

Flexibility of the Pyranose Ring in α - and β -D-Glucoses*

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Synopsis

Conformational energies of α - and β -D-glucopyranoses were computed by varying all the ring bond angles and torsional angles using semiempirical potential functions. Solvent accessibility calculations were also performed to obtain a measure of solvent interaction.

The results indicate that the 4C_1 (D) chair is the most favored conformation, both by potential energy and solvent accessibility criteria. The 4C_1 (D) chair conformation is also found to be somewhat flexible, being able to accommodate variations up to 10° in the ring torsional angles without appreciable change in energy. Observed solid-state conformations of these sugars and their derivatives lie in the minimum-energy region, suggesting that the substituents and crystal field forces play a minor role in influencing the pyranose ring conformation. Theory also predicts the variations in the ring torsional angles, i.e., CCCC < CCCO < CCOC, in agreement with the experimental results. The boat and twist-boat conformations are found to be at least 5 kcal mol^{-1} higher in energy compared to the 4C_1 (D) chair, suggesting that these forms are unlikely to be present in a polysaccharide chain. The 1C_4 (D) chair has energy intermediate between that of the 4C_1 (D) chair and that of the twist-boat conformation. The calculated energy barrier between 4C_1 (D) and 1C_4 (D) conformations is high—about 11 kcal mol^{-1} .

INTRODUCTION

Recently, application of conformational energy calculations have led to a number of interesting results in the field of carbohydrates, both in the solid state and in solution.¹⁻¹⁹ Since the exact pyranose ring conformation is not known in large molecules, the average atomic coordinates derived from x-ray crystal structure studies on simple sugars and their derivatives have been used as input parameters in such calculations, assuming a rigid geometry for the pyranose ring. The various possible chain conformations have been obtained by allowing rotations about the C—O bonds of the glycosidic bridge, and the corresponding energies have been calculated using appropriate potential functions. However, a careful examination of x-ray crystal structure data reveals that the ring torsional angles deviate considerably from their average values, raising doubts about the validity of the use of average parameters for the pyranose ring in the energy calcula-

* A part of this paper was presented at the International Symposium on Biomolecular Structure, Function, Conformation and Evolution held at Madras, India, January 4-7, 1978.

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tions. In fact, the length of α -D-glucopyranose is found to vary from 4.1 to 4.8 Å in different derivatives.^{20,21} Such differences have also been noted for β -D-glucose.²² In recent studies, a slightly flexible pyranose ring geometry has been used in refining the x-ray fiber diffraction data of polysaccharides,²³ without considering the ring distortion energies. In calculating the unperturbed dimensions of cellulose, Goebel et al.¹⁵ permitted a certain percentage of sugar residues to be in 1S_3 , 1S_5 , and 3S_5 besides the 4C_1 conformation. However, there is no direct experimental evidence for the existence of the β -D-glucose residues in twist-boat conformations either in solution or in the solid state. Recently, Kildeby et al.²⁴ have minimized the energies of the chair, boat, and twist-boat conformations of α -D-glucose with respect to bond lengths, bond angles, and torsional angles. These studies have indicated that the boat and twist-boat conformations are unlikely for α -D-glucopyranose as they have 5–6 kcal mol⁻¹ higher energy than the global minimum, the 4C_1 chair conformation. However, these studies indicate neither the possible distortions in the ring nor the energies involved in producing such distortions. Also, if the energy difference between two conformations is small, a polar solvent may stabilize the one which exposes its hydroxyl groups for a favorable interaction. Hence an attempt has been made to construct the energy and solvent accessibility surfaces of α - and β -D-glucopyranoses to study the flexibility of the pyranose ring and also to arrive at the best parameters to use in conformational studies of polysaccharides. A comparison of these results with crystal structure data also indicates the effect of crystal field forces on the pyranose ring.

METHOD OF CALCULATION

Since in the present work we are interested in studying the flexibility of the pyranose ring, it is necessary to vary all the ring bond angles and ring torsional angles. This can be conveniently done using the set of internal parameters shown in Fig. 1. Various ring conformations can be generated by varying the conformational angles α_1 , α_2 , and α_3 , which denote rotations about the virtual bonds O₅C₂, C₂C₄, and C₄O₅. In this process, all the ring torsional angles vary and so do the ring bond angles at O₅, C₂, and C₄. While minimizing the energy, the other bond angles—i.e., β_1 , β_2 , and β_3 at atoms C₁, C₃, and C₅, respectively—are also varied. Thus in the present study, variations in all the ring bond angles and ring torsional angles are taken into consideration. Variations of α_1 , α_2 , and α_3 in the range -75° to $+75^\circ$ generate all the conformations of the pyranose ring.

