1,3-(4-Biphenylyl)-2-propanone (6). To a solution of 4-phenylbenzylmagnesium chloride obtained from 6.2 g (0.0306 mol) of 4-phenylbenzyl chloride (Aldrich Chemical Co.) and 0.75 g (0.0306 g-atom) of magnesium in 100 ml of dry ether was added a solution of 2.96 g (0.015 mol) of 4-phenylphenylacetonitrile (Aldrich Chemical Co.) in 100 ml of dry ether. The mixture was heated at the reflux temperature for 3 hr, 100 ml of benzene was then added, the ether was removed, and the mixture was hydrolyzed with 30% hydrochloric acid by heating at the reflux temperature for 18 hr. The mixture was cooled and the benzene layer was separated and dried over magnesium sulfate. The benzene was removed at reduced pressure and the residue was recrystallized from 95% ethanol to give 2.3 g (41.6%), mp 146–148°. The ir spectrum showed a carbonyl peak at 1720 cm^{-1} and the nmr contained one nonaromatic peak at δ 3.77 (singlet).

Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.55; H, 6.59.

2,5-(4-Biphenylyl)-3,4-diphenylcyclopentadienone (7). A mixture of 1.0 g (2.8 mmol) of 1,3-(4-biphenylyl)-2-propanone (9) and 0.6 g (2.8 mmol) of benzil in 10 ml of triethylene glycol was heated to 100° and held there until solution was complete. Benzyltrimethylammonium hydroxide, 40% in methanol (1 ml), was added and the solution was heated at 100° for 10 min. The mixture was cooled, 60 ml of methanol was added, and the product was filtered to give 0.93 g (61.9%), mp 264–266°. The carbonyl absorption in the ir region appeared at 1710 cm^{-1}. The uv-vis spectrum showed λ_{max} at 350 (6.65×10^3) and 533 nm (ϵ 2.4×10^3).

Anal. Calcd for $C_{41}H_{28}O$: C, 91.76; H, 5.26. Found: C, 92.32; H, 5.29.

2′′,3′′,5′′-Triphenyl-*p*-quinquephenyl (5). A mixture of 0.1160 g (0.114 mmol) of phenylacetylene and 0.6000 g (0.114 mmol) of 2,5-(4-biphenylyl)-3,4-diphenylcyclopentadienone (7) in 8 ml of reagent grade toluene was placed in a polymerization tube. After three freeze–thaw cycles at liquid nitrogen temperatures, the tube was sealed *in vacuo* and placed in a 500-ml Paar pressure reactor containing 50 ml of toluene. The reaction was carried out at 200° for 18 hr. The mixture was cooled, the toluene was removed at reduced pressure, and the white solid was recrystallized from cyclohexane to give 0.5921 g (85%) of product, mp 275–277°.

Anal. Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.00; H, 5.85.

Poly(2,3,6,2′′′,3′′′,6′′′-hexaphenyl-*p*-pentaphenylene-4′,1′′-oxide-4,4′′′′-ylene (1). Polymerizations for the determination of the rate constants were carried out by the same method; a typical polymerization to yield poly(2,3,6,2′,3′′′,6′′′-hexaphenyl-*p*-pentaphenylene-4′,1′′-oxide-4,4′′′′-ylene) follows. A mixture of 0.2153 g (0.171 mmol) of freshly sublimed *p*-diethynylbenzene[23] (mp 94.5°) and 0.13362 g (0.171 mmol) of 3,3′-(oxydi-*p*-phenylene)bis-(2,4,5-triphenylcyclopentadienone)[14] (**12**), which had been purified by column chromatography on Woelm neutral alumina with benzene (mp 270°), was placed in a 20-ml polymerization tube with 2.06 ml of toluene. The contents of the tube were degassed by three freeze–thaw cycles at liquid nitrogen temperatures and then sealed *in vacuo*. Toluene (50 ml) was added to a 500-ml pressure bomb, the tube was placed inside, and the reactor was closed and heated to the desired temperature for the desired time. Then the pressure bomb was immediately cooled to room temperature by means of a cold water bath, the solution in the tube was filtered to removed solid impurities, and the toluene was removed at reduced pressure. The resultant polymers were freeze-dried from reagent grade benzene and the viscosities were taken. The results are summarized in Table II.

