ₃	C-6	C-1'	C-2'	C-3'	C-4'	C-5'
T_1	2.21	0.60	0.54	0.35	0.60	0.59	0.30
NOE	2.85	3.0	2.95	3.08	3.0	2.95	3.05

a. pH = 7.65.

Figure 2. NT_1 Values of Furanose Ring Carbons

shorter T_1 in the nucleotides. c) There is a general decrease in going from the sugars to the nucleotides in the order deoxyribose > AMP > TMP. d) T_1 in 3' and 5' derivatives of TMP are smaller except for slight decreases at C3' and C2' and a slight increase for C1'. The motions of C2' and C3' are coupled.

Analogy with Ring Puckering in Proline

The relaxation data summarized above are closely analogous to corresponding data for the five membered pyrrolidine ring of proline. As an illustration of this point, ^{13}C spin lattice relaxation data for hydroxyproline, proline, and several proline containing peptides are summarized in figure 3. Introduction of the hydroxyl substituent at C-4 results in nearly identical NT_1 values for all of the carbons in the ring, similar to the relaxation behavior observed for ribose. Alternatively, pronounced NT_1 differences are observed in free proline and in the proline-containing peptides, analogous to the observations in deoxyribose

Figure 3. NT₁ Values of Proline Ring Carbons

and the deoxynucleotides. The larger molecular weight peptides exhibit shorter NT₁ values, however the ratios of these values within the ring remain similar in all cases. For the deoxyribose-containing molecules studies here, the ratio of the NT₁ value of C-2' to that for the carbon having the shortest value (C-1' or C-4') varies within a relatively narrow range: 1.3 in 3'-TMP to 1.8 in 0.15 M 5'-dAMP. In addition to these experimental similarities, there are corresponding theoretical similarities between the two systems. In both cases, conformational energy calculations indicate two conformational minima^{42,28} supporting the validity of a bistable jump dynamic model to describe the puckering of the five membered ring. Thus, in both cases the effect of the substituents is to destabilize many of the possible puckered conformations which would otherwise be expected, on the basis of the analogy with

cyclopentane, to lead to pseudorotational motion. In view of these similarities, many of the general conclusions previously obtained using a bistable jump model to describe the relaxation resulting from puckering of the pyrrolidine ring of proline can be applied to the relaxation resulting from puckering of the deoxyribose ring.

Although originally given in a somewhat more complex form³⁶, the model can be formulated in terms of a relatively simple spectral density function which describes the effects of an instantaneous jump between two stable states, A and B, with corresponding lifetimes τ_A and τ_B , a rotational correlation time for overall, isotropic molecular diffusion τ_0 , and a jump range of 2θ . In addition, the parameter β describes the angle between the jump axis and the relaxation (C-H) vector.⁴³

$$J(\omega) = (1 - C) \frac{\tau_0}{1 + \omega^2 \tau_0^2} + C \cdot \frac{(1/\tau_0 + 1/\tau_0)^{-1}}{1 + \omega^2 (1/\tau_0 + 1/\tau_0)^{-2}}$$

where
$$\frac{1}{\tau_0} = \frac{1}{\tau_A} + \frac{1}{\tau_B}$$

and
$$C = \frac{3 \tau_A \tau_B}{(\tau_A + \tau_B)^2} \left[\sin^2 \beta (1 - \cos 2\theta) \right] \cdot \left[2 - \sin^2 \beta (1 - \cos 2\theta) \right]$$

Carbon-13 relaxation times can readily be calculated from the above spectral density function using standard formulas.⁴⁴ As noted previously, β and θ are not uniquely defined. One approach to this problem is the visualization of the jump as the limit of a rotational motion, allowing a unique description in terms of both angles β and θ . Since only motions with β relatively close to 90° will have a significant effect on the relaxation parameters, a second reasonable approximation involves setting $\beta = 90^\circ$ and then obtaining approximate values for the range 2θ . As in the example of proline, the overall molecular motion of deoxyribose is characterized by a relatively short rotational correlation time, $\tau_0 = 2.3 \times 10^{-11}$ s, so that the internal puckering rate must be at least this rapid. Based on the very low barriers obtained theoretically for the interconversion of puckered forms, a rapid τ motion, characterized by $\tau_A = \tau_B \approx 10^{-12}$ s, as used in the analysis of the proline relaxation, is reasonable. Determining τ_0 from the T_1 value of the carbon with the shortest relax-

ation time, the NT_1 value for C-2' can be predicted using jump range of 40°-50°.