Pickett and Strauss²⁵ have described a system of coordinates which very nearly gives an ideal description of the chair \rightarrow boat \rightarrow twist-boat change. The coordinates r , θ , and ϕ of this system are related to α_1 , α_2 , and α_3 (Fig. 1) by the expression

$$\alpha_i = r \left[\cos \theta + 2 \sin \theta \cos \left(\frac{4\pi i}{3} - \frac{2\pi}{3} + \phi \right) \right] \quad (1)$$

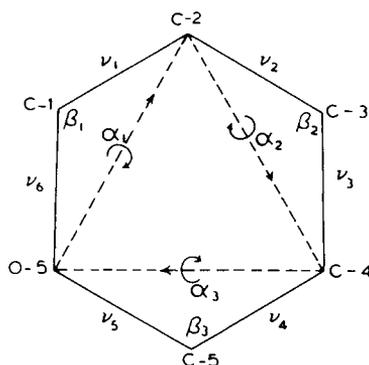


Fig. 1. Numbering of the ring atoms and definition of the conformational parameters α_1 , α_2 , α_3 and β_1 , β_2 , β_3 . Clockwise rotations about the virtual bonds are taken as positive. Figure shows the initial conformation. ($\alpha_1 = \alpha_2 = \alpha_3 = 0$.) The ring torsional angles are denoted by ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , and ν_6 .

The coordinate r is a measure of the deviation of the ring from planarity. Studies on cyclohexane have indicated that r for minimum-energy conformations remains relatively constant over the whole range of θ and ϕ . Thus only two coordinates, θ and ϕ , are necessary to define a conformation.

ENERGY CALCULATIONS

The total conformational energy of the molecule can be expressed as

$$E_{\text{tot}} = E_{\text{nb}} + E_{\text{es}} + E_{\text{tor}} + E_{\text{abs}} \quad (2)$$

where the subscripts tot, nb, es, tor, and abs refer to the total energy and its nonbonded, electrostatic, torsional, and angle bending strain components.

The nonbonded energy is computed using Kitaigorodsky's²⁶ function

$$E_{\text{nb}} = 3.5 \left(8600 \exp(-13Z) - \frac{0.14}{Z^6} \right) \quad (3)$$

$$Z = r_{ij}/r_{0,ij}$$

where r_{ij} is the distance (in Å) between the interacting atoms i and j and $r_{0,ij}$ is their equilibrium distance.

In these calculations, OH and CH₂OH groups were treated as spherical groups. The values of r_0 involving these groups are as follows:

$$\text{H}\cdots\text{OH} = 3.00, \quad \text{O}\cdots\text{OH} = 3.22, \quad \text{C}\cdots\text{OH} = 3.55$$

$$\text{OH}\cdots\text{OH} = 3.30, \quad \text{H}\cdots\text{CH}_2\text{OH} = 3.56, \quad \text{O}\cdots\text{CH}_2\text{OH} = 3.80$$

$$\text{C}\cdots\text{CH}_2\text{OH} = 4.11, \quad \text{OH}\cdots\text{CH}_2\text{OH} = 3.90$$

The value of r_0 for these interacting pairs is assumed to be 10% higher than the sum of their van der Waals radii, similar to the assumptions followed

