

# CONFORMATION OF RANDOM POLYNUCLEOTIDE CHAINS—FREE ROTATIONAL DIMENSIONS

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## ABSTRACT

Free rotational dimensions ( $C_f$ ) of polynucleotide chains, with four different types of rigid sugar residues, have been computed as a function of the linkage angle ( $\tau$ ), using the single virtual bond approach. The computed  $C_f$  values for the freely rotating polynucleotides are close to unity, indicating that the above polymer behaves quite similar to freely jointed chains. No significant difference is found in the computed  $C_f$  values for a fixed  $\tau$ , for all the four types of polynucleotides. Small variations in  $\tau$  do not effect  $C_f$  values significantly.

## INTRODUCTION

THE stiffness of polymeric chains is generally characterised by  $\sigma = \{ \langle r^2 \rangle_o / \langle r^2 \rangle_{o,f} \}^{1/2}$  where  $\langle r^2 \rangle_o$  is the unperturbed mean square end-to-end distance and  $\langle r^2 \rangle_{o,f}$  is that calculated from a model assuming free rotation of the monomeric units about the single bonds linking the adjacent units. The free rotational dimensions for polypeptides<sup>1,2</sup> and polysaccharides<sup>3</sup> have been reported by treating the chains comprising N monomeric units as a sequence of N virtual bonds of constant length  $l_v$ . Similar methods have been followed in computing the dimensions of hindered polypeptides<sup>1,2,4,5</sup>, polysaccharides<sup>6-8</sup> and polynucleotides<sup>9</sup>. Presently, we have attempted to compute the  $C_f (= \langle r^2 \rangle_{o,f} / Nl_v^2)$  values of freely rotating polynucleotides following the single virtual bond scheme<sup>a</sup> by Olson<sup>9</sup>. The polynucleotides

have been assumed to comprise of four types of rigid sugar residues, viz., C<sub>3'</sub>-endo, C<sub>2'</sub>-exo, C<sub>2'</sub>-endo and C<sub>3'</sub>-exo with a fixed valence angle ( $\tau$ ) at the linking phosphorus atoms. In view of the observed variations of this angle from 100° to 106°<sup>10-14</sup>, a systematic study was undertaken to compute the  $C_f$  values using the single virtual bond approach for polynucleotides with four different types of rigid sugar residues, as a function of  $\tau$ . These results may help in understanding the effect of variations in the linkage angle on the free-rotational dimensions and on comparison with the experimental values, may also furnish information about the stiffness of the various polynucleotide chains.

## THEORETICAL TREATMENT

A section of the backbone of a polynucleotide chain showing the virtual bonds is shown in Fig 1. The bond lengths and valence bond angles of the chain

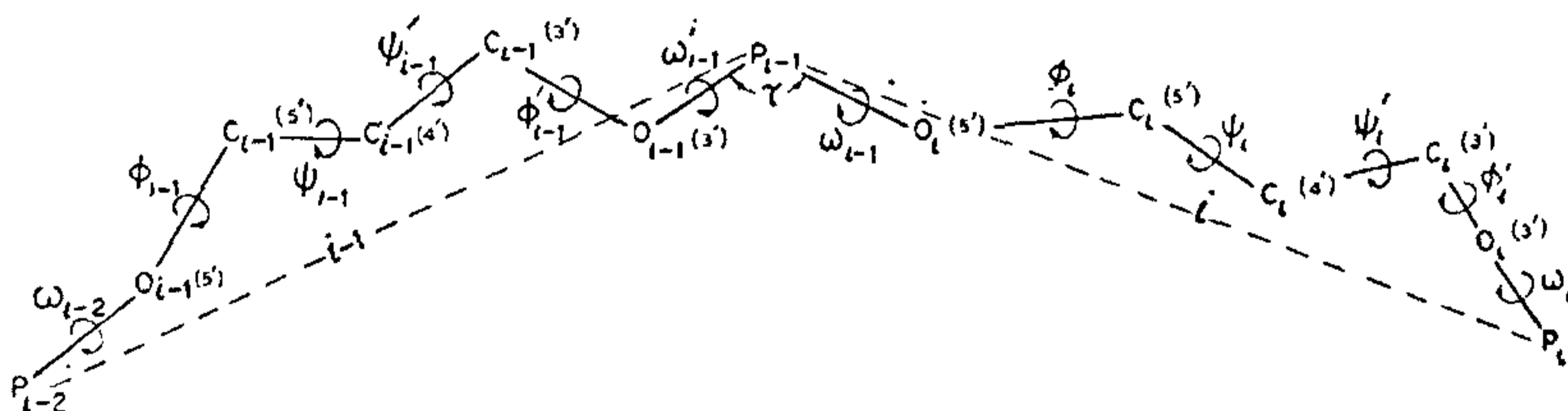


FIG. 1. Section of the backbone of a polynucleotide chain showing the rotational angles and virtual bonds (dashed lines).

