Carbohydrate Research, 90 (1981) 173–185
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THE CONFORMATIONAL PROPERTIES OF THE GLYCOSIDIC LINKAGE*

IGOR TVAROŠKA†
Institute of Chemistry, Slovak Academy of Sciences, 809 33 Bratislava (Czechoslovakia)
AND TIBOR KOŽAR
Institute of Neurobiology, Slovak Academy of Sciences, 040 01 Košice (Czechoslovakia)

(Received September 17th, 1980; accepted for publication, September 30th, 1980)

ABSTRACT

Stereochemical properties of the glycosidic linkage have been studied by the quantum-chemical PCILO method, using 2-methoxytetrahydropyran as a model. Calculations of the two-dimensional, conformational (Φ,Ψ) maps showed that the rotation around the C-1–O-1 bond is more hindered than that around the O-1–C-6 bond, and that there are differences in the shape of the energy curve for the axial and equatorial forms of 2-methoxytetrahydropyran. The observed population of the five stable conformers at equilibrium (GG:GT:TG$_1$:TG$_2$:TT = 70.8:6.0:19.9:2.0:1.3) is consistent with the prediction of the anomeric and exo-anomeric effects. The calculated abundance (76.8%) of the axial form of 2-methoxytetrahydropyran is comparable with experimental results (77–80%) obtained by n.m.r. measurements in non-polar solvents. The energies found for individual conformers made it possible to calculate the magnitude of the anomeric effect (3 kJ/mol) and to determine, for the first time, the values of the exo-anomeric effect for axial (6 kJ/mol) and equatorial 2-methoxytetrahydropyran (7 kJ/mol). The calculated variations of the geometry arising from rotation around the C-1–O-1 bond are consistent with results obtained by statistical analysis of experimental data for α- and β-glycosides. The results obtained, indicating that the energy, geometry, and electronic structure of glycosides are largely affected by the conformation of the acetal segment, are discussed from the point of view of conformational analysis of oligo- and poly-saccharides.

INTRODUCTION

The glycosidic linkage consists of a molecular segment where two electronegative atoms bearing lone pairs of electrons are linked to the anomeric carbon atom. The electronic structure in the vicinity of this arrangement affects markedly the geometry and conformation of a molecule, the overall consequences being termed

---

*Theoretical Studies on the Conformation of Saccharides, Part II. For Part I, see ref. 7.
†To whom correspondence should be addressed.

