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Anisotropic rotation in nucleic acid fragments: significance for determination of structures from NMR data

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Abstract. Proton-proton relaxation rate constants depend on the angle between the internuclear vector and the principal axis of rotation in symmetric top molecules. It is possible to determine to rotational correlation times of the equivalent ellipsoid for DNA fragments from a knowledge of the axial ratio and the cross-relaxation rate constant for the cytosine H6-H5 vectors. The cross-relaxation rate constants for the cytosine H6-H5 vectors have been measured in the 14-base-pair sequence dGCTGTTGACAATTA.dTAATTGTCAACAGC at four temperatures. The results, along with literature data for DNA fragments ranging from 6 to 20 base pairs can be accounted for by a simple hydrodynamic equation based on the formalism of Woessner (1962). The measured cross-relaxation rate constant is independent of position in the sequence and is consistent with the absence of large amplitude internal motions on the Larmor time scale. All the data can be described by a simple hydrodynamic model, which accounts for the rotational anisotropy of the DNA fragments and allows the correlation time for end-over-end tumbling to be determined if the approximate rise per base pair is known. This is the correlation time that dominates the spectral density functions for internucleotide vectors and is significantly different from that calculated for a sphere of the same hydrodynamic volume for fragments containing more than about 14 base pairs. This method therefore allows NOE intensities used for structure calculation of nucleic acids to be treated more rigorously.

Key words: DNA hydrodynamics – Cross relaxation

Introduction

The ready availability of chemically synthesised oligonucleotides of defined sequence has given a great impetus to the determination of the confirmations of genetically important sequences of nucleic acids with drugs and proteins, using single crystal X-ray diffraction and high-resolution NMR.

Although there are several methods of deriving conformation from NMR data, including distance geometry (Patel et al. 1987) restrained molecular dynamics and molecular mechanics (Nilges et al. 1987a, b), direct analysis of NMR data by least squares fitting (Lefèvre et al. 1987; Borgias and James 1988) and constrained conformation-space searching (Lane 1990), all of these approaches have hitherto assumed that double-stranded oligonucleotides behave as rigid isotropic rotors. While the isotropic rotor model may be adequate for short oligonucleotides (e.g. in the range six to ten base pairs), it certainly is not appropriate for longer sequences. For example, many operator sites are of the order 20 or more base-pairs in length. In the B-DNA confirmation, a 20-mer can be approximated by a cylinder of length 68 Å and diameter 22 Å, giving an axial ratio of nearly 3:1. Hence, distances estimated from NOE intensities assuming an isotropic rotor can be significantly in error, leading to incorrect conformations being produced.

In this communication, we show how the appropriate correlation times (and therefore spectral density functions) can be determined for rotation about the long and short axes of an oligonucleotide using cross-relaxation rate constants measured for ^1H-^1H vectors of known, fixed length. The limitations and potential errors are assessed, and calculations compared with data for several oligonucleotides ranging from 6 to 20 base pairs, measured as a function of temperature. Correlation times are calculated both for prolate ellipsoids of revolution, and as a rigid cylinder, and the results compared with the experimental data.

Materials and methods

Cross-relaxation rate constants for the cytosine H6-H5 vectors were determined as a function of temperature from NOE time courses as previously described (Lane et al. 1986; Lane 1989) for a non-self-complementary 14

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base-pair fragment of DNA. The DNA strands of sequence dGCTGTTGACAATTA and dTAATTGTCAACAGC (P35) were synthesised on a Beckman synthesiser using phosphoramidite chemistry and purified by ion exchange chromatography as previously described (Lane 1989). The two strands were mixed in equal amounts according to the absorbance at 258 nm, and further purified by chromatography on Sephadex G50. The peak eluting just after the void volume was duplex, which was lyophilised, dialysed against 50 m*M* KCl, 5 m*M* sodium phosphate, pH 7, and relyophilised.

Results and discussion

Owing to its symmetry, double-stranded DNA is expected to behave hydrodynamically as a symmetric top, for which the NMR spectral density functions have been given by Woessner (1962). Two possible appropriate symmetric top models are prolate ellipsoids of revolution, for which exact analytical formulae for the two rotational correlation times are known: the Perrin equations (Cantor and Schimmel 1980) and the rigid cylinder. Improved expressions for the rotational correlation times (or diffusion constants) for rigid cylinders have been recently given (Tirado and de La Torre 1979, 1980), which have been recently compared with the results of light-scattering and NMR experiments on DNA fragments (Eimer et al. 1990) models. However, the range of validity of these expressions for oligomers of small axial ratio that are accessible to detailed NMR studies is uncertain. Further, although B-DNA may appear more cylindrical than ellipsoidal, the precise dimensions of the equivalent cylinder are not obvious, because of the deep grooves. For this reason, we have calculated the rotational correlation times for both prolate ellipsoids and circular cylinders.

