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MOLECULAR MODELING OF THE SOLUTION BEHAVIOR OF CELLULOSIC CHAINS

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Theoretical conformational analysis (Brant, 1976), together with the statistical mechanical theory of polymer chain configuration (Flory, 1974), provides the basis for an interpretation of polysaccharide solution behavior in terms of the chemist's fundamental structural parameters, i.e. bond lengths, valence angles and bond rotation angles. The statistical mechanical theory involves minimal mathematical approximation; uncertainties in the detailed features of the conformational energy surface are always the limiting factor in determining the accuracy of the predictions made using this approach (Brant, 1980). However, the importance for polysaccharide solution configuration of such questions as intramolecular hydrogen bonding, solvation and the range of sugar ring and linkage geometries accessible remains to be generally understood.

Despite these uncertainties, considerable information about the comparative solution configurations of a series of polysaccharides can be obtained, even when rather coarse approximations to the true conformational potential energy surfaces are employed (Brant, 1980; Rees & Scott, 1971; Brant & Burton, 1981; Burton & Brant, 1982). Perspective drawings in Figs 1–6 of representative solution configurations of several glucans illustrate the dramatic differences in configuration that can be recognized solely on the basis of *unrefined* conformational energy surfaces.

Confidence in a polysaccharide chain model can be established only when it has been refined to yield calculated values of a variety of observable properties which are found to be in agreement with experiment (Brant, 1976; Brant, 1980). The unperturbed dimensions of the polymer chain are among the most suitable parameters against which to compare theoretical and experimental results. Hydrodynamic and, especially, scattering measurements yield chain dimensions directly, and dimensions, because they are strictly geometric characteristics, are readily calculated from theory without resort to assumptions or approximations (Brant & Goebel, 1975). The temperature coefficient of any observable property can be particularly important because

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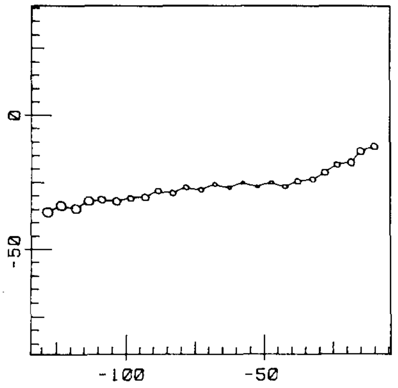

Fig. 1. Perspective drawing of a β-1,4-linked glucan (cellulose). Circles: glycosidic oxygens. Lines: virtual bonds spanning the sugar residues (not shown). Ordinate and abscissa scales measure distances in Ångstrom units. Drawing based on a polymer chain chosen as representative from a large Monte Carlo sample which was generated to be consistent with an unrefined conformational potential surface for the polymer (Jordan *et al.*, 1978).

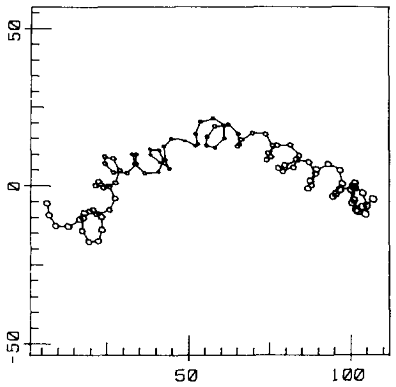

Fig. 2. Perspective drawing of an α-1,4-linked glucan. (See legend to Fig. 1.)

it provides information about the shapes of energy contours removed from the least energetic conformation (Brant, 1976; Brant, 1980).