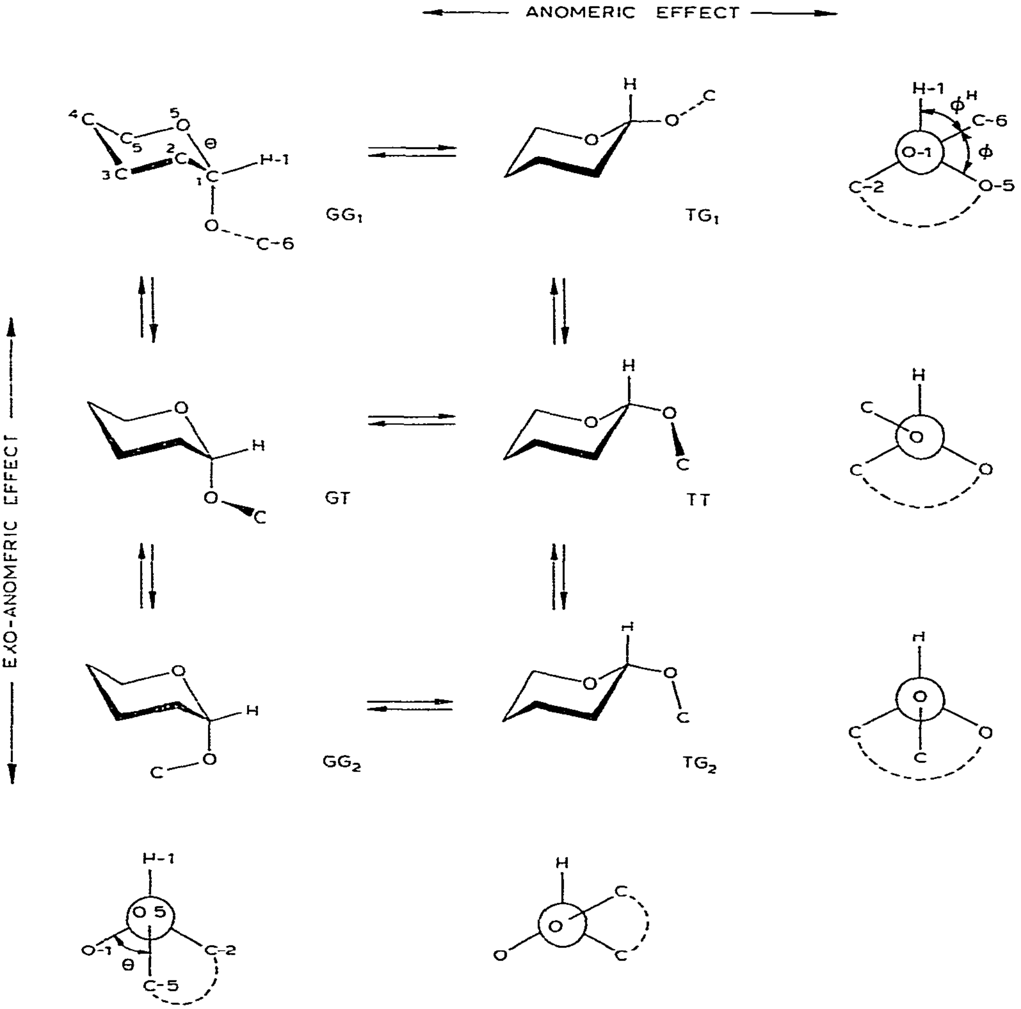

Fig 1 The differences between the anomeric and exo-anomeric effects, exemplified with the conformers of 2-methoxytetrahydropyran

anomeric and exo-anomeric effects[1] [2] Although the physical basis of the anomeric and exo-anomeric effects is the same, each affects a different portion of the acetal segment, so that two terms have been introduced to describe the same general phenomenon The anomeric effect is related to the preference of the axial orientation of the aglycon group in pyranosides, *i e* , the preference of a synclinal arrangement around the C-1–O-5 bond in the C-5–O-5–C-1–O-1 segment The exo-anomeric effect is related to the preference of the aglycon carbon atom for a position close to the synclinal orientation towards the ring oxygen and anomeric carbon in the O-5–C-1–O-1–C-X segment The two effects are illustrated in Fig 1, which shows the six possible conformations of 2-methoxytetrahydropyran Obviously, the most important outcome of the exo-anomeric effect is concerned with the relative stability of mutual orientations of neighbouring saccharide units in oligo- and poly-saccharides In this case, the conformational importance of the exo-anomeric effect surpasses that of the anomeric effect

Recently, anomeric and exo-anomeric effects have been extensively studied, both theoretically and experimentally Theoretical, quantum-chemical studies[3-6] of dimethoxymethane, an acyclic model for the acetal segment, demonstrate correctly the preference of the synclinal over the antiperiplanar orientation, and show the changes in the bonding angles as well as bond lengths Nevertheless, from the point of view of the behaviour of glycosidic structures, there are shortcomings In acyclic molecules, the conformational surface is largely symmetrical and thus does not allow differentiation between the magnitude of the anomeric and exo-anomeric effects, or between the stability of the two synclinal orientations resulting from the interactions with the pyranoid ring and its substituents

Our previous work[7] was devoted to studies of the conformational flexibility of the pyranoid ring, in which the semi-empirical, quantum-chemical PCILO method was applied to 2-methoxytetrahydropyran as a model substance The results showed that, in agreement with the anomeric and exo-anomeric effects, the most stable orientations are axial and synclinal for the methoxyl and methyl groups, respectively Also, the results indicated that there is a relation between the geometrical parameters and the conformation of the acetal segment We now report on the conformational properties of the glycosidic linkage and consider (*a*) the effect of the geometry adopted on the potential of rotation around the glycosidic linkage and the mutual stability of the conformers, and (*b*) the changes of the geometry of a pyranoid ring and of the acetal segment as a result of the changed conformation of the acetal segment

THE MODEL AND THE APPLIED METHOD

Conformational properties of the glycosidic linkage have been studied by using 2-methoxytetrahydropyran as a model, for numbering of the atoms and the designation of dihedral angles, see Fig 1 A detailed description of the nomenclature has been published[7] The rotation around the glycosidic linkage is given by the angles Φ and Ψ, and the angle θ determines the orientation of the methoxyl group The designation of stable conformers is based on the conformation of the acetal segment (Fig 1) and is given by the values of θ and Φ The individual conformer energies were calculated by the PCILO method with standard parameters When calculating the two-dimensional conformation (Φ,Ψ) maps, constant geometry corresponding to the most stable conformation of the given anomer was used, *i e*, GG_1 and TG_1 for axial and equatorial orientations of the methoxyl group, respectively In calculations involving optimisation of the geometry, 21 geometrical parameters were optimised[7]

RESULTS AND DISCUSSION

Conformation energy (*Φ*,*Ψ*) *maps* — Figs 2 and 3 show the energies of 2-methoxytetrahydropyran conformers having axial and equatorial methoxyl groups (A-MTHP and E-MTHP, respectively) obtained by rotation within 10° around the C-1–O-1 and O-1–C-6 bonds, in the form of two-dimensional contour, conformational energy (*Φ*,*Ψ*) maps As expected, the rotation around the O-1–C-6 bond is less restricted as compared with that around the C-1–O-1 bond The conformation energy map in the direction of the *Ψ* co-ordinate may be divided into three equal parts, each involving a 120° interval The symmetry follows from the symmetry of the methyl group The most stable arrangement is that involving a synclinal orientation of the reference hydrogen atom The rotation around the C-1–O-1 bond is hindered mainly by steric interactions of the methyl group with the methylene group of the pyranoid ring These interactions are more pronounced for A-MTHP, which is manifested by different space requirements for this conformer, as compared with E-MTHP In the direction of the *Φ* co-ordinate, the main minimum for A-MTHP holds for the synclinal arrangement, corresponding to GG_1 (further GG) conformer For E-MTHP, the minimum in the direction of the *Φ* co-ordinate again lies in the synclinal arrangement, and corresponds to the TG_1 conformer Surprisingly the two (*Φ*,*Ψ*) conformational maps indicate the existence of only one minimum in the direction of the *Φ* co-ordinate, although the existence of other minima, corresponding to conformers