There are two intrinsic correlation times for the rotation of a symmetric top molecule. In the following, we concentrate on prolate ellipsoids, though the same principles apply to circular cylinders, expressions for which are given in Tirado and de La Torre (1979, 1980) and Eimer et al. (1990). The correlation times for rotation about the long and short axes will be denoted τ_L and τ_S, respectively. According to Woessner (1962), the spectral density function is given by:

$$J(\omega) = a_1 J(\omega, \tau_1) + a_2 J(\omega, \tau_2) + a_3 J(\omega, \tau_3) \quad (1)$$

where

$$J(\omega, \tau) = \tau/(1 + \omega^2 \tau^2) \quad (2)$$

The amplitudes, a_i are given by:

$$a_1 = 0.25\ (3\cos^2\beta - 1)^2 \quad (3A)$$

$$a_2 = 3\cos^2\beta \sin^2\beta \quad (3B)$$

$$a_3 = 0.75 \sin^4\beta \quad (3C)$$

where β is the angle the vector makes with the principal axis of the diffusion tensor, in this case the long axis of the molecule. The correlation times $\tau_{1,2,3}$ are composite correlation times defined as:

$$\tau_1 = \tau_L \quad (4A)$$

$$\tau_2 = 6\tau_L \tau_S/(\tau_L + 5\tau_S) \quad (4B)$$

$$\tau_3 = 3\tau_L \tau_S/(2\tau_L + \tau_S) \quad (4C)$$

The correlation times τ_L, τ_S are related to the axial ratio, γ, defined as the ratio of the short axis to the long axis of the prolate ellipsoid of revolution by the Perrin equations (Cantor and Schimmel 1980):

$$\tau_L = 4(1-\gamma^4)\,\eta V/3kT\,\gamma^2(S(2-\gamma^2)-2) = f_L \cdot \tau_R \quad (5A)$$

$$\tau_S = 4(1-\gamma^2)\,\eta V/3kT(2-\gamma^2 S) \quad = f_S \cdot \tau_R \quad (5B)$$

where

$$S = [2/(1-\gamma^2)^{1/2}]\ln[1 + (1-\gamma^2)^{1/2}]/\gamma \quad (5C)$$

V is the hydrated volume, η is the viscosity and τ_R is the rotational correlation time for a sphere of equal volume.

The ratio of the correlation times, $\Gamma = \tau_L/\tau_S$, is then

$$\Gamma = (2-\gamma^2 S)(1+\gamma^2)\gamma^2\,(S(2-\gamma^2)-2) \quad (6)$$

The cross relaxation constant, σ, for any given vector, is given by:

$$\sigma = [56.92/r^6][6J(2\omega) - J(0)] \quad (7)$$

where r is the interproton separation in Å and the spectral density functions are in ns. From (1) to (7), it is clear that the cross-relaxation rate constant depends on the correlation times and the angle the vector makes with the long axis of the molecule. Figure 1 shows how the function $\sigma' = 6J(2\omega) - J(0)$ varies as a function of β for different axial ratios. The function has been normalised to the correlation time expected for a sphere of the same hydrodynamic volume. For angles near zero and near 90°, the correlation function has a weak dependence on the angle β; the function varies most rapidly for angles near the magic angle ($\beta = \cos^{-1}(1/3)^{1/2} = 54.74°$). Indeed, for modest axial ratios, and for rotation about axes in the slow tumbling regime, the function decreases monotonically.

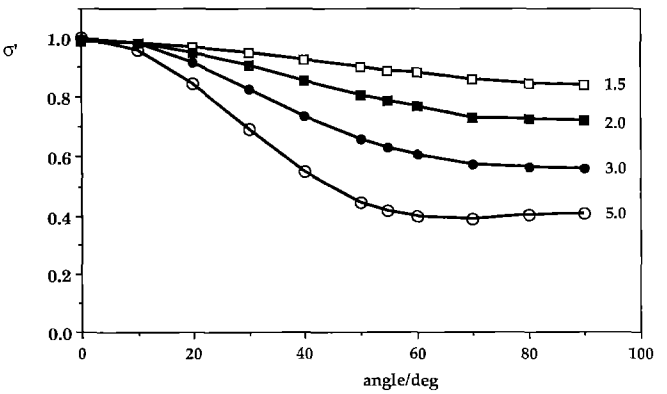

Fig. 1. Dependence of the cross-relaxation rate constant on the angle to the helix axis. The cross-relaxation rate constant was calculated for a prolate ellipsoid of axial ratio γ as described in the text. The cross-relaxation rate constant was normalised to give σ' as described in the text. The correlation time of the equivalent sphere was 5 ns. The axial ratio is shown at the right