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Conformational Statistics of 1,3- and 1,4-Linked Homopolysaccharides

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ABSTRACT: Unperturbed dimensions have been calculated for several 1,3- and 1,4-linked homopolysaccharides. The characteristic ratio depends strongly on the bonding geometry and on the degree of rotational freedom about the glycosidic bonds. It appears that unperturbed dimensions can be predicted qualitatively from a knowledge of the regular conformations of the polysaccharide.

A number of authors have attempted to calculate the unperturbed dimensions of polysaccharides such as amylose,[1,2] cellulose,[3] and alginic acid,[4] from an assumed skeletal geometry and an assumed potential function which allows hindered rotation about the glycosidic bonds. Most of this work has been directed toward obtaining detailed information on particular homopolysaccharides, though a preliminary study has been made of the effects of bonding geometry and substituent position on the unperturbed dimensions of a range of 1,4-linked homopolysaccharides.[5]

Rees and Scott[6] have recently published an extensive surve of the regular conformations of a variety of 1,2-, 1,3-, 1,4-, and 1,6-linked pyranoglycans using a computer model-building approach based on a hard-sphere potential function. They find that polysaccharides can be categorized as (A) extended chains, (B) wide helices, (C) crumpled and contorted, and (D) flexible, but, on average, extended. It has been suggested[2] that the solution properties of polysaccharides can be predicted, at least qualitatively, from their regular conformations, and detailed calculations for 1,4-linked systems[5] indicate that this is generally true, with some reservations.

The primary aim of this work is to calculate characteristic ratios of a range of 1,3- and 1,4-linked homopolysaccharides

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[1] V. S. R. Rao, N. Yathindra, and P. R. Sundararajan, *Biopolymers*, **8**, 325 (1969).

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[3] N. Yathindra and V. S. R. Rao, *Biopolymers*, **9**, 783 (1970).

[4] S. G. Whittington, *ibid.*, **10**, 1481 (1971).

[5] S. G. Whittington, *Macromolecules*, **4**, 569 (1971).

[6] D. A. Rees and W. E. Scott, *J. Chem. Soc. B*, 469 (1971).

TABLE I
PARAMETERS USED FOR KITAYGORODSKY POTENTIAL

Atom pair	Kitaygorodsky parameter, r_0
C···C	3.80
C···O(H)	3.55
C···H	3.15
O(H)···O(H)	3.33
O(H)···H	3.00
H···H	2.60
C···CH₂OH	4.45
O(H)···CH₂OH	4.215
H···CH₂OH	3.85
CH₂OH···CH₂OH	5.1

TABLE II
CHARACTERISTIC RATIOS FOR 1,3-LINKED HOMOPOLYSACCHARIDES[a]

Monomer	Bonding	C_∞	Z
α-D-Glucose	a–e	37	16
β-D-Glucose	e–e	6.1	27
α-D-Mannose	a–e	14	31
β-D-Mannose	e–e	2.7	45
α-D-Galactose	a–e	32	18
β-D-Galactose	e–e	3.7	43
α-D-Xylose	a–e	36	18
β-D-Xylose	e–e	5.7	27
α-L-Arabinose	e–e	3.3	45

[a] The calculations were carried out using a bridge angle of 116°.

and to seek correlations between the unperturbed dimensions and the bonding geometry of the polysaccharide. We shall confine our attention to pyranoglycans with the Reeves C1 ring conformation. We omit a study of 1,2-linked systems, since these occur only rarely (*e.g.*, rhamnose in pectic substances), and the assumption of separable conformational energies may not be a valid assumption in the treatment of their conformational statistics.

Previous workers have considered the $-CH_2OH$ group as a single group and do not consider rotation about the C5–C6 bond. In this paper we wish to propose an approximate method by which this rotation can be taken into account.

