

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228127892>

Relaxed potential energy surfaces of maltose

ARTICLE *in* BIOPOLYMERS · FEBRUARY 1989

Impact Factor: 2.39 · DOI: 10.1002/bip.360280211

CITATIONS

68

READS

11

4 AUTHORS, INCLUDING:



Alain Buléon

French National Institute for Agricultural Research

181 PUBLICATIONS 7,459 CITATIONS

[SEE PROFILE](#)



Serge Perez

French National Centre for Scientific Research - Grenoble Universit...

296 PUBLICATIONS 8,185 CITATIONS

[SEE PROFILE](#)

Relaxed Potential Energy Surfaces of Maltose*

VINH TRAN, ALAIN BULEON,, *Laboratoire de Physicochimie des Macromolécules, I.N.R.A., B.P. 527, Nantes, Cédex F-44026*; ANNE IMBERTY, *Centre de Recherches sur les Macromolécules Végétales, C.N.R.S., B.P. 53X, Grenoble Cédex, F-38041*; and SERGE PEREZ, *Laboratoire de Physicochimie des Macromolécules, I.N.R.A., B.P. 527, Nantes, Cédex, F-44026, France*

Synopsis

Experimentally observed solution conformations of carbohydrate molecules might correspond to a dynamical average of several interconverting conformers in solution. In order to understand and describe more precisely molecular flexibility and motions, new computational routes have to be envisaged. Compared to conventional approaches where sugar residues are treated as rigid, the optimization of all the internal parameters—i.e., bond angles, valence angles, and all torsional angles—is an important step toward more realistic information. Here we report the calculations of potential energy surfaces where all the internal coordinates of the molecules were “relaxed” and minimized through an extensive molecular mechanics scheme. For this work, a prototypical carbohydrate system, the disaccharide α -maltose, was selected. The inclusion of the relaxed principle into conformational description of maltose does not generally alter the overall shape of the allowed low-energy regions, or the position of the local minima. However, flexibility within the ring plays a crucial role. Its principle effect is the lowering of energy barriers to conformational transitions about the glycosidic bonds, permitting pathways among the low-energy minima. This occurs with retaining the overall 4C_1 conformation of the glucose residues. The torsional angles corresponding to the orientations of the hydroxyl groups, especially the primary hydroxyl ones, display stable arrangements separated by energy barriers. They create subpopulations of stable conformers and it has not been possible to take into consideration interconversion of one subpopulation to another one. A “synthetic” relaxed potential energy surface is proposed, which can provide a realistic starting base for further investigation of solution behavior of dynamic simulations.

INTRODUCTION

In order to correlate the chemical structure of biopolymers with their physical and biological properties, accurate representations of the conformational space of oligomeric units have to be sought.¹ Among other structurally oriented methods, conformational energy calculations have been extensively used to characterize simple carbohydrates and polysaccharides.² Considerable successes were achieved despite the fact that relatively simplistic concepts were used. Monosaccharides are the simplest building units in carbohydrate-containing molecules. Accumulations of structural information derived from crystal structure elucidations of oligosaccharides have justified the assumption that, in general, the internal parameters could be divided into rigid monomeric groups and flexible glycosidic linkages. Also, because of the spatial separation of these “rigid” entities, which are interposed between the flexible linkages, there is an almost total independence between successive sets of

*Please note it was the intent of the authors that this article be read in conjunction with and prior to the article “Conformational Analysis and Molecular Dynamics Simulations of Maltose” by S. N. Ha, L. J. Madsen, and J. W. Brady, *Biopolymers*, Vol. 27, No. 12, pp. 1927–1952 (1988).

glycosidic torsional angles.³ For these reasons, the assessment of preferred conformations is usually performed on disaccharides entities, by assessing, using molecular mechanics calculations, the space that is available for rotations about the glycosidic junction.⁴ In addition to the conventional use of these kinds of map in the elucidation of solid state conformations of oligo- and polysaccharides, one can expect to be in a position to understand and describe more precisely molecular flexibility and motions. Surveys of known carbohydrate crystal structures have revealed considerable alterations occurring in ring geometry.^{5,6} Compared to these approaches where carbohydrate entities are treated as rigid or semirigid, the optimization of all the internal parameters—i.e., bond lengths, valence angles, and all torsional angles—is an important step toward more realistic information.^{7,8} Moreover, experimentally observed solution conformations of disaccharide molecules might correspond to a dynamical average of several interconverting conformers in equilibrium.⁹ There is therefore a need to investigate how carbohydrate flexibility can be taken into account.

In the case of amylose, which has received more attention than any other polysaccharide except perhaps cellulose, accumulation of crystalline data on several linear and cyclic maltodextrins has shown that several conformations can occur.¹⁰ They provide a set of experimental data that should ideally be reproduced by energy calculations.^{11,12} For this purpose, the disaccharide maltose, which is the fundamental repeat unit of amylose, has been the subject of a number of conformational energy investigations.¹¹⁻¹⁸ Here we report the calculations of potential energy surfaces where all the internal coordinates of the molecules were “relaxed” and minimized through an extensive molecular mechanics scheme. An accompanying paper¹⁹ presents the results of calculations of similar surfaces using an alternative molecular mechanics computation.