Foot Note 'a': The rigid nucleotide concept and the connected virtual bond scheme have evolved from the original work of M. Sundaralingam and his associates. (Sundaralingam, M. (1973). In 'Conformation of Biological Molecules and Polymers', *The Jerusalem Symposium on Quant. Chem. Biochem.* Ed. Bergmann and B. Pullman, 5, 417-456, Academic Press, New York; Yathindra, N. and Sundaralingam, M. (1975), In *Structure and Conformation of Nucleic Acids and Protein—Nucleic Acid Interaction*, Ed. M. Sundaralingam and S. T. Rao, 729-748, University Press, Baltimore).

backbone were taken from the compilation of Arnott<sup>14</sup>. The sugar residues in the different polynucleotides studied in the present work were fixed in C<sub>3'</sub>-endo, C<sub>2'</sub>-exo, C<sub>2'</sub>-endo and C<sub>3'</sub>-exo conformations with the rigid nucleotide geometries used by Olson<sup>9</sup>. The recently recommended<sup>15</sup> notation and conventions were followed in describing the chain parameters.

The general expression for calculating the chain characteristic ratio of an infinitely large polynucleotide chain was obtained by using the expression<sup>9</sup>

$$\langle r^2 \rangle_o / Nl_v^2 = [(E + (T)) (L - (T))^{-1}]_{ii} \quad (1)$$

were  $E$  is the identity matrix of order 3 and  $\langle T \rangle$  is the statistical mechanical averaged matrix. (However, Olson<sup>9</sup> expresses the characteristic ratio as  $\langle r^2 \rangle_0/nl^2$  where  $n$  is the total number of chemical bonds in the chain backbone and  $l^2$ , the mean square bond length). The subscript 22 denotes the (2, 2) element of the final matrix. The transformation matrix  $T_i$ , which transforms a vector presented in the coordinate system associated with the virtual bond  $i$  to the coordinate system of  $i-1$  was formed following the procedure of Rao *et al.*<sup>6</sup>

#### RESULTS AND DISCUSSION

Since in a freely rotating polynucleotide chain all the orientations of the monomer units are equally probable, the characteristic ratios,  $C_f$ , of such a chain may be calculated by using equation 1 by giving equal statistical weights to all the conformational states. The  $C_f$  values computed for polynucleotides with different types of sugar puckerings for different values of  $\tau$  are given in Table I. It is seen from Table I that the

TABLE I

Calculated values of the characteristic ratio  $C_f$  of freely rotating linear polynucleotide chains.

Type of sugar pucker in the polynucleotide chains	Values of $C_f$ for different values of angle $\tau$				
	100°	101.4°	103°	104.5°	106°
$C_2'$ -endo	1.12	1.13	1.15	1.17	1.18
$C_2'$ -exo	1.13	1.14	1.16	1.18	1.20
$C_3'$ -endo	1.21	1.24	1.27	1.30	1.33
$C_3'$ -exo	1.23	1.26	1.30	1.34	1.38

computed  $C_f$  values for the freely rotating polynucleotide chains are close to unity, indicating that the above polymer behaves quite similar to freely jointed chains. This happens because the angle between the virtual bonds varies (though the angle  $\tau$  is kept constant) when the nucleotide units are rotated about the linking single bonds. Thus the chain formed by the virtual bonds tends to attain the character of a freely jointed chain. No significant difference is found in the computed  $C_f$  values for a fixed  $\tau$  for all the four types of polynucleotides. This indicates that the different rigid geometries for the nucleotides in the polynucleotide chains have little effect on the free rotational dimensions.

Table I also shows that there is no significant change in the  $C_f$  values of all the polynucleotide chains for different  $\tau$  values. This again indicates that the free rotational dimensions of polynucleotides do not depend on the valence angle at the linking phosphorus atom. This behaviour is in contrast to that of polypeptides<sup>2</sup> and polysaccharides<sup>3</sup> for which  $C_f$  is generally found to increase significantly with increase in  $\tau$ .

*Note added in proof:* Since this paper was submitted for publication the author has learnt from Dr. N. Yathindra of the University of Wisconsin that he has obtained similar results in independent calculations but his results are yet unpublished.

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