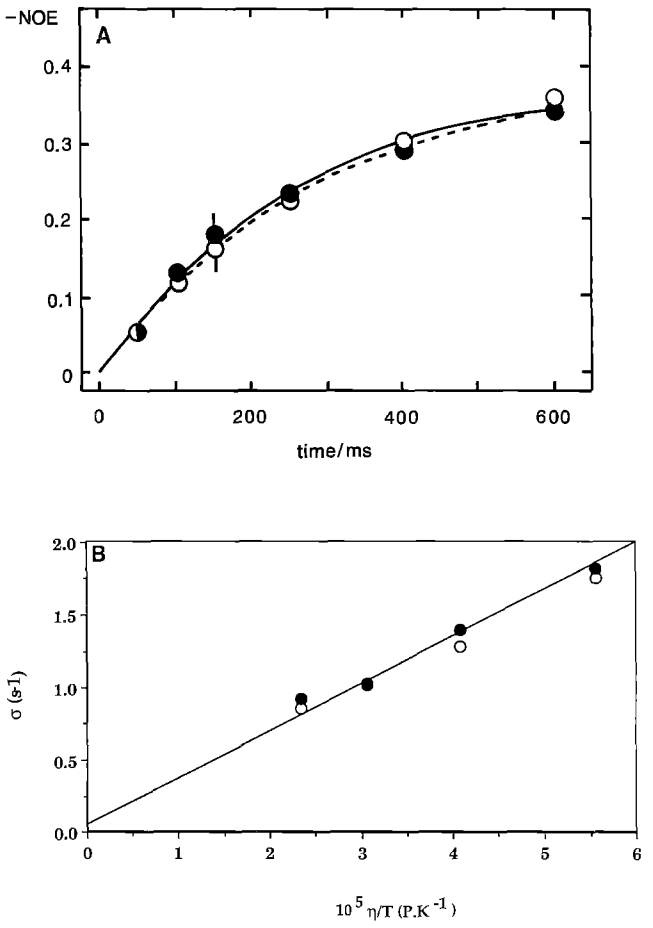

Fig. 2 A, B. Cross relaxation in the 14 base-pair promoter fragment. NOEs were measured as described in the Materials and methods. **A** NOE build-up curves for cytosines 2 (○) and 22 (●) at 20 °C. Curves are non-linear regression fits to the equation $\text{NOE} = (\sigma/\varrho)[1 - \exp - \varrho t]$. **B** Perrin plot of the cross-relaxation rate constant, σ, for cytosines 2 and 22 versus the ratio of the viscosity to the absolute temperature. The line is drawn according to the best fit linear regression

