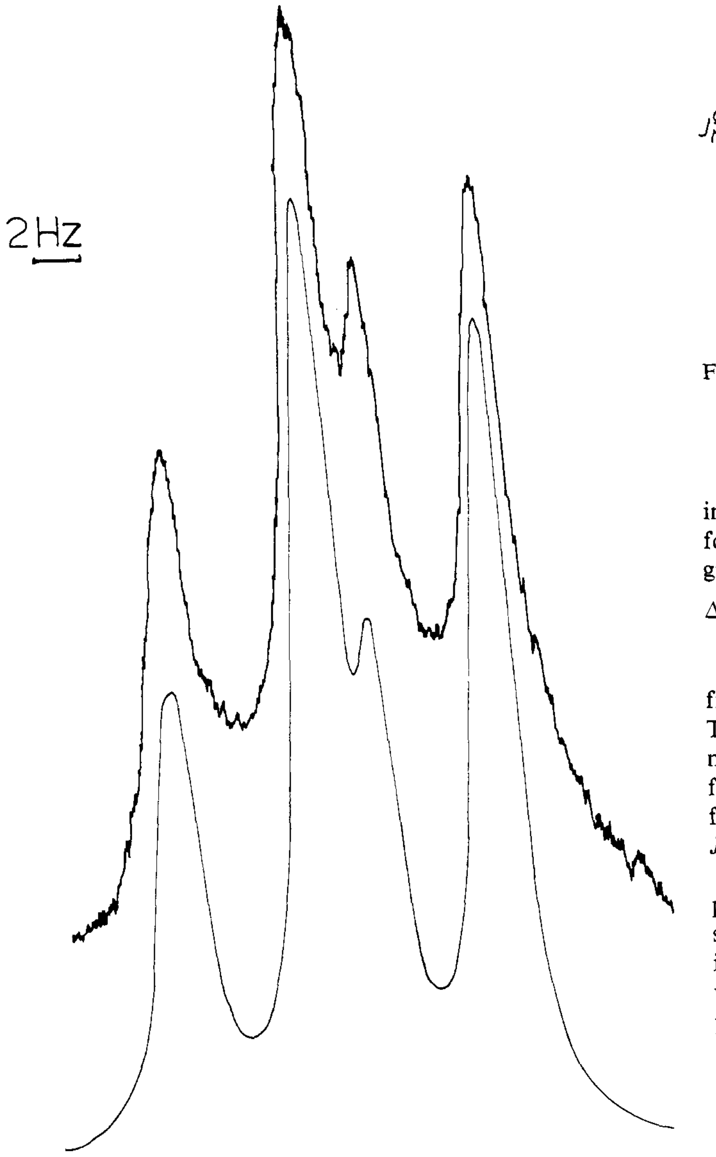

Figure 1. ^{13}C satellite pmr spectrum of poly(perdeuterioethylene-*co*-1-^{13}C-enriched ethylene) (upper trace, observed; lower trace, calculated).

$K = -26$ Hz,[2] $N = 14.8$ Hz, and different values of L, and, by comparison with the experimental spectrum, we got the best fit for $L = -2.9 \pm 0.3$ Hz. This gives $J = 5.95 \pm 0.16$ and $J' = 8.75 \pm 0.16$. Of course the sign of L is not given by this procedure.

Within the hypothesis of rotational isomerism, let us assume that the CH$_2$CH$_2$ fragment conformation is an equilibrium between the forms of Figure 2, where P indicates the polymer chain. The energy difference $\Delta E° = E_g° - E_t°$ is given by the expression

$$\Delta E° = RT \ln 2 \frac{n_t}{n_g} \tag{1}$$

where $E_t°$, $E_g°$, and n_t, n_g are the energies and molar fractions respectively, of the trans and gauche rotamers, and $n_t + n_g = 1$. The vicinal interproton coupling constants J and J' are the molar average of the individual couplings[3] (Figure 2). Superscripts indicate the orientation of the protons involved in the coupling, and subscripts indicate the conformers. Combining the relationships 1 and 2 or 1 and 3 gives, respectively:

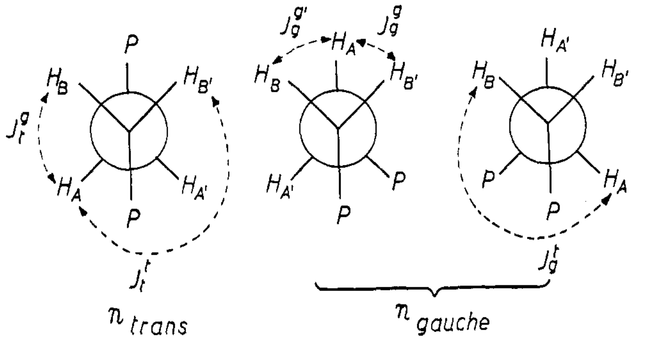

Figure 2. Rotational isomers of CH$_2$–CH$_2$ fragment.

$$J = n_t J_t^g + n_g(J_g^t + J_g^{g'})/2 \tag{2}$$

$$J' = n_t J_t^t + n_g J_g^g \tag{3}$$

$$\Delta E° = RT \ln 2\,(J' - J_g^g)/(J_t^t - J') = RT \ln\,(J_t^g + J_g^{g'} - 2J)/(J - J_t^g))$$

from which is possible to calculate $\Delta E°$ in two different ways. The individual conformer parameters were obtained from model compounds: 1,2-di-*tert*-butylethane[3] for the trans form and 1,1,4-tetradeuteriocyclohexane[2] for the gauche form: $J_t^g = 12.94$; $J_t^g = 4.30$; $J_g^t = J_{aa} = 13.12$; $J_g^g = J_{ae} = 3.65$; and $J_g^{g'} = J_{ee} = 2.96$.

The values of $\Delta E°$ obtained using the above relations and parameters were 0.70 ± 0.05 and 0.72 ± 0.15 kcal/mole, respectively, from J' and J. In view of the approximation used in obtaining the L parameter, we also have calculated the $\Delta E°$ value on the basis of the measurement of N only. For this purpose we recall[3] that the sum of the vicinal coupling is again a molar average of N_g and N_t where $N_t = J_t^g + J_t^t$ and

$$N = n_t N_t + n_g N_g \tag{4}$$

$N_g = [(J_g^t + J_g^{g'})/2] + J_g^g$. Combining relations 1 and 4 gives $\Delta E° = [RT \ln 2](N - N_g)/(N_t - N)$, from which a value of $\Delta E° = 0.68 \pm 0.06$ kcal/mole has been obtained, in fairly good agreement with the above values. Although this fact does not prove that the analysis is exact, it shows that it is not obviously wrong.

We can conclude that a reasonable value of $\Delta E°$ is 0.7 ± 0.15 kcal/mole where the quoted error is a combination of the experimental accuracy and of the approximation of taking the values of the individual J's from the model compounds.

The obtained value is a measure of the ratio of trans and gauche monomeric units of the polymer and, of course, does not give any information about the conformation of larger units. However, as far as we are aware, it is the first experimental determination of the average conformational energy of polyethylene.

L. Zetta,* G. Gatti
Istituto di Chimica delle Macromolecole, C.N.R.
20133 Milan, Italy

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Evidence for the Occurrence of Flexible Sugar Ring Conformers in Cellulosic Chains

Several workers have attempted recently to provide an interpretation of the observed unperturbed polymer coil dimensions of cellulose derivatives in terms of the structural characteristics of the cellulose chain skeleton.[1,2] Empirical conformational energy calculations[3] have been employed in conjunction with the statistical mechanical theory of polymer chain configuration[4] to calculate unperturbed chain dimensions for comparison with experimental results. Theoretical results that have been reported[1,2] fail to accord with the available experimental findings. The structural models for cellulosic chains employed to date[1,2] restrict the β-glucose residues of the cellulose backbone to the favored C1 chair conformation.[5] Chain flexibility is thereby assumed to arise solely from the torsional freedom about the two C–O bonds of the successive glycosidic bridges.