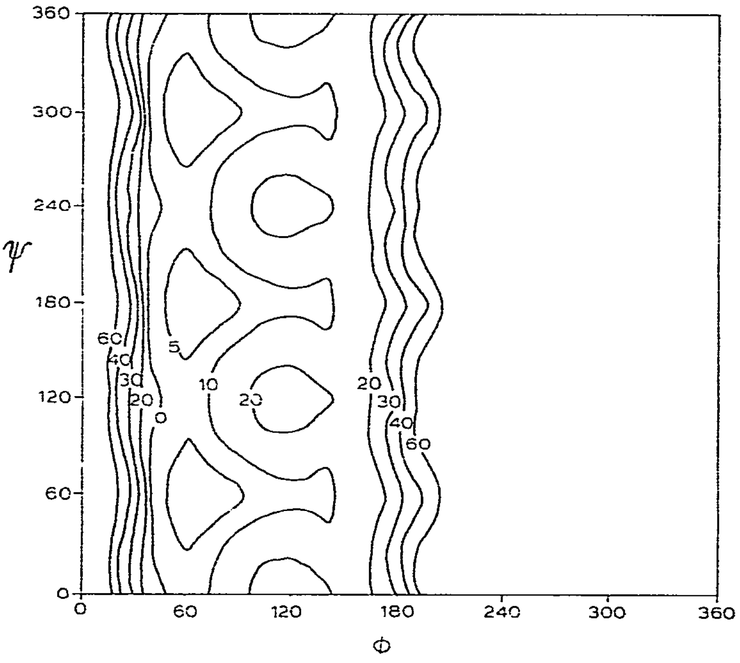

Fig 2 The conformational energy map for A-MTHP (in kJ/mol)

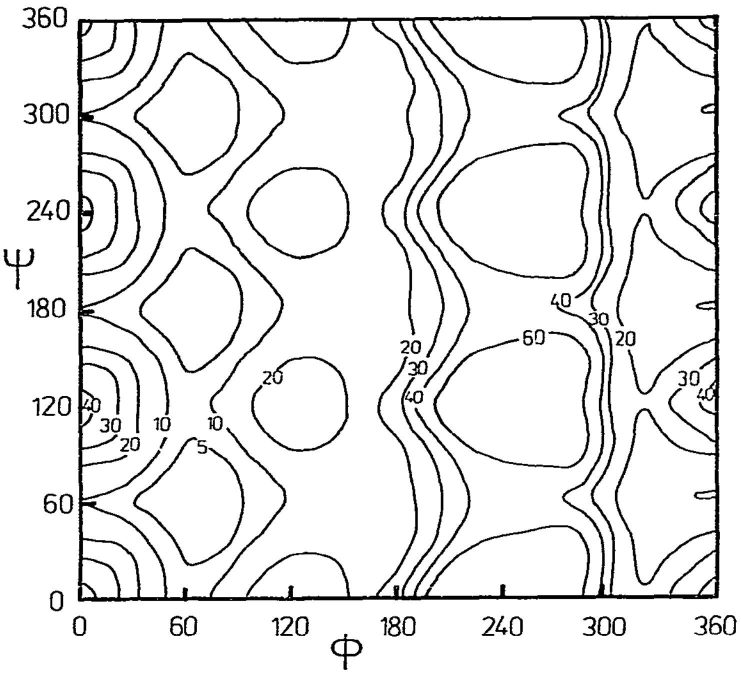

Fig 3 The conformational energy map for E-MTHP (in kJ/mol)

shown in Fig 1, would also be expected In regions corresponding to the GT, TG_2 and TT conformers, only slight indications of the existence of more stable areas are visible and, in the region of the GG_2 conformer, a pronounced maximum is present (Fig 2) This problem is discussed below

The effect of the geometry selected on the energy of rotation around the C-1–O-1 bond — The fact that only slight indications of minima for certain conformers were present on the (Φ,Ψ) maps calculated with fixed GG and TG_1 geometry for A-MTHP and E-MTHP, respectively, led to a further study of the effect of the geometry on the energy of 2-methoxytetrahydropyran conformers For the sake of clarity and because of the symmetry in the direction of the Ψ co-ordinate, only sections through (Φ,Ψ) maps for $\Psi = 60°$ were calculated

The pertinent results are illustrated in Figs 4 and 5 The dashed lines correspond to the energy of 2-methoxytetrahydropyran calculated with a fixed geometry in the most stable conformation of its individual forms The dot-dashed lines, corresponding to the fixed geometry of the GT and TT conformers, were calculated in a similar manner The full lines illustrate the energy curve involving the optimisation of 21 geometrical parameters[7] for an interval of $\Phi = 10°$ Figs 3 and 4 both show a pronounced dependence of the potential energy of the rotation around the C-1–O-1 bond on the selected geometry, *viz* , the inadequacy of the use of constant geometry in studies of the conformation of molecules that contain an acetal segment A com-