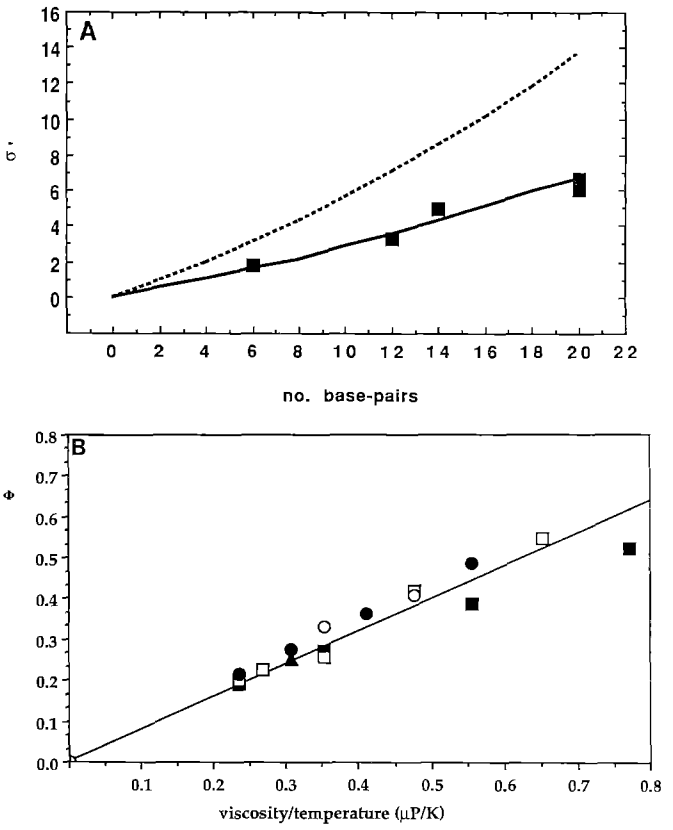

Fig. 3 A, B. Dependence of the correlation time on DNA length and viscosity. The cross-relaxation rate constants for cytosine H6-H5 vectors were averaged over each residue in each molecule as described in the text. **A** dependence of the normalised cross-relaxation rate constant, σ' on the number of base pairs n (——) calculation for a prolate ellipsoid of length $3.4 \times n$ and diameter 23 Å, (- - - -) calculation for a circular cylinder of diameter 20 Å. **B** dependence of the function ϕ on the ratio of the viscosity to the temperature. The line is the regression fit to all of the data (16 points $r^2 = 0.94$). (■) trp operator (20 base pairs), (□) trp operator mutant (20 base pairs), (●) P35 (14 base pairs), (▲) EcoR1 dodecamer, (○) hexamer

There are three special angles to consider,when one or two of the amplitude terms becomes zero. These are $\beta = 0$, when $a_1 = 1$; $\beta = 54.74°$, when $a_1 = 0$, $a_2 = 0.667$, $a_3 = 0.333$; and $\beta = 90°$, when $a_1 = 0.25$, $a_3 = 0.75$. When $\beta = 0$, the spectral density terms depend only on the tumbling of the long axis. The rotation of many of the conformationally sensitive internucleotide vectors is dominated by this motion. When $\beta = 90°$, the spectral density terms are determined by both τ_L and τ_S, but $a_2 = 0$. This corresponds to vectors lying in the plane of the bases in B-DNA. Indeed, for slowly tumbling molecules, where $6J(2\omega) \ll J(0)$, the cross relaxation rate constant for $\beta = 0$ and 90° becomes

$$\sigma_{(\beta=0)} = -[56.92/r^6]\tau_L \quad (8\,\text{A})$$

$$\sigma_{(\beta=90)} = -[56.92/r^6][\tau_L/4 + 2.25\,\tau_L\tau_S/(2\tau_L + \tau_S)] \quad (8\,\text{B})$$

If the axial ratio of the ellipsoid or cylinder is known, (8 B) can be rewritten in terms of the ratio of the correlation times $\Gamma = \tau_L/\tau_S$:

$$\sigma_{(\beta=90)} = -[56.92/r^6][1/4 + 2.25/(2\Gamma + 1)]\tau_L \quad (9)$$

Note that $\sigma_{(\beta=90)}$ is a relatively weak functions of the axial ratio and therefore of Γ (see Fig. 1). For example, for $\tau_R = 5$ ns, increasing Γ from 2 to 3 increases $\sigma_{(\beta=90)}$ by a factor of only 1.056. Hence, Γ does not need to be known with high accuracy to calculate $\sigma_{(\beta=90)}$. Conversely, if a value of $\sigma_{(\beta=90)}$ is known from measurement, the value of τ_L can be readily calculated. Thus,

$$\tau_L = -2(2\Gamma + 1)r^6\,\sigma_{(\beta=90)}/56.92(\Gamma + 5) \quad (10)$$

A suitable reference vector in nucleic acids is the Cyt H6-H5 vector, whose length is fixed and known (2.46 Å), and which lies in the plane perpendicular to the long axis of the molecule (i.e. $\beta = 90°$). Indeed, the angle this vector makes with the principal axis is affected only by the base tilt (the base roll is about an axis parallel to this vector), which in B-like DNA at least is usually small. Thus, as Fig. 1 shows, even if β is 80°, the cross-relaxation rate constant is not significantly larger than for $\beta = 90°$. Hence, the cytosine H6-H5 cross-relaxation rate constant is very convenient for determining the rotational dynamics of DNA.