Calculations and Results

Since the primary aim of this work is to compare the unperturbed dimensions of a wide range of polysaccharides, it was felt that the advantage of using a single consistent set of residue coordinates outweighed any consideration that more accurate values for a particular molecule might be obtained by using residue coordinates derived by X-ray diffraction of appropriate monomers or dimers. We have used the monomer coordinates given by Settineri and Marchessault[7] for β-D-xylose and have derived the coordinates of other monomers by suitable epimerizations and by the addition of an equatorial $-CH_2OH$ group using standard bond lengths and bond angles.

1,3-Linked Homopolysaccharides. If the ring conformation of each monomer is assumed to be fixed, then the polysaccharide chain can be regarded as a sequence of virtual bonds of constant length joining adjcaent bridge oxygens. Examination of molecular models suggests that the interaction between a monomer and its next nearest neighbor is small compared to the interaction between nearest-neighbor monomers so that, to a good approximation, the conformational energy of the polymer can be written as the sum of the conformational energies of the dimers. (This is known as the assumption of separable conformational energies and has been adopted in all previous calculations on 1,4-linked systems.[1-5]) If this assumption is valid, then the treatment of the conformational statistics is completely standard and the characteristic ratio, C_∞, can be calculated as

$$C_\infty = [(\mathbf{I} + \langle\mathbf{T}\rangle)(\mathbf{I} - \langle\mathbf{T}\rangle)^{-1}]_{11}$$

where **I** is the 3 × 3 unit matrix and $\langle\mathbf{T}\rangle$ is the average value of the matrix which transforms, apart from translation, from the coordinate system situated on one virtual bond to that on the neighboring virtual bond.[1-5] $\langle\mathbf{T}\rangle$ depends only on the conformation of the dimer and can readily be calculated for any given potential function. We have used a Kitaygorodsky function[8] for nonbonded interactions

$$V(r) = 3.5\,(-0.04/s^6 + 8.6 \times 10^3 \exp(-13s))\ \text{kcal/mol}$$

where $s = r/r_0$, r is the distance between the nonbonded atoms' and r_0 is a parameter depending on the nature of the nonbonded atoms. The Kitaygorodsky parameters used were mainly those used by Rao, *et al.*,[1,3] and are given in Table I. We have used two sets of parameters to characterize the $-CH_2OH$ group, treating it both as a single carbon atom (which probably underestimates the steric effect of the group) and as a rather bulky group with the parameter for the CH_2OH-CH_2OH interaction taken as 5.1 Å (which must overestimate the steric effect of the group).[5]

The matrix $\langle\mathbf{T}\rangle$ was calculated as

$$\langle\mathbf{T}\rangle = \sum_{\phi}\sum_{\psi}\mathbf{T}(\phi,\psi)\exp(-E(\phi,\psi)/RT)/Z$$

where

$$Z = \sum_{\phi}\sum_{\psi}\exp(-E(\phi,\psi)/RT)$$

The summations are over 10° intervals of the dihedral angles ϕ and ψ about the C1–O and O–C3′ bonds, T is the absolute temperature (assumed throughout to be 300°K), and R is the gas constant. $E(\phi, \psi)$ is the dimer energy in conformation (ϕ, ψ) with the energy of the minimum-energy conformation taken as zero. Z is proportional to the contribution (from hindered rotation) to the configuration integral of the dimer and is a measure of the degree of rotational freedom about the glycosidic bonds in the dimer.

We have calculated C_∞ and Z for a number of 1,3-linked homopolysaccharides, and the results are almost independent of the Kitaygorodsky parameter used to characterize the $-CH_2OH$ group. Since this group is apparently unimportant in determining the unperturbed dimensions of 1,3-linked polysaccharides, no attempt was made to take cognizance of the rotation about the C5–C6 bond. Results (using r_0 $(CH_2OH-CH_2OH) = 5.1$ Å) are given in Table II.