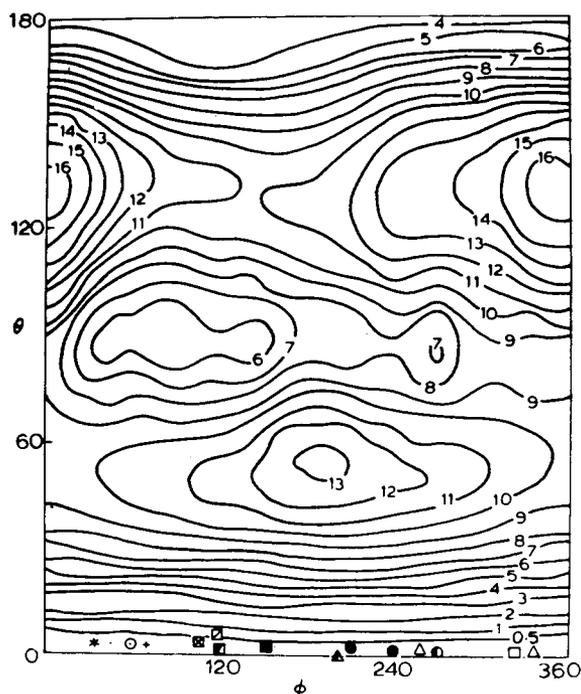


Fig. 2. Conformational energy map for α -D-glucopyranose. Numbers on contours indicate relative energies in kcal mol⁻¹. Minimum-energy contour coincides with the ϕ axis. The observed conformations of α -D-glycopyranose residue in various crystal structures are indicated: ●, *cyclo*(hexaamylose), 3 residues (Ref. 35); ▲, plateose dihydrate (Ref. 36); ○, methyl α -D-glucose (Ref. 37); △, β -maltose monohydrate (Ref. 38); ▲, raffinose pentahydrate (Ref. 39); □, dipotassium-1 phosphate (Ref. 40); ■, α -D-glucose urea complex (Ref. 41); ■, α -D-glucose (neutron diffraction; Ref. 42); ○, *N*-acetyl glucoseamine (Ref. 43); +, plant sulfolipid (Ref. 44); *, methyl- β -maltoside (Ref. 45); □, 1-kestose (Ref. 46); ■, α -D-glucosamine hydrochloride (Ref. 47).

in obtaining the r_0 values of other interacting pairs. The constants used for the other interacting pairs have been reported previously.²⁷⁻³²

As the ring takes different conformations, the bond angles at the carbon atoms vary asymmetrically, causing the torsional angles across a C—C bond to be unequal. This variation is taken care of by following the procedure adopted by Allinger et al.,³³ wherein the torsional energy for each fragment X—C—C—Y is evaluated separately using the expression

$$E_{\text{tor}} = V_0/2 (1 + \cos 3\theta), \quad 0^\circ \leq \theta \leq 60^\circ \quad (4)$$

$$= 0, \quad 60^\circ < \theta$$

The value of V_0 is taken to be 0.8 kcal mol⁻¹ for both C—O and C—C bonds. This gives a total of 2.4 kcal mol⁻¹ for the intrinsic torsional barrier about the C—C single bond, in agreement with the values used by the earlier workers.¹⁶

The form of the functions and the constants used for computing bond angle bending strain energy are the same as described previously.²⁷⁻³²

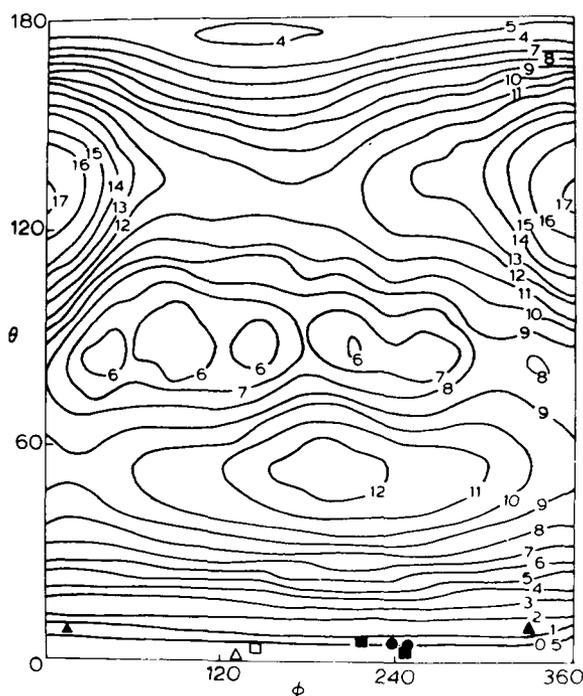


Fig. 3. Conformational energy map for β -D-glucopyranose. Numbers on contours indicate relative energies in kcal mol⁻¹. Minimum-energy contour coincides with the ϕ axis. The observed conformations of β -D-glucopyranose residue in various crystal structures are indicated: Δ , β -maltose (Ref. 38); \bullet , β -cellobiose, 2 residues (Ref. 48); \square , β -D-glucose (Ref. 49); \blacksquare , cellobiose, 2 residues (Ref. 49); \blacktriangle , methyl cellobioside, 2 residues (Ref. 50).

The bond lengths were kept constant throughout the calculations.