Figure 2A shows typical NOE build-up curves for the H6-H5 vectors of Cytosines 2 and 22 of the 14-mer P35 at 293 K. The values of the cross-relaxation rate constants are -1.3 and $-1.4\ s^{-1}$, respectively; they are not significantly different from one another. We have determined the cross-relaxation rate constant for each cytosine H6-H5 vector at 10, 20, 30 and 40 °C. Figure 2B shows the Perrin plot for the different cytosines. The data all lie on the same straight line of slope 0.32 ± 0.01 that passes through the origin. This indicates either that the molecule is rigid, or that any internal motions are both sufficiently fast and affect each residue in the same way. An Eyring plot of the data (not shown) gave apparent activation energies of 4.2 kcal/mol, which is equal to the apparent activation energy for the viscosity of D_2O (Wilbur et al. 1976). The slope of the Perrin plot is proportional to the hydrodynamic volume of the molecule. From the Stokes-Einstein equation, and (4–7), the slope of the Perrin plot is:

$$\text{slope} = (56.92/r^6)\, f_L [0.25 + 2.25/(2\Gamma + 1)]\, V/R \qquad (11)$$

where V is the hydrated volume and R is the gas constant. For 14 base-pairs of B-like DNA, the axial ratio is expected to be about 2:1, from which f_L can be calculated to be about 1.6 (Cantor and Schimmel, 1980 and see 5A), and the value of Γ to be about 2. Using $r = 2.46$ Å, the hydrated volume V can be calculated as 8900 Å^3. The hydrated volume is given by:

$$V = M\,(v + h) \qquad (12)$$

where v is the partial specific volume and h is the hydration. The partial specific volume of DNA is 0.5 ml/g, and it has been estimated that the value of h is about 0.6. Using these value of v and h yields a molecular weight of 8100, which compares well with the chemical molecular weight of 8400. On the other hand, using the chemical molecular weight, the hydration would be 0.55 g/g.

Equation (5) indicates that τ_L is a linear function of the ratio of the viscosity to the absolute temperature (η/T), and of its hydrated volume V. From (5) to (10), the cross relaxation rate constant for a vector perpendicular to the helix axis can be expressed as:

$$\sigma = (-56.92/r^6)[0.25 + 2.25/(2\Gamma + 1)]\, f_L \cdot \eta V/RT \qquad (13)$$

The hydrated volume is proportional to the number of base-pairs, n. Assuming a molecular weight of 600 per base-pair, the volume is $600\, n\,(v + h)$. Hence, at a given temperature, the cross-relaxation rate constant should be proportional to the number of base-pairs, n, and to the frictional ratio f_L, whose value depends on the model used. Figure 3A shows the dependence of $\sigma' = \sigma/(-56.92/r^6)$ on the number of base pairs at 298 K in D_2O. As expected for modest axial ratios, the correlation time increases nearly linearly with the number of base pairs. The two model lines in Fig. 3A were calculated for a prolate ellipsoid of diameter 23 Å, and for a circular cylinder of diameter 20 Å. The lengths were calculated as $3.4 \times n$. Interestingly, the reduced correlation time calculated for the ellipsoid is very close to the experimental data, whereas that calculated for the cylinder is considerably higher. The correlation times can be made smaller by decreasing the axial rise, though unphysical values are needed for the cylindrical model to force agreement with the experimental data. Therefore, either the calculations of rigid cylinders, assuming reasonable dimensions, overestimate the true dimensions of the hydrodynamically equivalent cylinder appropriate for B-DNA, or the experimental data underestimate the rotational corelation for a rigid cylinder. Eimer et al. (1990) found that the NMR correlation times were significantly smaller than those calculate for a rigid cylinder, which they attributed to internal motions of characterised by an order parameter of about 0.8. This is similar to the order parameter we have estimated from a combination of proton and phosphorus NMR for a DNA hexamer (Forster and Lane 1990).

Equation (13) indicates that if measured cross-relaxation rate constants for the cytosine H6-H5 vectors are normalised by division by the factor $(-56.92/r^6)[0.25 + 2.25/(2\Gamma + 1)]\, nf_L$, then data obtained for different numbers of base pairs should all fall on the same line when plotted against the ratio η/T. Figure 3B shows the dependence of the normalised cross-relaxation rate constant $\phi = \sigma/(-56.92/r^6)[0.25 + 2.25/(2\Gamma + 1)]\, nf_L$ for cytosine H6-H5 vectors on η/T for several DNA fragments of different length (see Table 1). In this plot, the cross-relaxation rate constants for the different cytosine residues in each fragment have been averaged. The value of f_L was calculated for a prolate ellipsoid of diameter 23 Å; this value is similar to that quoted by Eimer et al. (1990). A similar calculation using the expressions for a rigid cylinder yields values for ϕ about a factor of two smaller. Figure 3B shows that the data lie close to a line passing through the origin, with a slope of 8000 ± 950. The correlation coefficient for all data (17 points) was 0.94. From (13), the slope of the plot in Fig. 3B is $600\,(v + h)/R$.