We wish to report here our progress in obtaining improved agreement between theoretical and experimental results for the unperturbed cellulosic coil dimensions using an alternative structural model for the chain skeleton. It is our further purpose to emphasize the importance in studies of the type described here of comparisons of theoretical and experimental estimates of the temperature dependence of observable properties. Only through such comparisons can the detailed contours of a proposed conformational energy surface for a representative chain segment be subjected to a significant test of physical reality. Consistency of a particular theoretical potential surface with the magnitude of an observed property and simultaneously with the temperature dependence of that property is a decidedly more rigorous criterion of suitability than is consistency with the magnitude of the property alone.

Restriction of the β-glucose residues in cellulosic chains to the C1 conformation in theoretical calculations of the characteristic ratio C_∞[4] yields, for reasonable values of the structural and conformational energy parameters, chain dimensions significantly larger than those observed.[6–10] Moreover, the theoretical temperature coefficient d ln $C_\infty/\mathrm{d}T$ is smaller in magnitude by a factor of 2 than the estimated experimental value,[6–10] *ca.* −0.006/°K. We have found it necessary, in order to explain satisfactorily the observed chain dimensions and their large negative temperature coefficient, to remove the restriction of β-glucose residues to the C1 conformation. Occasional occurrence of residues in conformations belonging to the flexible cycle of conformations of the boat–skew class serves to introduce dramatic changes in the direction of propagation of a chain composed predominantly of C1 β-glucose residues. The calculated chain dimensions are accordingly reduced. Simultaneous recognition of the sizable positive energy difference between the flexible conformers and the favored C1 form can account for the large negative temperature coefficient of C_∞, which is then understood to be a consequence of the resultant rapid increase in the occurrence of flexible conformers with increasing temperature. No other potential source of flexibility in the cellulose skeleton appears capable of yielding a sufficiently large temperature dependence; valence angle distortions and the possible occurrence in cellulose of sugar residues other than β-glucose have been considered explicitly. The possible origin in solvation effects of the large negative temperature coefficient of the coil dimensions of cellulosic chains has been debated.[2,7,11,12] The occurrence of large negative values for d ln $[\eta]/\mathrm{d}T$ for several cellulose derivatives in a variety of solvent systems[6–10] suggests strongly that the rapid decrease in chain dimensions with increasing temperature is not an effect of strong solvation, but originates instead in the structural features of the cellulose skeleton.

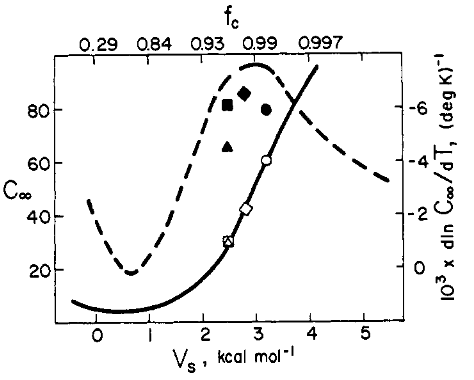

Figure 1. Theoretical characteristic ratio C_∞ (solid curve) and temperature coefficient d ln $C_\infty/\mathrm{d}T$ (broken curve) for cellulosic chain containing C1 and B1 conformers at 25° plotted *vs.* the self-energy V_s of the B1 form relative to the C1 form and *vs.* the fraction of C1 residues f_c. Experimental values of C_∞ (open symbols) and d ln $C_\infty/\mathrm{d}T$ (filled symbols): (◇, ◆) cellulose trinitrate in acetone,[6–8] (○, ●) cellulose trinitrate in ethyl acetate,[7,8] (△, ▲) hydroxyethylcellulose (MS = 1.67) in water,[9] (□, ■) sodium carboxymethylcellulose (DS = 1.0) in aqueous 0.2 *M* NaCl.[10]