For a given conformation (θ, ϕ), the total potential energy was minimized with respect to $\beta_1, \beta_2, \beta_3$ and r . This was carried out at intervals of 5° in θ and 15° in ϕ .

Conformational energy contours drawn at 1 kcal mol⁻¹ in the ϕ - θ plane for α - and β -D-glucoses are shown in Figs. 2 and 3, respectively. The calculated energy and the conformational parameters of minimum-energy conformations are given in Tables I and II.

Accessibility Calculations

The method of Lee and Richards³⁴ was used to calculate the solvent accessibilities of different conformations.

An atom or a group of atoms in a molecule is said to be accessible to a solvent molecule if (1) its distance from the center of the solvent molecule is equal to the sum of its van der Waals radius and that of the solvent molecule, (2) the distance between the solvent molecule in that position and any other atom in the molecule is greater than the sum of their van der Waals radii.

TABLE I
Conformational Energy and Parameters for the Chair, Boat, and Twist-Boat
Conformations of α -D-Glucose

Confor- mation	α_1 (deg)	α_2 (deg)	α_3 (deg)	θ (deg)	ϕ (deg)	r (deg)	E^a (kcal mol ⁻¹)
⁴ C ₁	-32.8	-32.8	-32.8	0.0	0-360	-32.8	0
¹ C ₄	32.7	32.7	24.8	175.0	120.0	-30.2	3.3
B _{3,0}	25.8	-68.3	25.8	80.0	0.0	-31.9	8.4
¹ S ₃	54.8	-60.6	-2.9	85.0	30.0	-33.4	6.0
^{1,4} B	63.7	-31.8	-31.8	90.0	60.0	-31.8	5.8
¹ S ₅	56.2	0.0	-56.2	90.0	90.0	-32.5	5.0
B _{2,5}	30.4	30.4	-60.9	90.0	120.0	-30.4	6.0
³ S ₅	0.0	57.2	-57.2	90.0	150.0	-33.1	5.5
^{3,0} B	-32.3	64.7	-32.3	90.0	180.0	-32.4	7.3
³ S ₁	-54.4	54.4	0.0	90.0	210.0	-31.4	7.0
B _{1,4}	-58.9	25.8	25.8	85.0	240.0	-28.4	8.2
⁵ S ₁	-54.5	-2.6	49.2	85.0	270.0	-30.1	6.9
^{2,5} B	-30.3	-30.3	53.2	85.0	300.0	-27.2	8.9
⁵ S ₃	-2.7	-55.4	50.0	85.0	330.0	-30.5	8.4

^a Energies are expressed with respect to the ⁴C₁ conformation.

The solute molecule, represented as a set of interlocking spheres, is divided into equidistant planar sections. The solvent molecule is rolled along the periphery of each section. If for a given atom, L_i is the arc length in the i th section along which conditions (1) and (2) are satisfied, the total accessible area of that atom is given by

$$A = \sum_i \frac{R}{R^2 - Z_i^2} DL_i$$

TABLE II
Conformational Energy and Parameters for the Chair, Boat, and Twist-Boat
Conformations of β -D-Glucose

Confor- mation	α_1 (deg)	α_2 (deg)	α_3 (deg)	θ (deg)	ϕ (deg)	r (deg)	E^a (kcal mol ⁻¹)
⁴ C ₁	-33.2	-33.2	-33.2	0.0	0-360	-33.2	0
¹ C ₄	29.0	33.4	24.6	175.0	150.0	-29.2	3.7
B _{3,0}	25.3	-67.0	25.3	80.0	0.0	-31.3	8.0
¹ S ₃	55.3	-59.0	-2.8	85.0	30.0	-32.6	5.7
^{1,4} B	58.3	-33.3	-33.3	85.0	60.0	-30.8	5.9
¹ S ₅	55.2	0.0	-55.2	90.0	90.0	-31.9	5.0
B _{2,5}	27.8	27.8	-63.5	85.0	120.0	-30.6	6.0
³ S ₅	0.0	56.7	-56.7	90.0	150.0	-32.8	5.5
^{3,0} B	-32.7	65.5	-32.7	90.0	180.0	-32.8	7.0
³ S ₁	-59.9	54.1	-2.9	85.0	210.0	-33.1	5.9
B _{1,4}	-62.5	27.3	27.3	85.0	240.0	-30.1	6.7
⁵ S ₁	-55.4	-2.7	50.0	85.0	270.0	-30.1	6.7
^{2,5} B	-30.4	-30.4	53.4	85.0	300.0	-28.1	8.8
⁵ S ₃	-5.3	-57.8	47.1	80.0	330.0	-30.8	7.9