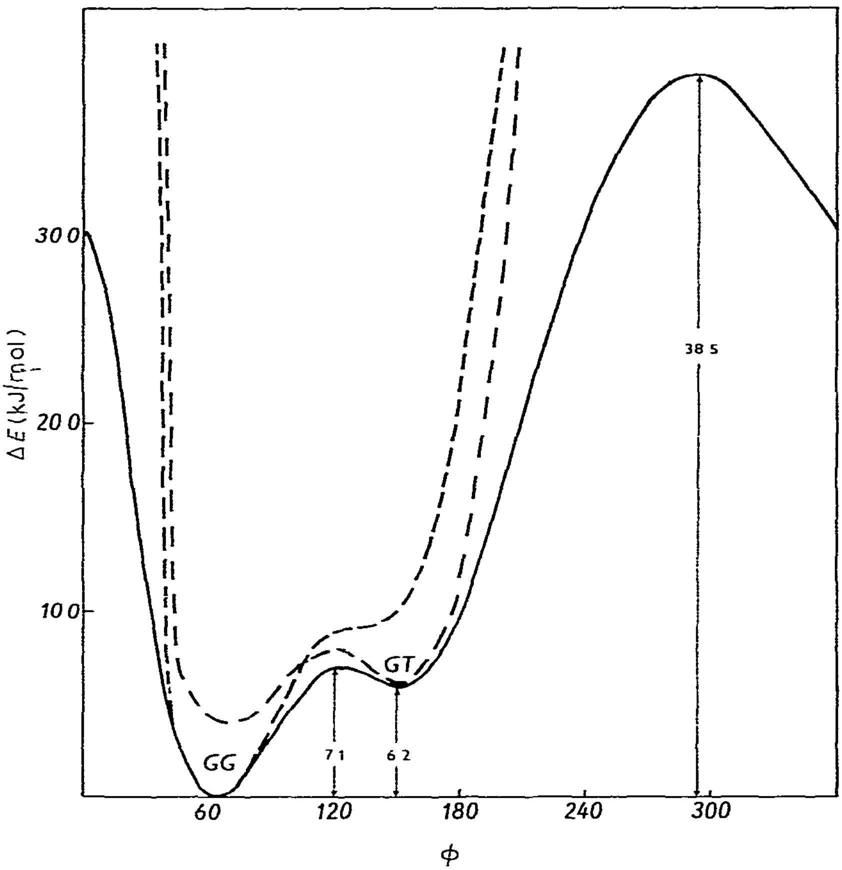

Fig 4 A section through conformational energy maps (Ψ = 60°) for A-MTHP with optimised geometry (——) and fixed geometry corresponding to GG (– – – –) or GT (– –) conformers (in kJ/mol)

parison of the curves demonstrates that the use of constant geometry leads to an unreal shape of the energy curves, whereas the curves approach the region of "correct" (optimised) energies only in the region of the minimum, corresponding to the geometry used The barriers of transitions among the individual conformers are excessively high

An undesirable consequence of the use of constant geometry, corresponding to certain of the stable conformations, is the erroneous description of the course of the energy in its further minima It may sometimes lead to such a situation that some of the minima remain undisclosed Only when the geometry is optimised are the general features of the energy profiles such as would be expected by analogy with the conformation properties of acyclic model compounds[3]. The most stable conformation of dimethoxymethane is the twice-degenerate one, $G_1G_1(G_2G_2)$ The next minimum (3 37 kJ/mol higher) is the four-times degenerate G_1T (TG_1, G_2T, TG_2) conformation The last minimum is the TT conformation, which has an energy 13 69 kJ/mol