METHODS

Nomenclature

The recommendations and symbols proposed by the Commission on Nomenclature^{20,21} are used throughout this paper. A schematic drawing of the maltose disaccharide, along with the labeling of the atoms, is given in Fig. 1. The relative orientation of a pair of contiguous glucose residues is described by a set of two torsional angles:

$$\Phi = O(5)-C(1)-O(1)-C(4') \text{ or } \Phi^H = H(1)-C(1)-O(1)-C(4')$$

$$\Psi = C(1)-O(1)-C(4')-C(5') \text{ or } \Psi^H = C(1)-O(1)-C(4')-H(4')$$

The orientation of the primary hydroxyl groups (Ω) is referred to as either *gauche-trans* (GT), *gauche-gauche* (GG), or *trans-gauche* (TG).²² In this terminology, the torsion angle O(5)-C(5)-C(6)-O(6) is stated first, and the torsion angle C(4)-C(5)-C(6)-O(6) second. The orientation of the hydroxylic hydrogen atoms is described by X(i):H-O(i)-O(i)-C(i)-H(i).

Protocol

In a first step, the conformational energy was evaluated by including the partitioned contributions arising from van der Waals interactions, torsional

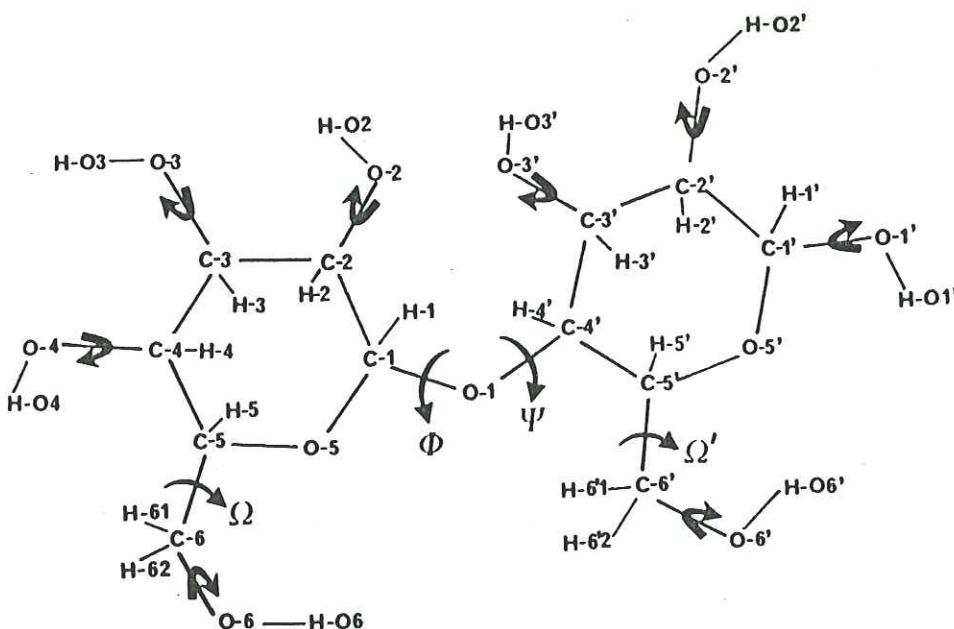


Fig. 1. Schematic representation of the maltose molecule, along with the labeling of the atoms and the torsional angles of interest.

and exo-anomeric potential.⁷ The starting geometry for the disaccharide was taken from standard glucose geometry; the coordinates of the hydrogen atoms were determined using a C-H bond vector of 1.10 Å, and a bond vector appropriately set to the C-C and C-O vectors. Hydroxylic hydrogen atoms were not considered. At this stage, both the ring geometry and pendent groups were left invariant; only the glycosidic torsional angles Φ, Ψ were allowed to vary at intervals of 5°, over the whole angular range from -180° to 180°. With respect to the global energy minimum, the iso-energy contours were drawn by interpolation at 1 kcal/mol intervals; the 10 kcal/mol contour was selected as the outer limit. Such a map, which will be referred to as the "rigid potential energy surface," is shown in Fig. 2.

In a second step, the low-energy portion of the rigid potential energy surface was divided into a 10° by 10° grid. Each conformer was submitted to energy optimization through the MM2CARB method.⁷ MM2CARB is the MM2 force-field program²⁴ (Quantum Chemistry Program Exchange no. 395) modified with the acetal-segment parameters of Jeffrey and Taylor.²⁵ As already demonstrated, these parameters, along with the introduction of lone pairs on the oxygen atoms, especially within the acetal sequence C(5)-O(5)-C(1)-O(1)-C(x), reproduce, in an adequate fashion, the dependence of geometry upon variations of glycosidic torsion angles, as observed in crystalline carbohydrate structures.⁷ The potential energy function used in these studies was a typical MM2-type molecular mechanics energy function:

$$E_{\text{conf}} = E_{\text{streh}} + E_{\text{bend}} + E_{\text{streh-bend}} + E_{\text{tor}} + E_{\text{dip}} + E_{\text{vdw}}$$

All these calculations were performed in vacuo since neither an explicit additional hydrogen-bond term nor a partial charge increase was added. The original DRIVER option of MM2 permits 1 or 2 torsion angles to be changed in increments while other structural details are optimized at each set. For the starting geometry of each new Φ, Ψ combination, the dihedral driver takes the optimized coordinates of the preceding conformation. Such a computing