Table 1. DNA sequences and conditions used for measuring correlation times

No. base pairs	Sequence	Temperature (K)	Reference
6	$(CGTACG)_2$	288, 293	Lane and Forster (1989)
12	$(CGCGAATTCGCG)_2$	303	Lane, Jenkins, Brown, and Neidle (unpublished data)
14	GCTGTTGACAATTA CGACAACTGTTAAT	283, 293, 303, 313	this work
20	$(CGTACTAGTTAACTAGTACG)_2$	273, 283, 298, 313	Lane et al. (1986)
20	$(CGTACTGATTAATCATGTACG)_2$	278, 288, 298, 308, 313	Lane (1989)

Hence, the average value of $v + h = 1.11$, which implies a degree of hydration, on average, of about 0.5 g/g DNA.

The preceding analysis has assumed that there are no internal motions that affect the cross-relaxation of the H6-H5 vector. The linearity of the Perrin plot (Fig. 2 B) is evidence that any internal motion that does occur is rapid on the Larmor timescale. Further, the close agreement between the estimated molecular weight and the calculated molecular weight argues against large amplitude motions. As has been previously argued (Lane et al. 1986), internal motions would have to be of the order 30° angular of angular fluctuation to have a significant effect on the relaxation. A 30° angular fluctuation within a cone is equivalent to an order parameter $S^2 = 0.65$ which is simply a scaling factor for the spectral density functions (Lipari and Szabo 1981, 1982, Lane and Forster, 1989). We conclude that librational motions of the bases do not exceed 20 to 30°. Nevertheless, Eimer et al. (1990) have compared dynamic light scattering and NMR relaxation rates to show that the bases do fluctuate up to 20–30° in solution. Comparison of correlation times determined for the cytosine H6-H5 vectors and for reorientation of the chemical shift anisotropy tensor of the phosphates in a DNA hexamer is also consistent with a small degree of internal motion of the bases (Forster and Lane 1990). This, in turn, implies that the hydration of DNA, as far as rotation is concerned, must be significantly larger than 0.6 g/g (see above).

Conclusions

The observation that a single treatment of data acquired on different lengths of DNA of unrelated sequences accounts for all of the data obtained over a wide range of conditions suggests that the simple hydrodynamic model adequately accounts for the rotation of these DNA fragments. It is clear that the effects of anisotropic rotation become significant for vectors oriented nearly parallel to the long axis of the molecule; internucleotide distances derived from NOE intensities, assuming isotropic reorientation, will be significantly underestimated when the axial ratio exceeds about 2.5. Fortunately, the appropriate correlation time for end-over-end tumbling can be readily calculated from the cross-relaxation rate constant for cytosine H6-H5 vectors.

For the analysis of conformations of DNA using the nuclear Overhauser effect, it is important to use correlation times that reproduce observed enhancements. As the bases are thought to be more rigid than the sugars (McCammon and Harvey, 1987), the NMR-determined correlation times may be more appropriate in practice than the larger values determined from other methods, as they already include the (small) influence of internal motion. There does not seem to be a clear choice between the model of the hydrodynamic rotor; a rigid prolate ellipsoid accurately reproduces the observed relaxation behaviour of the cytosine vectors with no additional assumptions, whereas the cylinder model requires use of an order parameter of magnitude approximately 0.8 to account for the relaxation.

To achieve the agreement with the data the GC base-pair tilts must be small ($< 10°$), and the average rise per base pair is not dramatically different from 3.4 Å, unless unlikely cancellation of effects were occurring. This result gives confidence in the use of the simple hydrodynamic models of DNA fragments that become necessary to take into account the effects of anisotropic rotation on the intensities of NOEs for internucleotide vectors. We note also that all five nucleotides studied must be essentially straight. In short oligonucleotides, the influence of large amplitude bending motions of the kind observed in long fragments of DNA (Hogan and Jardetzky 1979, 1980) motions seems to be minimal. Further, large bends or an unusual average rise per base pair would cause deviations from the line in Fig. 3 B. We note that the cytosine H6-H5 cross-relaxation rate constants for the EcoR1 dodecamer lie on the best fit line, implying that under the conditions of the experiment, this dodecamer does not have sharp bends or kinds that significantly affect its rotational friction behaviour (Nerdal et al. 1989).

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