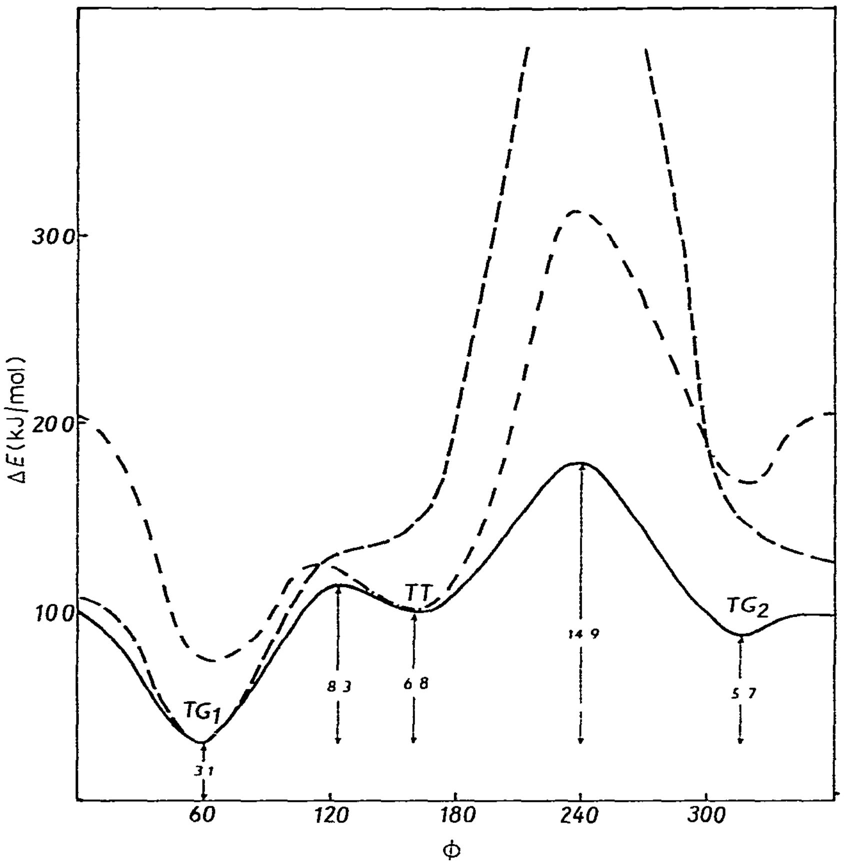

Fig 5 A section through conformational energy maps (Ψ = 60°) for E-MTHP with optimised geometry (——) and fixed geometry corresponding to TG_1 (– – – –) or TT (– –) conformers (in kJ/mol)

above the absolute minimum In comparison with dimethoxymethane, the ring structure of 2-methoxytetrahydropyran results in a lower symmetry of the conformation surface, and the individual conformers therefore differ in their energy For A-MTHP, the lowest minimum appeared at 63° (GG) and the next (GT), with ~6 2 kJ/mol higher energy, at 152 2° In the range of the third, expected GG_2 minimum between —150° and 20°, there is a broad maximum caused by steric interactions of the methyl group and the ring with its substituents For E-MTHP, there are three minima, corresponding to three different, eclipsed arrangements around the glycosidic linkage Energetically most favoured is the TG_1 conformer, having 3 1 kJ/mol higher energy than the GG conformer of A-MTHP The TG_2 and TT conformers are 5 7 and 6 8 kJ/mol, respectively, higher than the TG_1 conformer The maximum at ~ —120° is caused by interactions of the methyl group and H-2 and H-3 Based on the energies calculated for the individual conformers, the equilibrium distribution GG GT TG_1 TG_2 TT = 70 8 6 0 19 9 2 0 1 3 has been calculated It shows that the equilibrium A-MTHP E-MTHP = 76 8 23 2 is shifted in favour of A-MTHP, which is in agreement with data for non-polar solvents (*cf* ~77–80% for A-MTHP[2 8 11])

Coupling of the 2-methoxytetrahydropyran structure with the glycosidic torsional angle — A difference of bonding parameters for α- and β-pyranosides has been observed Theoretical calculations for acyclic models follow these trends as a function of the change of the conformation, and explain the differences as resulting from the delocalisation of free electron-pairs at the oxygen atom[5 6 12] However, the acyclic models do not allow determination of the effect of rotation around the glycosidic linkage (characterised by angle Φ) on the shape of the pyranoid ring, and of the ring on the structure of the glycosidic linkage The high degree of dependence of the rotation energy on the chosen geometry indicates changes in the structure of both forms of 2-methoxytetrahydropyran, depending upon the orientation of the methyl group Table I shows selected geometrical parameters for the five most-stable conformations of 2-methoxytetrahydropyran The Cremer–Pople parameters (Q, Θ_2,φ_2) show changes of ring puckering depending upon the change in conformation of the acetal segment The larger φ_2 values calculated for E-MTHP conformations agree with experimental data extracted from X-ray analysis and neutron diffraction studies[13] The bond lengths follow qualitatively the experimentally found changes The differences however, are not as pronounced as for the experimental values Similar results for bond lengths calculated by the PCILO method have been observed[7], and they can probably be accounted for by the approximations involved in the PCILO method

TABLE I

CALCULATED RELATIVE ENERGY VALUES (ΔE_t) AND SELECTED GEOMETRICAL PARAMETERS OF THE MOST STABLE CONFORMERS OF 2-METHOXYTETRAHYDROPYRAN

	A-MTHP		*E-MTHP*		
	GG	*GT*	*TG*$_1$	*TG*$_2$	*TT*
ΔE_t (kJ/mol)	0 0	6 1	3 1	8 8	9 9
Θ (deg)	66 0	66 3	−178 5	174 2	179 1
Φ (deg)	63 0	151 2	58 2	−44 4	159 5
Ψ (deg)	60 0	60 0	60 0	60 0	60 0
Q (pm)	57 4	57 6	57 1	57 6	57 1
Θ_2 (deg)	3 6	2 6	4 4	3 9	4 4
φ_2 (deg)	201 8	199 6	208 3	197 7	208 5
r(C-1 O-1) (pm)	139 4	139 7	139 2	139 4	139 4
r(C-1–O-5) (pm)	139 9	139 9	140 0	140 0	139 8
α(1) (deg)	110 5	106 4	106 6	107 2	102 3
α(6) (deg)	111 9	111 4	112 4	111 9	112 7
β (deg)	108 8	108 6	108 5	109 5	108 9
r(O-1–HO-4) (pm)	421 1	416 4	511 1	514 3	510 4
r(O-1–HO-3) (pm)	390 7	394 5	452 4	458 0	456 9
r(O-1–HO-6) (pm)	377 4	368 9	428 2	429 2	421 8