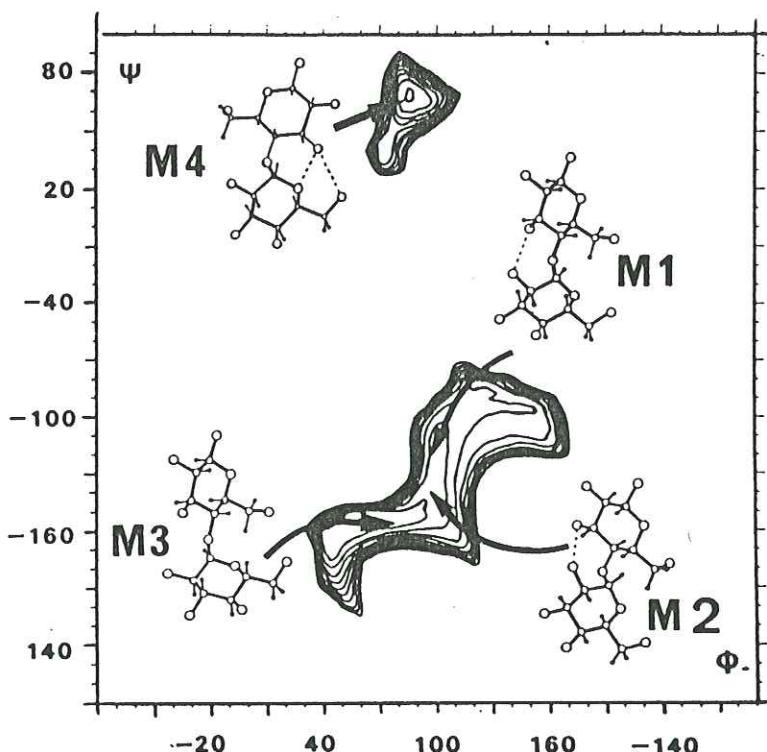


Fig. 2. Rigid potential energy surface of maltose, along with the representation of the four stable conformers (M1, M2, M3, and M4).

scheme is sound, providing the magnitude of the increment is not too large. Since the present problem deals with a minimum of 4 essential torsion angles ($\Phi, \Psi, \Omega, \Omega'$), we have extended the DRIVER option to 4 torsional angles. In practice, the above-mentioned scheme cannot be applied to Ω and Ω' since the increment to go from one stable conformation to another one is 120° . The extension of the DRIVER option was used: (1) to increment Φ, Ψ angles and (2) to maintain a specific orientation about Ω and Ω' . This explains why separate relaxed (Φ, Ψ) potential energy surfaces have to be computed.

Within an hyperdimensional space there is no assurance that any minimization algorithm based upon the derivative of the energy function yields the lowest conformation. Actually, such an algorithm will converge toward the closest minimum not separated from the starting point by any energy barrier. There is, therefore, a need to identify essential parameters other than the glycosidic torsional angles. There is ample evidence in the carbohydrate literature that the conformation of the primary hydroxyl groups may play a role in the intramolecular energy. Consequently, they were considered and given, in a systematic fashion, their low-energy orientations. As there are three conformational subpopulations, i.e., GG, GT, and TG,²² nine possible combinations have to be considered for this disaccharide. However, according to crystallographic considerations, we have excluded all the cases involving a TG orientation of the primary hydroxyl group at the reducing glucose residue. Such a conformation would correspond to an unstable 1–3 type of interaction,²² or Hassel–Ottar effect,²⁶ which can only occur with an intramolecular hydrogen bond involving the glycosidic oxygen atom. Such a scheme has never been detected in the solid state. A similar case cannot be made for eliminating the TG position for the nonreducing residue. Thus, six exocyclic conformations

(GG-GG, GG-GT, GT-GG, GT-GT, TG-GG, and TG-GT) were considered. In this terminology, the orientation of the primary exocyclic group of the nonreducing residue is stated first. Therefore, six partial "relaxed" Φ, Ψ potential energy surfaces were computed.

Despite the high functionality provided by the new DRIVER option, it is not possible to compute the different potential energy surfaces in a single computer run. It rapidly became obvious that the starting orientations of the hydroxylic hydrogen atoms were inducing false energy minima. Because of the high number of such conformational parameters [$X(i)$] along with their almost free rotation, it is impossible to claim that the lowest minimized energy has been found for a given set of Φ, Ψ and Ω, Ω' . For each map, we tried to minimize such effects by manually testing different starting orientations of the dihedral angles $X(6)$ and $X(6')$ and checking the continuity of these values.

All the calculations were performed on the PRIME 750 computer of the I.N.R.A. Research Centre in Nantes. The present investigation required about 450 h of cpu time. The molecular drawings were realized with the program PITMOS.²⁶ The graphic software package DISSPLA (Computer Associates, San Diego, CA) was used to draw the two-dimensional and three-dimensional iso-energy contours.

RESULTS AND DISCUSSION

In Fig. 3, the relaxed isoenergy maps corresponding to the six conformational types investigated are shown. Contours are in 1 kcal/mol intervals from 1.0 to 8.0 kcal/mol above the absolute energy minimum found for $\Phi = 60^\circ$, $\Psi = -160^\circ$, on the TG-GG map. The similarities between the low-energy domains, i.e., localization of the energy minima along with the general features of the external contours, is striking. This corroborates previous statements¹⁶ about the minor role played by the orientation of the primary hydroxyl groups on the low-energy domain. However, it must be emphasized that each map is associated with a specific type of conformation dictated by the starting orientation of the primary hydroxyl groups. It was also noticed that once the constraints on Ω and Ω' were relieved, none of the minimizations performed yield another type of orientation. This was observed regardless of whether the (Φ, Ψ) conformations belong to a low-energy domain or not. This in a sense corroborates our choice of Ω and Ω' as fundamental parameters in addition to the glycosidic angles. It is also clear from Fig. 3 that on these relaxed maps, minor differences appear such as the magnitude of the relative energies associated with local minima. These are summarized in Table I. From all these results, it is possible to detect six local minima, which occur in almost all the potential energy surfaces. They are designated as A, B, C, D, E, and F, and can be visualized on the final map (Fig. 5). For each of these local minima, we have selected the combination of Ω and Ω' yielding the lowest energy. The corresponding molecular representations are displayed in Fig. 4. Further energy minimizations were performed, relieving the constraints on Φ , Ψ , Ω , and Ω' . It was found that whereas the energy decreased by 0.1 to 0.5 kcal/mol, the final orientations about the torsional angles remained, within a few degrees, identical to the starting values.