^a Energies are expressed with respect to the ⁴C₁ conformation.

where R is the van der Waals radius of the atom, Z_i is the distance of the i th section from the center of the sphere, and D is the distance between two adjacent sections. The accessibility S of the atom is then given by

$$S = 100A/4\pi R^2$$

The solvent molecule (water) was assumed to be a sphere of radius 1.4 Å. For a polar solvent like water, interactions with the polar groups would be of much more significance than the nonpolar ones. Hence the accessibilities of the polar groups were added to give the total solvent accessibility for that conformation.

Solvent accessibilities were calculated for the entire range of θ and ϕ . At every point, the hydroxymethyl group was fixed in all three staggered orientations, and the accessibility of the molecule was calculated separately for each case. Of the three orientations of the hydroxymethyl group, the one leading to the highest accessibility was taken into consideration for plotting the isoaccessibility contours. In most of the cases, the *trans* orientation ($O_6C_6C_5C_4 = 180^\circ$) was found to have high solvent accessibility.

Isoaccessibility curves plotted in the ϕ - θ plane are shown in Figs. 4 and 5.

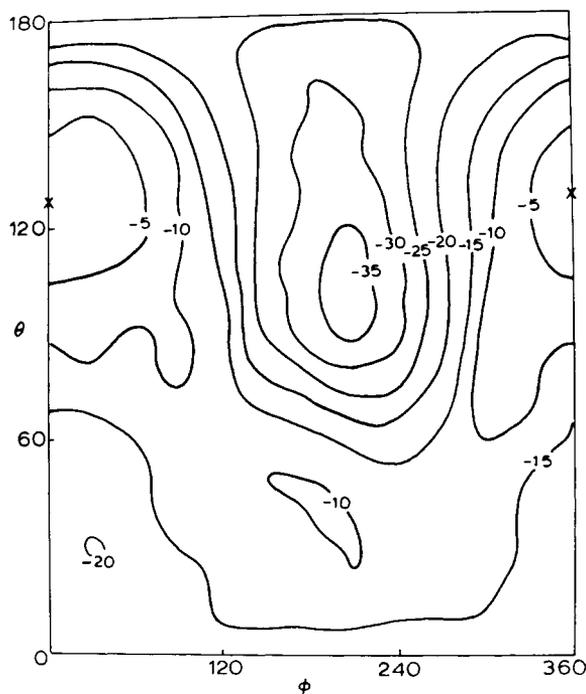


Fig. 4. Solvent accessibility map for α -D-glucopyranose. Sum of the accessibilities for O-1, O-2, O-3, O-4, O-5, and O-6 is plotted. Isoaccessibility contours are drawn with respect to the maximum value, marked with \times ($S_{\max} = 221$).

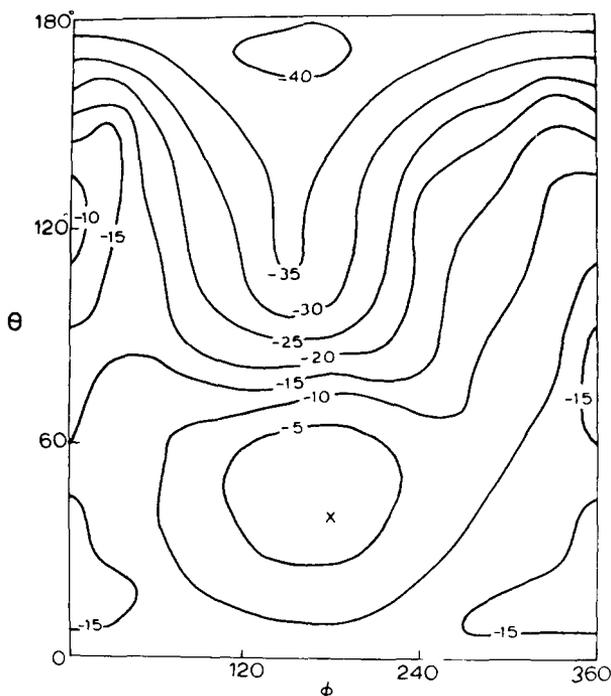


Fig. 5. Solvent accessibility map for β -D-glucopyranose. Sum of the accessibilities for O-1, O-2, O-3, O-4, O-5, and O-6 is plotted. Isoaccessibility contours are drawn with respect to the maximum value, marked with \times ($S_{\max} = 225$).