Among the flexible conformations the boats B1, 3B, and B2 and the intervening skew forms 3B1 and 3B2 have fewer axial substituents than do the conformers 1B, B3, 2B, 1B3, and 2B3.[13,14] Pseudorotational interconversions among the former set may occur without traversing the conformational domain of the latter. The potential surface for pseudorotation of β-glucose is unknown, but axial substituents may be presumed to have a destabilizing influence.[14,15] On these grounds we exclude from consideration the 1C chair conformer which possesses five axial substituents. We report here the results of calculations in which β-glucose residues were permitted to adopt, in addition to the C1 conformation, either the B1 or the B2 conformation, the latter two being chosen as representative of the class of flexible forms of lower energy, *i.e.*, possessing fewer axial substituents. The probability of occurrence of the B form was assumed to depend upon the self-energy V_s of an isolated B β-glucose residue relative to an isolated C1 residue and upon the mutual interaction energy V_m of a pair of adjacent residues. The latter quantity was estimated for C1–C1, C1–B, B–C1, and B–B dimers using conventional empirical conformational energy calculations;[3] the self-energy of the B conformer was treated as an adjustable parameter of the calculation. Parameters of the skeletal geometry were obtained from X-ray crystal structure analyses of low molecular weight analogs. Details of the calculation and more extensive results will be presented elsewhere. It should be noted that introduction of the pos-

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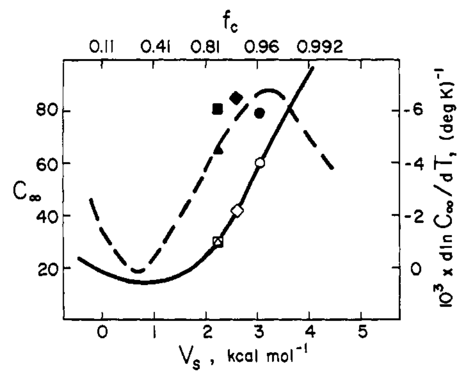

Figure 2. Same as Figure 1 but with theoretical curves for cellulosic chain containing C1 and B2 conformers.

sibility for alternative sugar ring conformers renders the chain unacceptable for statistical mechanical treatment in the independent unit approximation[16] employed in all polysaccharide treatments published to data.[1,2,16,17]

The results of the calculations appear in Figures 1 and 2, where C_∞ and d ln C_∞/dT are plotted *vs.* V_s and the fraction of C1 residues f_c. Representative experimental results for several cellulose derivatives are presented in Figures 1 and 2 for comparison; the measured quantities are plotted at values of V_s which cause the theoretical and estimated experimental values of C_∞ to coincide. The experimental estimates have been drawn from studies [6–10] which provide information concerning both C_∞ and its temperature dependence. Theoretical estimates of d ln C_∞/dT agree well with the observed values when either B1 or B2 is chosen to represent the class of flexible conformers. Correspondence of theory and experiment for C_∞ occurs for $V_s \simeq 3$ kcal mol^{-1} and at a fraction of flexible conformers given by $1 - f_c$. This fraction significantly exceeds the value 0.006 expected solely on the basis of the magnitude of V_s. Hence, the flexible form is stabilized relative to the C1 form by the mutual interactions which occur between neighboring residues in the polymer chain; examination of this effect discloses that both energetic and entropic factors contribute to the enhanced stability of the flexible forms of β-glucose within the polysaccharide chain. For cellulosic chains this mutual free energy effect evidently works to moderate the instability of the flexible conformers that is a consequence of their substantial self-energy relative to the C1 chair. Asymptotic values of C_∞ and d ln C_∞/dT calculated for large V_s, and therefore corresponding to exclusion of B residues, are 112 and -0.0029/°K, respectively.

A more realistic model for cellulosic chains than that used to calculate the results presented here has been developed. It allows for the occurrence of a diversity of possible flexible conformers and, hence, recognizes the significant self-entropy contribution to their stability relative to the C1 chair form. Preliminary calculations indicate that satisfactory agreement of theoretical and experimental results can be achieved for significantly larger, and therefore more satisfying, values of the self-energy of the flexible forms.

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David A. Brant,* Kenneth D. Goebel

Department of Chemistry, University of California
Irvine, California 92664

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