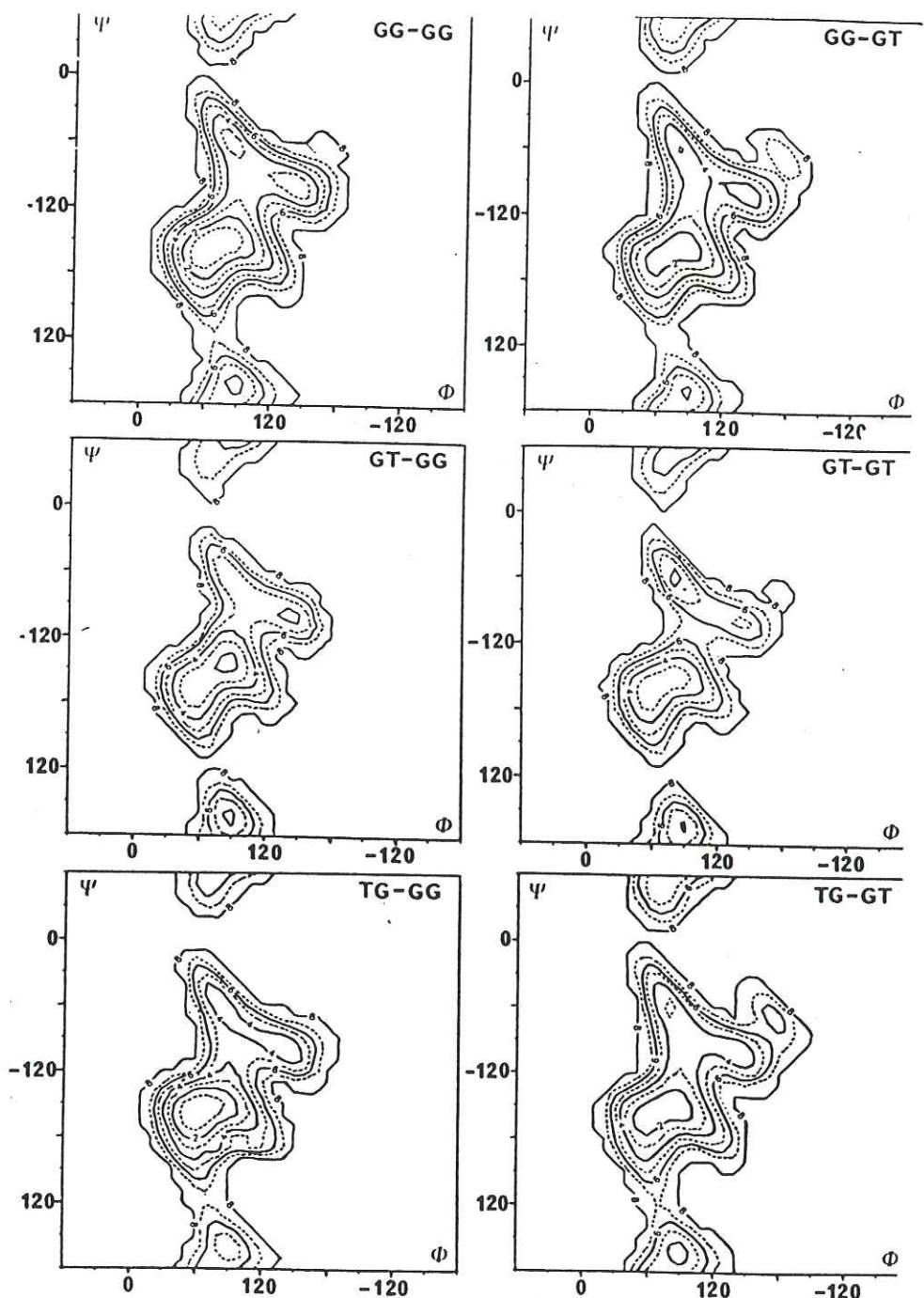


Fig. 3. Relaxed potential energy surfaces of maltose, as a function of the exo-cyclic conformations. Contours are in 1 kcal/mol intervals from 1.0 to 8.0 kcal above the absolute energy minimum found for $\Phi = 60^\circ$, $\Psi = -160^\circ$, on the TG-GG map.