The equilibrium ratio of the two states A and B is of critical importance for the relaxation analysis. Experimentally, the observation of a significantly longer NT_1 value for C-2' relative to other ring carbons suggests that the stabilities of the two puckered forms must be fairly close, i.e., differing by less than a factor of 5. This conclusion is again consistent with the theoretical similarities in stabilities of the C-2' endo and C-2' exo conformations predicted by Levitt and Warshel.²⁸ Alternatively, the relaxation data indicate that if the puckering motion of C-2' and C-3' are concerted, the amplitude of the puckering motion for C-3' must be smaller than that for C-2'. More generally, there are three possible explanations for the observation of longer NT_1 values for the hydroxylated carbons as compared with the methylene carbons in either the deoxyribose or the proline systems: (1) the amplitude of motion is smaller in the former case; (2) the lifetimes of the two puckered states differ more significantly for the hydroxylated carbons compared with the methylenes; (3) the rates of puckering are much longer for the hydroxylated carbons. Based on the low interconversion barrier predicted theoretically which separates the different puckered conformations²⁸, the third alternative listed above appears highly unlikely. However, there is generally insufficient data to distinguish between the first two alternatives. The second possibility noted above would imply that the puckering motion involving C-2' and C-3' is not concerted. This possibility could be evaluated more fully from a theoretical standpoint. However, it is important to note that the significant experimental differences noted here between ribose and deoxyribose are not predicted theoretically²⁸. Thus, Levitt and Warshel have concluded that the additional hydroxyl group in the former does not affect the conformational preferences of the ring. The observed dynamic differences which are reflected in the NT_1 values must be related to the stability of the various possible conformations. The differences between ribose and deoxyribose may arise in part as a result of hydrogen bonding interactions between the hydroxyl groups and the solvent.

EXPERIMENTAL

Materials and Sample Preparation

Ribose, 2'-deoxyribose, 5'-dAMP, 5'-TMP and 3'-TMP (sodium salts) were purchased from Sigma Chemical Company, paramagnetic free, 100% isotopically pure D₂O was purchased from Stohler Isotope Chemicals. All solutions were shaken with a small amount of Chelex for several hours in order to ensure that no paramagnetic impurities were present. After filtration a stream of dry nitrogen gas was passed through the solution for 10 minutes to flush out dissolved oxygen.

NMR Measurements

¹³C spin relaxation time measurements were made on a Bruker WM-360 widebore NMR spectrometer operating at 90.56 MHz. T₁'s were obtained using the fast inversion recovery pulse sequence,⁴⁵ using 12-13 tau values. The time domain signal was digitized using 4K data points during acquisition. Prior to Fourier transformation,

FID's were zero filled to 16K data points giving a digital resolution of 0.5 Hz in the final spectra. T₁ values were determined using a three parameter exponential fit.⁴⁶ Multiple runs on all of the data in Tables 1-3 were found to be consistent. NOE's were obtained using gated decoupling experiments, with pulse delays 10 times the longest T₁ being measured.

CONCLUSIONS

Spin-lattice relaxation times of carbons in the deoxyribose ring in DNA and in mononucleotides indicate that similar types of internal motion occur in the biopolymer and its subunits. NT₁ values for the deoxyribose sugar rings in free deoxyribose, d-AMP and in DNA are consistently larger for C2' than for the other ring carbons. This is in contrast to the approximately constant NT₁ values of the ring carbons of ribose. The general increase in NT₁ of C-2' for deoxyribose derivatives therefore reflects a specific dynamic process which occurs when the OH group is removed from C2'. A model which incorporates a fast internal jump between two stable conformations provides one explanation for this effect.

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