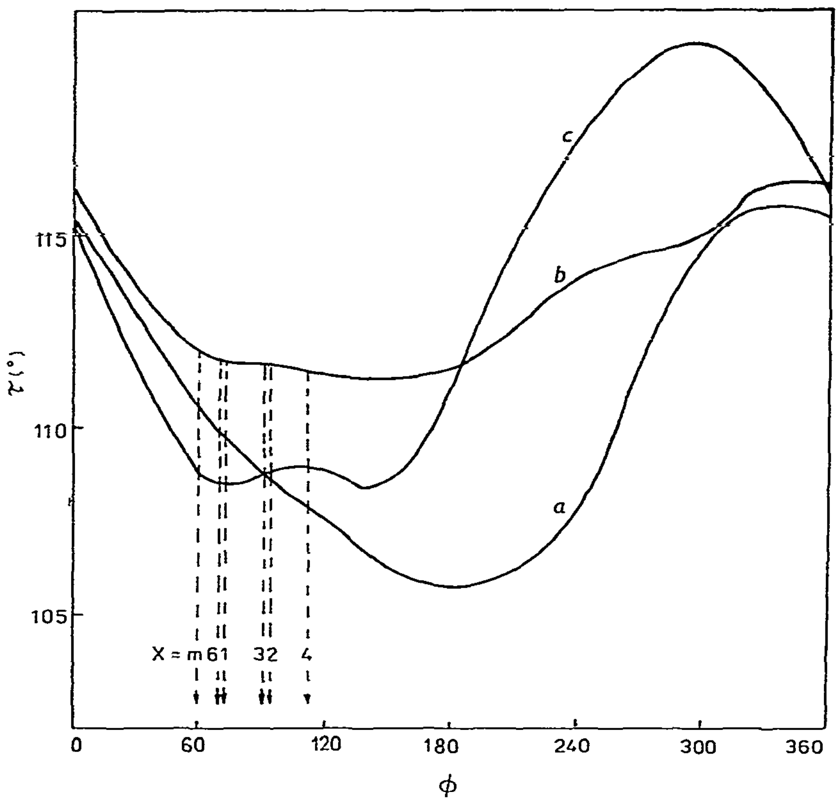

Fig. 6. Conformational dependence of bond angles a $\alpha(1)$, b, $\alpha(6)$, and c, β, for the rotation about the C-1–O-1 bond in A-MTHP. Broken lines correspond to mean values of angle Φ for different types of glycosides[14]

An analysis of geometrical parameters during rotation about the C-1–O-1 bond reveals that the most pronounced changes are in the bond angles of the acetal segment [$\alpha(1)$, $\alpha(6)$, and β]. Figs. 6 and 7 show these changes for A-MTHP and E-MTHP. The conformational dependence of these angles results from several effects. The most important are the relaxation of the geometry to minimise non-bonded interactions, and delocalization of a free electron-pair of the oxygen atom. The former factor manifests itself mainly in the region of energetically unfavourable conformations involving strong, steric interactions of the methyl group with ring atoms and substituents ($\Phi \sim -120$ to $-150°$). The unfavourable interactions become less pronounced at the expense of alterations of some inner geometrical parameters. The loss of energy needed to cause this change is overcome by the gain resulting from the elimination of steric repulsions by separation of the interacting groups. Since the valence angles are "softer" parameters than bond lengths, it is to be expected that the changes would affect most markedly only the valence angles, and mainly the glycosidic angle which is independent of the ring-closure conditions