Higher solvent accessibility for a conformation indicates only a high probability of association with solvent molecules and does not imply formation of the best hydrogen bond, as this requires proper mutual orientations of the polar groups and the solvent molecules.

RESULTS AND DISCUSSION

Conformational energy contours for α - and β -D-glucopyranoses are shown in Figs. 2 and 3, respectively. Their similar overall appearance indicates that the difference in the orientation of the hydroxyl group at C1 atom does not affect the favorable conformations significantly.

The global minimum occurs along the line $\theta = 0^\circ$ ($\phi = 0^\circ$ – 360°). This corresponds to the 4C_1 (D) chair conformation. The shallow local minimum at $\theta = 175^\circ$ ($\phi = 120^\circ$ for α -D glucose and $\phi = 150^\circ$ for β -D-glucose) corresponds to the 1C_4 chair form and is about 3 kcal mol $^{-1}$ higher than the 4C_1 chair. This is in agreement with the earlier studies.^{24,27,29} The isoaccessibility plots (Figs. 4 and 5) show that 4C_1 (D) has higher solvent accessibility than the 1C_4 (D). Thus the 4C_1 (D) chair conformation is favored both by potential energy and solvent accessibility criteria.

The global minimum (Figs. 2 and 3) is seen to be quite diffuse. As θ

varies from 0° to 5° and ϕ from 0° to 360° , there is only a slight change (<0.5 kcal mol $^{-1}$) in the conformational energy. It is interesting to note (Figs. 2 and 3) that the pyranose ring conformations observed in the solid state for simple sugars and their derivatives lie in the minimum-energy region, suggesting that the crystal field forces play only a minor role in influencing the favored ring conformations.

To illustrate the possible distortions in the chair conformations, the calculated endocyclic torsional angles and bond angles are plotted as functions of ϕ for $\theta = 5^\circ$ (since most of the experimental points lie very close to this line). It is interesting to note from Figs. 6 and 7 that the theory predicts large variations (up to 10°) in the ring torsional angles and small variations (up to 3°) in the ring bond angles, in agreement with the experimental data,²⁰ though the conformational energy is almost independent of ϕ in this region. This indicates that a large number of distorted chair conformations are possible which differ significantly in both torsional and bond angles, without appreciable change in the conformational energy. This suggests that the pyranose ring is flexible, not rigid.

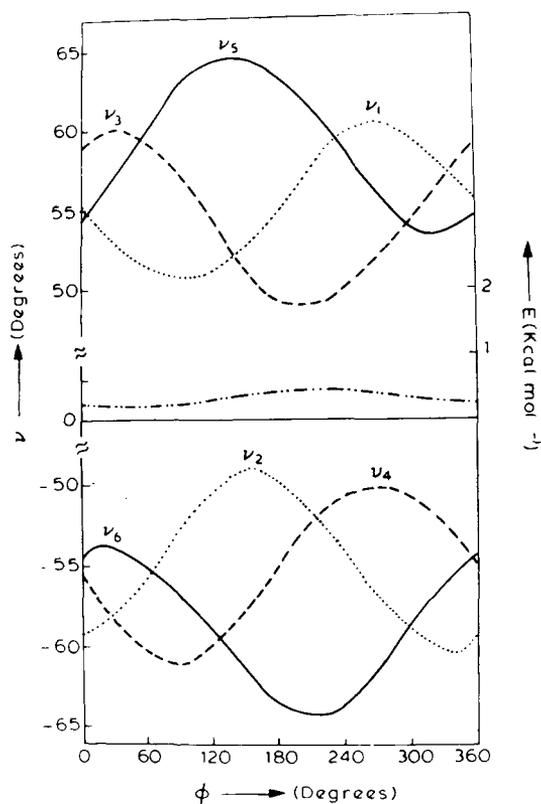


Fig. 6. Ring torsional angles ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , and ν_6 of α -D-glucopyranose are plotted against ϕ for $\theta = 5^\circ$. The torsional angles ν_1 - ν_6 are defined in Fig. 1. Variation of conformational energy E with ϕ is also indicated (---).