1,4-Linked Homopolysaccharides. Previous workers[1-5] have neglected rotation about the C5–C6 bond and have treated the $-CH_2OH$ group as a single group with size varying from a single carbon atom[1,3] to a very bulky group.[5] For 1,4-linked systems, the calculated characteristic ratio is very sensitive to the size assumed for this group. We wish to develop a method by which the rotation about the C5–C6 bond can be, at least approximately, included, since we regard

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[7] W. J. Settineri and R. H. Marchessault, *J. Polym. Sci., Part C*, No. 11, 253 (1965).

[8] A. I. Kitaygorodsky, *Tetrahedron*, **14**, 230 (1961).

this as a better model of the $-CH_2OH$ group than those previously employed.

Consider a typical 1,4-linked dimer of a D sugar in the Reeves C1 conformation. Let ϕ and ψ be the dihedral angles about the C1–O and O–C4′ bonds, let τ be the dihedral angle about the C5–C6 bond, and let χ be the dihedral angle about the C5′–C6′ bond. From inspection of molecular models, it appears that rotation about C5–C6 is almost independent of the other dihedral angles[9] so that we can write the conformational energy of the dimer as

$$E_1(\phi, \psi, \chi, \tau) \simeq E_2(\phi, \psi, \chi) + E_3(\tau)$$

If this separation is exact, then the averaged transformation matrix for a dimer can be written as

$$\langle \mathbf{T} \rangle = \frac{\int\int\int T(\phi, \psi) \exp(-E_2(\phi, \psi, \chi)/RT)\, \mathrm{d}\phi \mathrm{d}\psi \mathrm{d}\chi}{\int\int\int \exp(-E_2(\phi, \psi, \chi)/RT)\, \mathrm{d}\phi \mathrm{d}\psi \mathrm{d}\chi}$$

so that $\langle \mathbf{T} \rangle$ is independent of the rotation on the nonreducing monomer. If we now consider a polysaccharide chain and label the monomers $i = 1, 2, \ldots, N$, we can write χ_i for the dihedral angle of rotation about the C5–C6 bond on monomer i and ϕ_i, ψ_i for the dihedral angles about the glycosidic bonds between monomers $i - 1$ and i. If $\mathbf{T}_{i+1}$ is the transformation matrix from monomer $i + 1$ to i and $\mathbf{T}_i$ is the transformation matrix from monomer i to $i - 1$, then it is easy to show that

$$\langle \mathbf{T}_i \mathbf{T}_{i+1} \rangle = \langle \mathbf{T}_i \rangle \langle \mathbf{T}_{i+1} \rangle = \langle \mathbf{T} \rangle^2$$

for a homopolymer, so that the assumption of independence or of separable conformational energies still holds. It is straightforward to test the validity of the above treatment, since the calculated value of C_∞ should be essentially independent of the way the $-CH_2OH$ is treated in the nonreducing sugar. We have evaluated the $\langle \mathbf{T} \rangle$ matrix by taking sums over 10° intervals of ϕ and ψ and over 120° intervals of χ (so that the $-CH_2OH$ group is in gt, gg, and tg orientations), and assuming that τ is fixed so that, in one case the $-CH_2OH$ group in the nonreducing sugar was in the gt orientation, while in the second case it was in the gg orientation. With a C1–O bond length of 1.397 Å, an O–C4′ bond length of 1.446 Å, and a bridge angle of 116°, the calculated values of C_∞ for β-D-glucose are 93 and 91, respectively. For comparison, we have calculated C_∞ with the same parameters except that the $-CH_2OH$ groups were treated as single carbon atoms,[1,3] yielding $C_\infty = 74$, and assuming that both $-CH_2OH$ groups were fixed in the gt conformation, yielding $C_\infty = 85$. This suggests that, at least in the range of bridge parameters of interest for β sugars, the assumption of independence of τ and (ϕ, ψ, χ) is justified and that this treatment of the $-CH_2OH$ group leads to larger unperturbed dimensions than the other treatments described above. The value $C_\infty = 74$ calculated by treating the $-CH_2OH$ group as a single carbon atom can be compared with the calculation of Yathindra and Rao.[3] It appears from their graph of C_∞ against bridge angle that their calculations give $C_\infty \simeq 60$ for a bridge angle of 116°. Since the potential function used by Yathindra and Rao is that used in our calculation, the discrepancy must arise as a result of our use of different monomer geometries.