It is not surprising to observe that the essential features of the rigid map are preserved in each of the relaxed maps. Such a consistent description of the low-energy conformations of maltose is reached despite the fact that potential energy functions are partitioned differently in the rigid and relaxed approaches. The four families of stable (Φ, Ψ) conformations, designated as M1, M2, M3, and M4 in the rigid potential energy surface, occur in rather steep energy wells. In all the relaxed potential energy surfaces, they occur in more extended areas. Such an extension is an expected consequence of the relaxation. Conformers M1, M2, and M3 correspond closely to conformations found

TABLE I
Summary of the Φ and Ψ Locations of the Six Local Minima (A, B, C, D, E, and F) as a Function of the Type that is Defined by the Orientations of the Primary Hydroxyl Groups.^a

Type	A	B	C	D	E	F
GG-GG	(60, -160)	(80, -150)	(140, -100)	(80, -60)	(90, 80)	(70, 50)
ΔE	0.15	0.20	2.30	2.56	3.48	4.64
GG-GT	(60, -160)	(80, -150)	(140, -100)	(80, -60)	(90, 80)	(70, 50)
ΔE	1.47	1.25	3.37	2.83	3.74	4.26
GT-GG	(60, -170)	(80, -150)	(140, -100)	(80, -60)	(90, 80)	(70, 50)
ΔE	2.16	1.60	3.62	4.22	3.69	6.02
GT-GT	(60, -160)	(80, -150)	(140, -100)	(80, -60)	(90, 80)	(70, 50)
ΔE	2.33	2.44	4.73	3.51	3.92	5.42
TG-GG	(60, -160)	(80, -150)	(140, -100)	(80, -60)	(90, 80)	(70, 50)
ΔE	0.0	0.57	3.09	3.21	4.22	5.39
TG-GT	(60, -160)	(80, -150)	(140, -100)	(80, -60)	(90, 80)	(70, 50)
ΔE	1.27	1.17	3.06	2.64	3.42	4.06

^aThe corresponding relative energies are indicated in Kcal/mol.

in the solid state in cyclic or linear maltodextrins¹⁰ as well as in amylose polymorphs.^{28,29} In both the M1 and M2 types, intramolecular hydrogen bonds ($O(2) \cdots O(3')$) between contiguous glucoses are involved. Apparently, the omission of such a stabilizing feature in the present scheme of calculation does not prevent the occurrence of these energy minima. It may, however, explain some shifts in Φ, Ψ between the M1 conformation and the nearest (C) local minimum. Nevertheless, within the relaxed potential energy surfaces, M1 and M2 belong to the central low-energy zone. As for the M3 conformation, it corresponds precisely to the B local minimum, which is located in the lowest zone (1 kcal/mol contour). Actually, this zone also includes the lowest conformation (A) that corresponds to one arrangement about the (1 → 4)glycosidic linkage recently found in the crystal structure of a maltohexaoside molecule.³⁰ Similarly, M4 occurs in an energy well that shows two local energy minima (E and F) and corresponds precisely to E. The second local minimum F was already visible in the rigid map (Fig. 2). In the central low-energy part of the relaxed potential energy surfaces (4 kcal/mol contour) a new feature is detected. A low-energy domain is found centered about a local minimum (D). Within this domain, the conformation of the glucose residues is somewhat altered, but it still remains in the 4C_1 form (Fig. 5). A net consequence of the "relaxation" method is that introducing flexibility in the sugar ring geometry and conformation allows for more favorable situations to be reached. In the maltose case, this flexibility generates a nonuniform enlargement of the low-energy domains. Whereas there is no noticeable enlargement in the Φ dimension, the expansion observed along Ψ is such that the two distinct regions calculated with the rigid scheme (Fig. 2) are now fused (Fig. 3). There may exist two conformational pathways that allow all the low-energy minima to be contiguous. In another work, conformational behavior of maltose in different solvents was attempted through molecular modeling and high-resolution nmr spectroscopy.³¹ It was found that the contribution of the M4 type of conformation had to be taken into account, despite the fact that the two