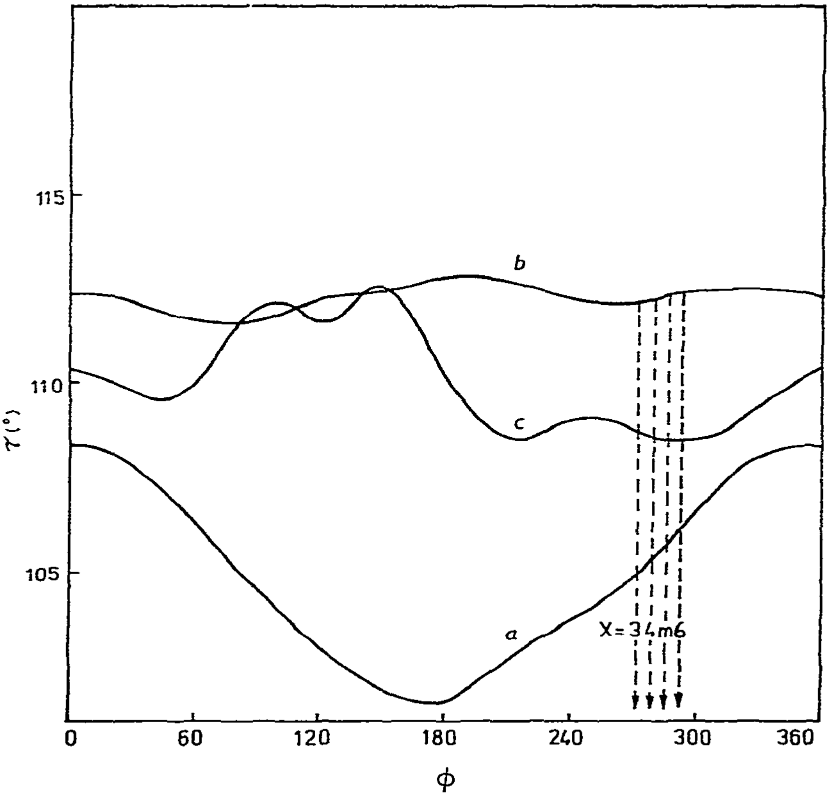

Fig 7 Conformational dependence of bond angles a, $\alpha(1)$, b, $\alpha(6)$, and c, β, for the rotation about the C-1–O-1 bond in E-MTHP Broken lines correspond to mean values of angle Φ for different types of glycosides[14]

with respect to other parameters in the ring It follows[12] from studies of the torsional dependence of orbital interactions in dimethoxymethane that, by virtue of through-bond interactions of free electron-pairs, each rotation from the antiperiplanar position around the C-O bond results in an increase of the O-C-O angle These factors are clearly reflected in the course of the torsional dependence of bonding angle α (Figs 6 and 7) For the purpose of comparison with experimental data from statistical analysis of available crystallographic data for methyl glycosides and for oligo- and poly-saccharides containing different types (1→X) of glycosidic linkage[14], the mean values of angle Φ are shown in Figs 6 and 7 as a dashed line These values make it possible to compare the alterations of valence angles calculated for 2-methoxytetrahydropyran with those of the mean, angle values for different types of glycosidic linkage In spite of the evident effect of chemical structure and the strengths of the crystal field, the changes, compared with the situation in 2-methoxytetrahydropyran, are qualitatively correct For example, of the values for glycosidic angles calculated according to experimental, mean, angle values for β-glycosides, the smallest value is observed for

TABLE II

CALCULATED, NET ATOMIC CHARGES[a] AND DIPOLE MOMENTS OF THE MOST STABLE CONFORMERS OF 2-METHOXYTETRAHYDROPYRAN

	A-MTHP		*E-MTHP*		
	GG	*GT*	*TG_1*	*TG_2*	*TT*
Q(C-1)	291 8	294 0	299 9	293 8	299 0
Q(C-2)	−21 0	−30 8	−25 3	−34 5	−35 2
Q(C-3)	45 0	44 7	40 9	42 6	43 4
Q(C-4)	0 4	0 6	0 1	−0 6	−0 6
Q(C-5)	160 0	160 0	156 5	156 5	154 7
Q(C-6)	100 6	97 8	102 6	104 6	95 3
Q(O-1)	−170 5	−171 3	−160 1	−169 1	−154 2
Q(O-5)	−194 2	−181 4	−187 5	−186 9	−168 3
Q(H-1)	−78 0	−75 4	−96 5	−76 9	−94 9
μ (D)[b]	0 284	2 169	2 134	2 360	3 181
μ_{ch} (D)	0 369	0 631	0 385	0 746	0 666
μ_{sp} (D)	0 175	1 619	2 031	1 749	2 715

[a] Q(i), in 10^{-3}e [b] 1D = 3 33 × 10^{-30} mAs

methyl derivatives, a larger one for (1→4)-linked oligosaccharides, and the greatest for (1→3)-linked oligosaccharides This fully agrees with the order found experimentally For α-glycosides, the theoretically predicted, glycosidic angle increases in the order (1→1), (1→6), methyl, (1→3), (1→2), and (1→4), which is very close to the order found experimentally (1→6), methyl, (1→1), (1→3), (1→2), and (1→4) (Figs. 6 and 7) The same qualitative agreement is observed for the dependence of angles $\alpha(1)$ and $\alpha(6)$ upon Φ

An important parameter in the conformational analysis and X-ray structure-determination of polysaccharides is the so-called virtual-bond length It is also an index of the cumulative effect of changes in the geometrical parameters of the monomeric units of polysaccharides For 2-methoxytetrahydropyran, the parameter analogous to the virtual-bond length will be taken as the distance between O-1 and the hydrogen atom at the position of the assumed glycosidic linkage Values for three such distances are given in Table I The different values of these distances indicate that the size and shape of the residues change with the change in the shape of the polysaccharide chain, which is determined mainly by angles Φ and Ψ These results support French's opinion[15], based on single-crystal studies of various polymorphs of amylose, that the size of α-D-glucopyranose varies from 410 to 480 pm and that the whole set of known geometrical residues should therefore be used in structural studies

Conformational dependence of intramolecular interactions and geometrical parameters is manifested also in calculations of electronic structures resulting from the change of conformation of the glycosidic linkage Table II shows changes in charge distribution of selected atoms, and changes of the dipole moment together with its components for the five most-stable conformers of 2-methoxytetrahydropyran.