TABLE III

CHARACTERISTIC RATIOS FOR 1,4-LINKED HOMOPOLYSACCHARIDES

Monomer	Bonding	C_∞	Ω
α-D-Glucose	a–e	4.5	9
α-D-Mannose	a–e	0.50	22
α-D-Galactose	a–a	235	13
β-D-Glucose	e–e	93	42
β-D-Mannose	e–e	67	62
β-D-Galactose	e–a	27	25

We have examined briefly the effect of bridge angle on the characteristic ratio for 1,4-linked polymers of α-D-glucose and β-D-glucose, using the Kitaygorodsky function and allowing rotation about C5′–C6′ as above, with the gt conformation for the $-CH_2OH$ group in the nonreducing sugar. For β-D-glucose, the value of C_∞ decreases from 131 at 112° to 47 at 120°, while, for α-D-glucose, C_∞ decreases from 10.2 at 110° (the value of the bridge angle assumed by Rao, *et al.*[1]) to 1.1 at 116°. In order to obtain a value of C_∞ of about 6 or 7 for amylose, as found experimentally by Banks and Greenwood,[10,11] the bridge angle would need to be about 111°, which is smaller than that reported for any X-ray determination of the structure of an oligosaccharide of glucose known to the authors. Similarly, in order to obtain a value of C_∞ for cellulose as low as, say, 40, the value of the bridge angle would have to be in excess of 120°. Of course, use of a different monomer geometry, different bridge bond lengths, or a different potential function might appreciably improve these results.[12]

We have calculated characteristic ratios for the 1,4-linked homopolymers of α- and β-glucose, -mannose, and -galactose using the above method, together with a quantity Ω, proportional to the contribution to the configuration integral from rotation about the glycosidic and C5–C6 bonds, given by

$$\Omega = \sum_{\phi}\sum_{\psi}\sum_{\chi} \exp(-E_2(\phi, \psi, \chi)/RT)$$

where the zero of E_2 is the energy of the minimum-energy conformation. We have assumed a bridge angle of 112° for the a–e cases and 116° otherwise. For a comparison between sugars in the same series, the angle assumed is less important than in any attempt to obtain quantitative data for a single polymer. The results are shown in Table III. Since we cannot separate the rotation about C5′–C6′ from the rotation about the glycosidic bonds, Ω is a less reliable estimator of the degree of rotational freedom in the bridge than is the quantity Z which we used for 1,3-linked systems.

Discussion

The calculated values of the characteristic ratios for amylose and cellulose are extremely dependent on the value chosen for the valence angle at the bridge oxygen, as found by other workers.[2,3] The form of potential function used to describe the steric effects also has a large effect on the calculated characteristic ratios, the values calculated using the Lennard-Jones potential[12] being even more dependent on bridge angle than those calculated using the Kitaygorodsky potential. With these uncertainties in mind, it seems more useful to attempt to draw general conclusions on the way in which

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(9) Rotation about C5′–C6′ is not independent of the rotations about the glycosidic bonds.

(10) W. Banks and C. T. Greenwood, *Carbohydr. Res.*, **7**, 349 (1968).

(11) W. Banks and C. T. Greenwood, *Makromol. Chem.*, **67**, 49 (1963).

(12) To investigate the effect of potential function, we have calculated C_∞ for amylose and cellulose using the Lennard-Jones potential used by Brant and Dimpfl.[2] For amylose this yields $C_\infty = 17$ for a bridge angle of 110°, 6 for a bridge angle of 112°, and 1 for a bridge angle of 116°. For cellulose the value of C_∞ decreases from 129 at 112° to 35 at 120°. The differences between the characteristic ratios calculated using the two potential functions give some idea of the uncertainty present in the quantitative values calculated for particular polymers.

unperturbed dimensions depend on such factors as bonding geometry, etc., than to attempt to obtain quantitative agreement between theory and experiment for particular molecules.