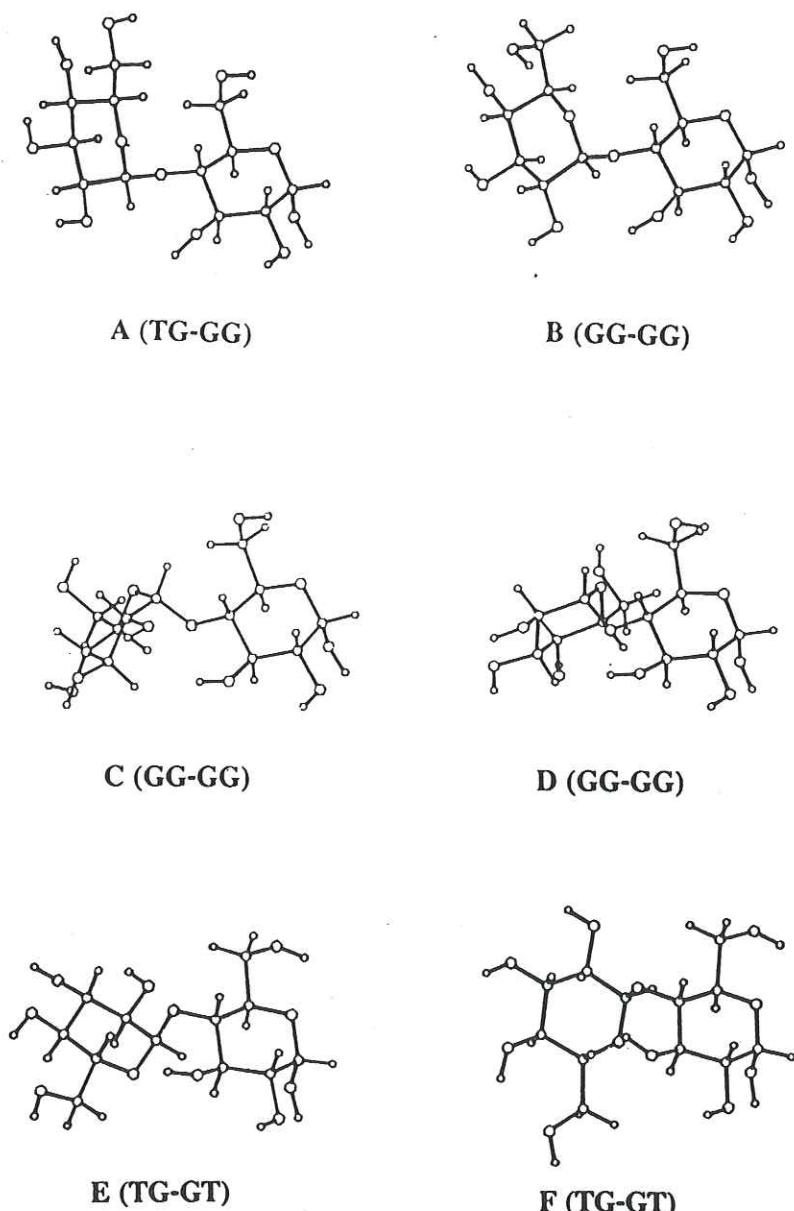


Fig. 4. Molecular representations of the stable conformations of maltose derived from the six local minima identified in the relaxed potential energy surfaces.

distinct regions in (Φ, Ψ) were not contiguous in "rigid" potential energy surface. The information provided by the relaxed surfaces indicate that the lowest barrier is about 7 kcal/mol higher than the most probable conformation. Although such a gap is important according to the Boltzmann principle, it yields some insight into the transitional state. It provides the missing link in understanding how low-energy conformations of maltose in solution can interchange. This clearly supports recent statements⁹ about the possibility that experimentally observed solution conformations of some disaccharides might be the dynamical average of several interconverting conformers in dynamic equilibrium.

One of the initial goals of this study was to produce a single relaxed (Φ, Ψ) potential energy surface that could be used for further modeling of maltose conformational analysis. This surface could be tested against those spectroscopic data that are particularly dependent on conformational changes about the glycosidic linkage. The synthesis of the six partial relaxed potential energy

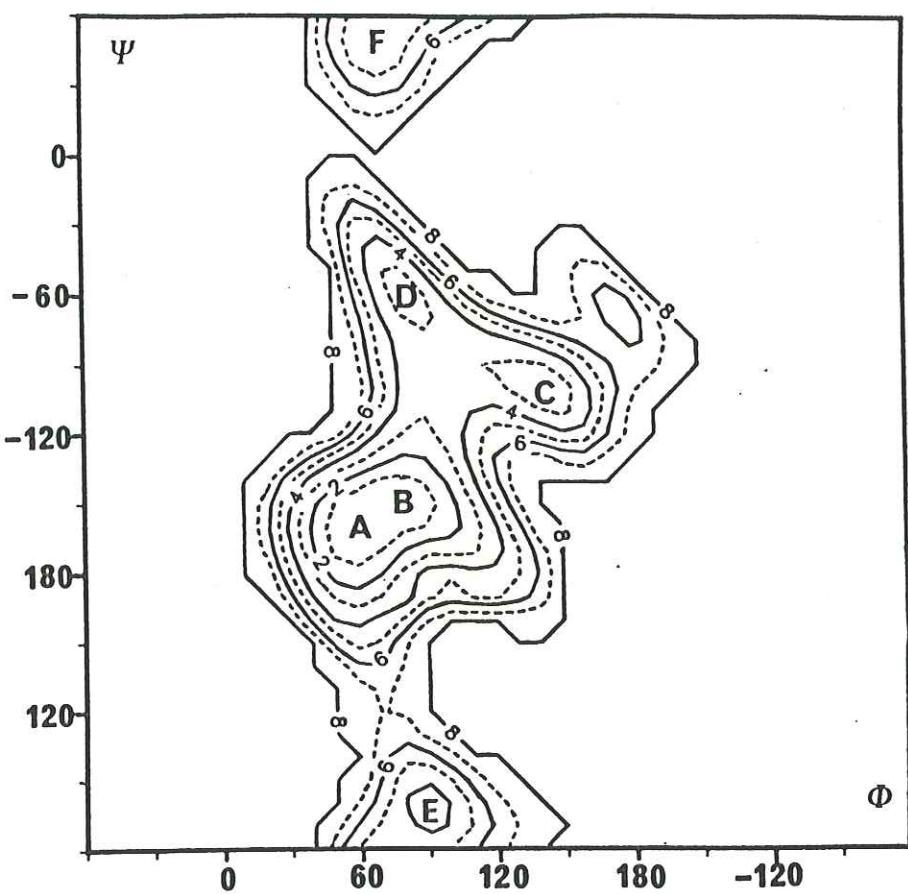


Fig. 5. Global relaxed potential energy surface of maltose synthesized from the six partial maps of Fig. 4. Each point of the surface corresponds to the conformation of lowest energy found among all those examined. The Φ, Ψ locations corresponding to the stable conformers A, B, C, D, E, and F are indicated. Contours are in 1 kcal/mol intervals from 1 to 8 kcal above the energy minimum.

surfaces was performed (Fig. 5). In this map each point of the grid corresponds to the conformation of lowest energy found among all those examined. As for the six local minima, they correspond to only three orientation types: TG-GG, TG-GT, and GG-GG. All partial relaxed potential energy surfaces, except the GT-GG one, contribute to the "synthetic" map. The use of such a synthetic potential energy surface must be done very carefully, because it represents a two-dimensional projection of a far more complex hyperspace. This reduction obviously suffers severe approximations in spite of the methodological approach chosen. In such a synthetic map the energy differences that go from one molecular type to another one are erased.