When the chain model leading to the representative cellulosic configuration in Fig. 1 is tested for its capacity to reproduce the observed magnitude and temperature coefficient of the unperturbed dimensions of cellulose acetate (DS = 2·45) (Tanner & Berry, 1974), it is found to overestimate the chain dimensions by a factor of three and to underestimate the temperature coefficient by approximately the same factor

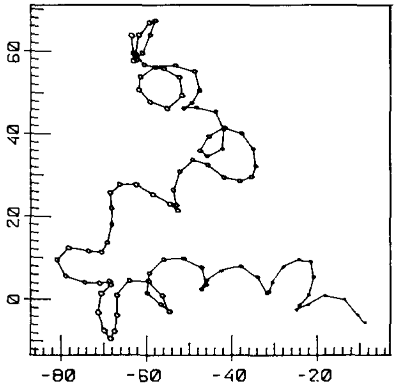

Fig. 3. Perspective drawing of a β-1,3-linked glucan. (See legend to Fig. 1.)

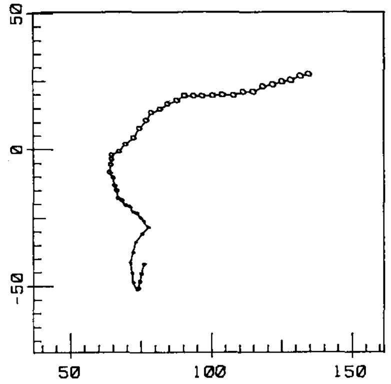

Fig. 4. Perspective drawing of an α-1,3-linked glucan. (See legend to Fig. 1.)

(Goebel *et al.*, 1976). Thus, an unrefined cellulosic chain model, based on the assumption of rigid C1 glucose ring geometry and standard estimates of the conformational energy for rotations about the glycosidic and aglycone bonds of the linkage region, suggests a much stiffer and more extended chain than observed experimentally. A satisfactory model requires an additional source of chain flexibility, which is strongly temperature dependent, to bring calculated values of the characteristic ratio C_∞ (Flory, 1974; Brant & Goebel, 1975) and its temperature coefficient $\mathrm{d}\ln C_\infty/\mathrm{d}T$ simultaneously into agreement with the experimental values (Tanner & Berry, 1974) of 36 and $-0{\cdot}0075$ degree^{-1}, respectively.

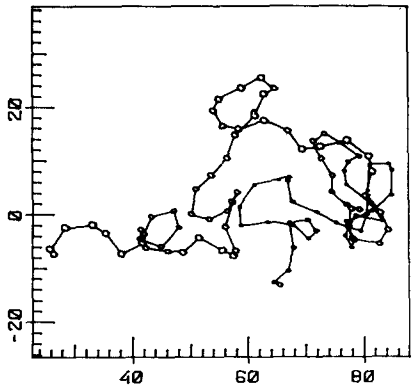

Fig. 5. Perspective drawing of a β-1,6-linked glucan. (See legend to Fig. 1.)

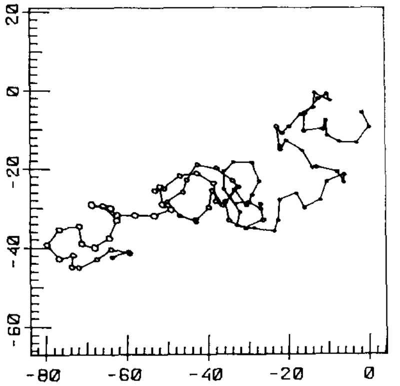

Fig. 6. Perspective drawing of an α-1,6-linked glucan. (See legend to Fig. 1.)

An exhaustive search for alternative models discloses that vibrational motions of the C1 glucose rings and the linkage region are alone insufficient as sources of additional temperature-dependent flexibility to bring theory and experiment into agreement (Goebel *et al.*, 1976; Brant & Hsu, 1982). The possibility of occasional conversion of the most stable C1 ring form into the alternative chair form 1C is also inadequate (Brant & Hsu, 1982). It is concluded that only if a small fraction of the glucose residues are allowed to exist at any instant in conformations of the flexible (boat–skew boat) class can the theory yield the experimentally observed values of C_∞ and $\mathrm{d}\ln C/\mathrm{d}T$. Figure 7 shows that for no energy $V^{\mathrm{s}}_{1\mathrm{C}}$ assigned to the 1C chair (relative to the energy of C1) does the theory yield simultaneously the observed C_∞ and $\mathrm{d}\ln C_\infty/\mathrm{d}T$ for chains constrained to contain only C1 and 1C glucose residues.