Characteristic ratios have previously been calculated for a variety of 1,4-linked homopolysaccharides, and it was noted that, in general, characteristic ratios were larger for equatorial–equatorial-linked systems than for axial–equatorial-linked systems and that, in both cases, the characteristic ratios decreased as the freedom of rotation about the glycosidic bonds increased. If we examine the results for 1,3-linked systems reported here, it is clear that the characteristic ratio is larger for axial–equatorial- than for equatorial–equatorial-linked systems and that, for each system, C_∞ decreases as Z increases.

For the 1,4-linked homopolysaccharides considered here, the results are in qualitative agreement with previous work.[5] Characteristic ratios decrease in the order a–a > e–e > e–a > a–e and for the e–e and a–e series, C_∞ decreases as Ω increases. Since Ω contains a contribution from the rotation about C5–C6, the results are not directly comparable with xylose or arabinose results.[5]

We can rationalize these results using the classification of Rees and Scott,[6] who noticed that 1,4-a–a, 1,4-e–e, and 1,3-a–e polymers are all of type A, while 1,4-e–a, 1,4-a–e, and 1,3-e–e polymers are all of type B. It appears that, in general, unperturbed dimensions of type A polymers are large and unperturbed dimensions of type B polymers are small, but that there are variations within these types depending on the details of the bonding geometry and on the degree of rotational freedom about the glycosidic bonds.

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Excluded Volume Expansion of a Polymer Chain in a Mixed Solvent

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ABSTRACT: A new theory of dilute solutions of polymers in mixed solvents has been developed. In this theory the solvent sea is divided into two regions, one consisting of the nearest neighbors of the segments of the polymer chain and the other the infinite sea beyond the isolated macromolecule. Expressions for the free energy and the Θ temperature for this model are obtained.

The theory of polymer solutions with a single solvent has been developed by many authors for both dilute solutions and concentrated solutions. Since the well-known lattice formulations of Flory[1] and Huggins[2] which were first published in the early 1940's, the subject has become highly developed and numerous treatments have appeared. The thermodynamic properties of a concentrated polymer solution have been more or less successfully explained by the lattice and the cell variant[3] of this theory, and some practical applications have been worked out. Another series of studies has been related to the characteristics of polymer molecules in a dilute solution, with the fundamental analysis being that of Flory.[4,5] The basic problem of dilute solutions is the calculation of the expansion factor α, which relates the true root-mean-square radius of gyration $\overline{s^2}$ of a swollen linear polymer molecule to that in the unperturbed state. According to Flory's theory,[5] this is given by

$$\alpha^5 - \alpha^3 = 2C_M\chi_1\left(1 - \frac{\Theta}{T}\right)M^{1/2} \qquad (1)$$

where M is molecular weight, T is the temperature, and ψ_1 and Θ are functions of the solvent quality. When Θ equals T, the expansion factor must be unity, which, as Flory points out, is the criterion of incipient precipitation. The parameter Θ is called the Flory Θ temperature. Equation 1 has direct application to the theory of intrinsic viscosity, as one may write

$$[\eta] = \Phi'\frac{(\overline{s^2})^{3/2}}{M} = [\eta]_\Theta\alpha^3 \qquad (2)$$

where $[\eta]_\Theta$ is the intrinsic viscosity under Θ conditions. More recent research[6-8] has been aimed at obtaining improved expressions for α.

In many practical applications, the system contains a mixture of two or more solvents rather than a single solvent. For example, in the process of fractional precipitation, a poor solvent is gradually added to a mixture of polymer and good solvent (at constant temperature). The apparent solvent power gradually decreases and the polymer molecules with high molecular weight begin to precipitate. A similar change

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