The contribution of the different energy terms to the total magnitude of the local minima was investigated. Among the main contributors to the energy are bending, stretch-bending, torsional, and to a certain extent, dipolar terms. Surprisingly, the contribution of the van der Waals term (repulsion and attractive components) is relatively flat. The repulsive component of these terms is only predominant in delineating the external contours, and introducing flexibility of the internal parameters cannot overcome steric conflicts. Within the low-energy section, these contributions are no longer important. As shown in Fig. 6, the energy variations for this term are always less than 1 kcal/mol, even in the two possible conformational transition pathways.

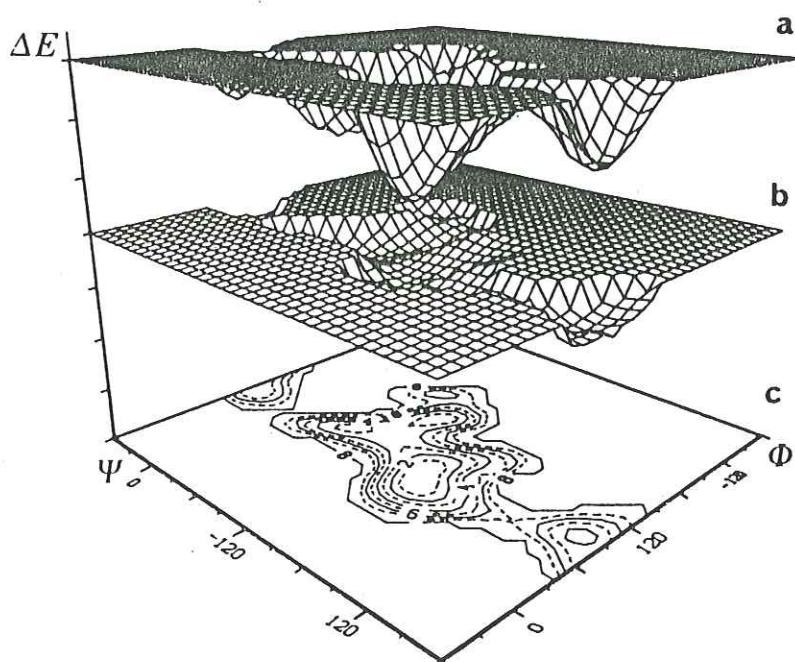


Fig. 6. (a) Perspective drawing of the three-dimensional shape of the global relaxed potential energy well of maltose for the full angular range of Φ and Ψ . The projected surface (c) is identical to that in Fig. 5. (b) Contribution of the van der Waals interactions to the overall relaxed potential energy well.

The accompanying paper¹⁹ presents a related study of the characterization of the static conformational behavior of the $\alpha(1-4)$ -linkage in the β -maltose case. In order to do so, an “adiabatic” map using CHARMM-type molecular mechanics calculations³² was produced. The parameters used were those selected for use with glucose,³³ with the glycosidic linkage treated the same as the ring C-O-C linkages. Therefore, the contribution of the exo-anomeric effect is neglected. The authors explicitly take into account the stabilizing effect of intramolecular hydrogen bonding by increasing the partial electrostatic atomic charges. As a net result, the relative orientations about X torsional angles has to be considered in a vacuum calculation. Despite these differences, the general agreement reached in both studies is satisfying. The only differences lie in the predominance of the TG conformation of the primary hydroxyl group of the nonreducing residue in their adiabatic map, along with the prediction of a local minima centered about $\Phi = 164^\circ$ and $\Psi = 104^\circ$. Using our MM2CARB potential, we have explored this conformation, which was found to be about 12 kcal/mol higher than our lowest minimum. Subsequent analysis of the contributions to the energy revealed that the dipolar terms were important in the establishment of such a conformation. Therefore, it may be that the increase in partial charges significantly contribute to the existence of such a local minimum. The same argument may be used to explain the predominance of the TG conformation for the nonreducing residue in their calculations.

CONCLUSIONS

The present work underlines the importance of relaxing all internal coordinates in predicting low-energy conformations. It represents a contribution toward the construction of more realistic potential energy surfaces. These

results demonstrate the adequacy of both the MM2 energy functions and MM2CARB constants when applied to carbohydrate molecules. The overall similarity of the results obtained with CHARMM potentials establishes credibility of both programs and strategies. Indeed, these calculations can reproduce experimentally characterized conformations. Other structural features are revealed, such as the location of new energy minima and the continuity within the low-energy domains. With respect to rigid modeling studies, these results indicate that flexible residues are a necessity for anything but locating minima.