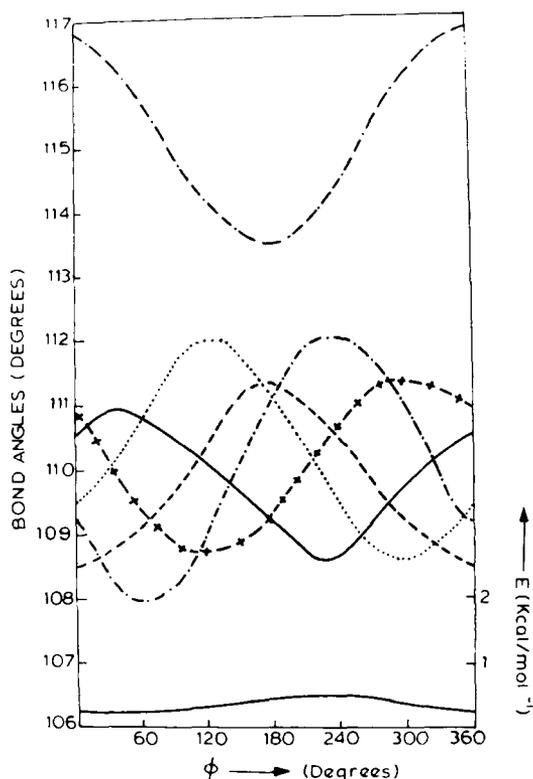


Fig. 7. Ring bond angles C5-O5-C1 (upper curve), O5-C1-C2 (—), C1-C2-C3 (---), C2-C3-C4 (---), C3-C4-C5 (---), and C4-C5-O5 (-+-) of α -D-glucopyranose are plotted against ϕ for $\theta = 5^\circ$. Variation of conformational energy with ϕ is also indicated by the solid line at the bottom of the figure.

The calculated ring torsional angles CCCC, OCCC, and CCOC for α -D-glucose at the global minimum are 55.3° , 56.0° , and 59.8° , respectively. Thus the theory not only predicts the qualitative behavior of these angles (CCCC < OCCC < CCOC), but also shows a good agreement with the average values (53.0, 55.8, and 61.7) obtained for the pyranose ring in solid state.²⁰ Thus justifies the use of average parameters obtained from crystal structure data as a first approximation in conformational studies on polysaccharides. However, calculations with flexible 4C_1 (D) chair conformation may offer a measure of refinement in comparing theory with the experiment, since the ring torsional angles can vary as much as 10° without much loss in energy.

A series of local maxima and minima (Figs. 2 and 3, and Tables I and II) corresponding to various boat and twist-boat conformations occur along $\theta \approx 90^\circ$. Their solvent accessibilities vary over a wide range. Among the flexible conformations for both α - and β -D-glucopyranoses (Figs. 4 and 5), the 1S_3 , 1S_5 , and 3S_5 twist-boats ($\theta = 90^\circ$, $\phi = 30^\circ$, 90° , and 150° , respectively) have low energies, which is in general agreement with the calculations

of Kildeby et al.²⁴ However, the 1S_5 conformation has high solvent accessibility, and hence it is the most favored among the boat and twist-boat conformations. It has about 5 kcal mol⁻¹ higher energy, as well as lower solvent accessibility, than the 4C_1 (D) chair conformation. Hence the possibility of the occurrence of α - or β -D-glucopyranoses in conformations other than the 4C_1 is highly unlikely.

The present study also indicates that the 1C_4 (D) conformation of these sugars has intermediate energy between 4C_1 (D) and boat or twist-boat conformations. This is in disagreement with the results of Brant¹⁴ that the boat and twistboats have energies intermediate between the 4C_1 (D) and 1C_4 (D) chairs. This discrepancy arises mainly due to the fact that the earlier results were based on ideal models, whereas in the present calculations, the energy was minimized with respect to all ring bond angles and ring torsional angles.

The half-chair conformations occur along $\theta \approx 55^\circ$ and $\theta \approx 130^\circ$. The energies of these conformations range from 10 to 17 kcal mol⁻¹ for α -D-glucose and 9 to 17 kcal mol⁻¹ for β -D-glucose. Some of these half-chairs have very high solvent accessibilities (Figs. 4 and 5). Hence the barrier height between the global and the local minima (about 11 kcal mol⁻¹ for both α - and β -D-glucoses) may be slightly lowered due to the favorable interactions with the solvent.

One of us (N.V.J.) thanks the Indian Institute of Science, Bangalore, for a fellowship. Partial financial support from D.S.T., Government of India is gratefully acknowledged.

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Received March 13, 1979

Accepted June 25, 1979