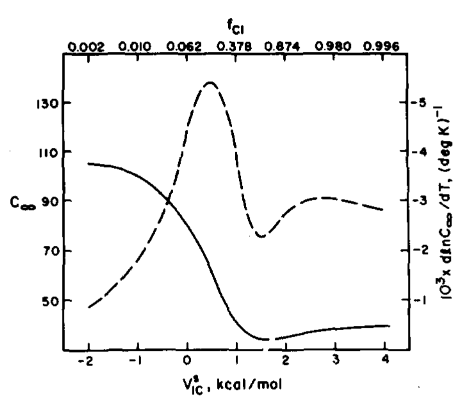

Fig. 7. Calculated magnitude (solid curve) and temperature coefficient (dashed curve) of the unperturbed dimensions as measured by the dimensionless characteristic ratio C_∞ (Flory, 1974; Brant & Goebel, 1975), plotted against the assumed energy, $V^{\mathrm{S}}_{1\mathrm{C}}$, of the 1C chair form relative to the C1 chair form for chains in which residues are restricted to the 1C and C1 forms. Chain is approximately pure 1C at the left margin and pure C1 at the right margin. The fraction, f_{C1}, of residues in the C1 form is shown at the top margin of the figure.

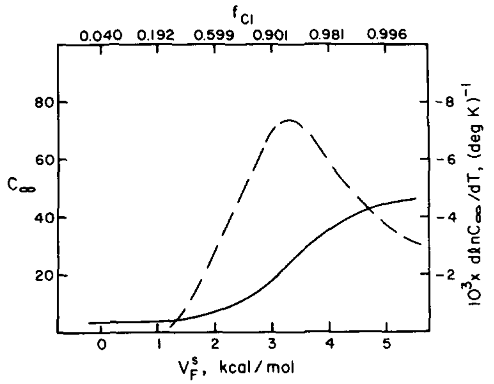

Fig. 8. The same as Fig. 7 except residues are restricted to either the C1 chair or the class of flexible (boat-skew boat) forms (Goebel *et al.*, 1976). Here $V^{\mathrm{S}}_{\mathrm{F}}$ is the energy assumed for the flexible forms relative to the C1 form. For $V^{\mathrm{S}}_{\mathrm{F}} \simeq 4{\cdot}0$ kcal/mol the calculated curves for C_∞ and $\mathrm{dln}\,C_\infty/\mathrm{d}T$ match the experimental results, and $f_{\mathrm{C1}} \simeq 0{\cdot}98$.

In Fig. 8 on on the other hand the experimental results are reproduced, using a model which allows both the C1 chair and flexible forms, for a relative energy $V^{\mathrm{S}}_{\mathrm{F}}$ of the flexible forms of about 4·0 kcal/mol. This value for $V^{\mathrm{S}}_{\mathrm{F}}$ appears realistic in the light of various estimates of the conformational energies of the glucose ring conformers (Brant & Hsu, 1982). Because of the favorable mutual energy contributions arising from interactions between the flexible form glucose residues and neighbouring residues in the chain, the relative self-energy $V_F^s \simeq 4{\cdot}0$ kcal/mol for the flexible forms is predicted by the model to generate about 2% of the glucose residues in the higher energy flexible forms (Goebel *et al.*, 1976). In a more realistic model, which would incorporate simultaneously all of the possible sources of temperature-dependent flexibility, it is anticipated that a smaller fraction of ring conformers in a form other than the most stable C1 chair would be required to fit the experimental data (Brant & Hsu, 1982).

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