When the relaxation principle is applied, a two-dimensional representation may not be adequate and suitable to display all conformational details. In the case of the maltose molecule, one must differentiate two kinds of geometrical parameters. On the one hand, relaxing the internal coordinates of the pyranose rings reflects the flexibility of these moieties, which is an essential feature to be considered for a realistic modeling. At this stage, the Φ, Ψ representation is reasonable. The enlargements of the low-energy domains are probably the most noticeable consequence. There exist conformational pathways that allow all the low-energy minima to interconvert; this occurs while maintaining the overall 4C_1 conformation of the glucose residues. In the rigid approximation, the repulsive terms of the van der Waals contributions dominate while the introduction of flexibility decreases such drastic effects since most of the steric conflicts are relieved through small variations of atomic positions. On the other hand, the torsional angles corresponding to the orientations of the hydroxyl groups, especially the primary hydroxyl ones, display stable arrangements separated by energy barriers. From these, false minima originate, which cannot be discarded by minimization algorithms. Such a drawback, along with the lack of accurate knowledge about the occurrence of intramolecular hydrogen bonds in solution, were partially overcome by considering six subpopulations. Each of these cases was thoroughly investigated. Within such a protocol, it is not possible to take into consideration interconversion of one subpopulation to another one even though it occurs. Therefore, the use of the synthetic relaxed potential energy surface as an "adiabatic" map may not be straightforward. Nevertheless, it provides a realistic starting base for further investigation of solution behavior or dynamic simulations.

The authors wish to thank M. M. Delage and B. Vigny for technical assistance, and J. Brady, L. Madsen, and S. Ha for helpful discussions. The help of J. L. Morat to implement the DISSPLA package is gratefully acknowledged.

References

1. Brant, D. A. (1976) *Quart. Rev. Biophys.* **9**, 527–596.
2. Rees, D. A. & Smith, P. J. C. (1970) *J. Chem. Soc. Perkin II*, 836–840.
3. Gagnaire, D., Pérez, S. & Tran, V. (1982) *Carbohydr. Polym.* **2** 171–191.
4. Rao, V. S. R., Sundararajan, P. R., Ramakrishnan, C. & Ramachandran, G. N. (1967) in *Conformation in Biopolymers*, Vol. 2, Ramachandran, G. N., Ed., Academic Press, London, pp. 721–737.
5. French, A. D. & Murphy, V. G. (1973) *Carbohydr. Res.* **27**, 391–406.
6. French, A. D. & Murphy, V. G. (1977) *Polymer* **18**, 489–494.
7. Tvaroska, I. & Pérez, S. (1986) *Carbohydr. Res.* **149**, 389–410.
8. Jimenez-Barbero, J., Noble, O., Pfeffer, C. & Pérez, S. *New J. Chem.*, in press.
9. Cumming, D. A. & Carver, J. P. (1987) *Biochemistry* **26**, 6664–6676.

10. Pangborn, W., Langs, D. & Pérez, S. (1985) *Int. J. Biol. Macromol.* **7**, 363-369.
11. Jordan, R. C., Brant, D. A. & Cesaro, A. (1978) *Biopolymers* **17**, 2617-2632.
12. Pérez, S. & Vergelati, C. (1987) *Polym. Bull.* **17**, 141-148.
13. Giacomini, M., Pullman, B. & Maigret, B. (1970) *Theor. Chem. Acta* **19**, 347-364.
14. Goehel, C. V., Dimpfl, W. L. & Brant, D. A. (1970) *Macromolecules* **3**, 644-654.
15. Kildeby, K., Melberg, S. & Rasmussen, K. (1977) *Acta Chem. Scand.* **A31**, 1-13.
16. Pérez, S., Roux, M., Revol, J. F. & Marchessault, R. H. (1979) *J. Mol. Biol.* **129**, 113-133.
17. Melberg, S. & Rasmussen, K. (1979) *Carbohydr. Res.* **69**, 27-31.
18. Shashkov, A. S., Lipkind, G. M. & Kochetkov, N. Y. (1986) *Carbohydr. Res.* **147**, 175-182.
19. Ha, S. N., Madsen, L. J. & Brady, J. W. (1988) *Biopolymers* **27**, 1927-1952.
20. IUPAC-IUB Commission on Biological Nomenclature (1970) *J. Mol. Biol.* **52**, 1-17.
21. IUPAC-IUB Commission on Biological Nomenclature (1971) *Arch. Biochem. Biophys.* **145**, 405-421.
22. Marchessault, R. H. & Pérez, S. (1979) *Biopolymers* **18**, 2369-2374.
23. Arnott, S. & Scott, S. E. (1972) *J. Chem. Soc. Perkin Trans. 2*, 324-335.
24. Allinger, N. L. (1977) *J. Am. Chem. Soc.* **99**, 8127-8134.
25. Jeffrey, G. A. & Taylor, R. (1980) *J. Comp. Chem.* **1**, 99-109.
26. Hassel, O. & Ottar, B. (1947) *Acta Chem. Scand.* **1**, 929-942.
27. Pérez, S. & Scaringe, R. P. (1986) *J. Appl. Crystallogr.* **19**, 65-66.
28. Imbert, A., Chanzy, H., Pérez, S., Buléon, A. & Tran, V. (1988) *J. Mol. Biol.* **201**, 365-378.
29. Imbert, A. & Pérez, S. (1988) *Biopolymers*, **27**, 1205-1221.
30. Hinrichs, H., Büttner, G., Steifa, M., Betzel, C., Zabel, V., Pfannemüller, B. & W. Saenger, W. (1987) *Science* **328**, 205-208.
31. Pérez, S., Taravel, F. & Vergelati, C. (1985) *Nouv. J. Chimie.* **9**, 561-564.
32. Brooks, B. R., Bruccoleri, R. E., Olafson, B. D., States, D. J., Swaminathan, S. & Karplus, M. (1983) *J. Comput. Chem.* **4** 187-217.
33. Ha, S. N., Giammona, A., Field, M. & Brady, J. W. (1988) *Carbohydr. Res.*, in press.

Received April 29, 1988

Accepted July 8, 1988