Although a certain dependence of net-charge values for the individual atoms on conformation can be observed, the most pronounced variation of electronic structure can be seen in the change of the dipole moment. The smallest dipole moment is exhibited by the GG conformer (0.284 D, 1 D = 3.33×10^{-30} mAs) and the highest one by the TT conformer (3.181 D). The mean value of the dipole moment (1.23 D) calculated by applying PCILO energies and dipole moments of the individual conformers is in a very good agreement with the experimental value (1.21 D) found[11] in CCl_4. The changes in dipole moment as a function of conformation are very important from the point of view of conformational equilibria in solution: conformers showing higher dipole moments are stabilised in more polar solvents. A comparison of dipole moment components shows that while the charge component, μ_{ch}, varies only slightly (from 0.37 to 0.75 D), the hybridisation dipoles, μ_{sp}, depend largely upon conformation (0.18–2.72 D). The value and the conformational dependence of μ_{sp} indicates the inadequacy of the use of charge distribution when the electrostatic term is calculated by the molecular-mechanics method, and confirms the need to modify this distribution by inclusion of the hybridisation dipoles[16].

Anomeric and exo-anomeric effects. — Although the physical basis of the two effects is the same, it is necessary to distinguish between the magnitude of the anomeric and exo-anomeric effects, and for the exo-anomeric effect, its magnitude for axial and equatorial forms. In contrast to acyclic models for which it is impossible to distinguish between the magnitude of the anomeric and exo-anomeric effects, based on our results and using energies of individual conformers, it is possible to calculate the effects for A-MTHP and E-MTHP. In this approximation, the anomeric effect is determined by the differences between the mean energies of conformations of A-MTHP and E-MTHP. Analogously, for the exo-anomeric effect, the difference can be taken between energies of synclinal and antiperiplanar conformers in individual 2-methoxytetrahydropyran forms. Based on calculated energies of individual conformers, the anomeric effect in 2-methoxytetrahydropyran amounts to 2.96 kJ/mol, and the exo-anomeric effects in A-MTHP and E-MTHP are 6.14 and 7.01 kJ/mol, respectively. This result implies that the exo-anomeric effect is stronger in β anomers. Owing to experimental difficulties involved in the determination of conformational equilibrium around the C-1–O-1 bond, the calculated magnitude of the anomeric effect can be compared only with data obtained in non-polar solvents, where the respective values range from 3.0 to 3.9 kJ/mol. It can be assumed, based on the good agreement between calculated and experimentally found values for the anomeric effect, that the values for the exo-anomeric effect (the first to have been reported) are also correct. The values for the exo-anomeric effect are roughly twice as high as those for the anomeric effect, which again emphasizes the importance of the exo-anomeric effect in governing the conformational properties of the glycosidic segment[17].

The foregoing results correspond to the so-called state of an isolated molecule. The conformational equilibrium of the conformers and the magnitudes of the anomeric and exo-anomeric effects depend, of course, upon the medium in which the glycosidic structures exist. Recent studies of the effect of media on the conformational properties of dimethoxymethane[18] and n m r studies of 2-alkoxytetrahydropyrans in solution[2 8 11] show that the solvent effect is an important factor upon which the abundance of the axial form of 2-methoxytetrahydropyran depends A detailed study of the effect of solvents upon the conformational properties of the glycosidic linkage and the magnitude of anomeric and exo-anomeric effects are presented elsewhere[19]

As a conclusion to this study, a few comments concerning the conformational analysis of oligo- and poly-saccharides are necessary The pronounced dependence of the torsional energy around the glycosidic linkage indicates that the approximation to a rigid residue may lead to erroneous results Care should be exercised in deriving conclusions in cases when only geometrical parameters from X-ray or neutron diffraction studies are available, because these correspond only to certain conformations A more suitable approximation would be the use of the so-called average parameters, for example, Arnott and Scott's geometrical parameters[20] Since some of the geometrical parameters alter considerably, it is necessary to include in calculations of the conformation of oligo- and poly-saccharides at least the most important parameters, *e g* , $\alpha(1)$ or the glycosidic angle This is particularly important in studies of the properties of polysaccharides in solutions, as the shape and properties of molecules are given by a dynamic equilibrium of many conformations The first approach of this type can be found in the work of Brant[21] who included, as another parameter, the glycosidic angle β in the configurational statistics of polysaccharides

It follows from the high values of the exo-anomeric effect that this factor is an important driving-force, comparable with other interactions, determining the conformational properties of the glycosidic linkage The exo-anomeric effect should therefore be included as a suitable parameter in the methods of molecular mechanics applied to conformational properties of oligo- and poly-saccharides

REFERENCES

1 R U Lemieux and N J Chu, *Abstr Pap Am Chem Soc Meet* , 133 (1958) 31N
2 R U Lemieux, A A Pavia, J C Martin, and K A Watanabe *Can J Chem* 47 (1969) 4427–4439
3 I Tvaroška and T Bleha *J Mol Struct* , 24 (1975) 249–259
4 I Tvaroška and T Bleha *Tetrahedron Lett* (1975) 249–252
5 D G Gorenstein and D Kar, *J Am Chem Soc* , 99 (1976) 672–677
6 G. A Jeffrey, J A Pople, J S Binkley, and S Vishveshwara *J Am Chem Soc* 100 (1978) 373–379
7 T Kožar and I Tvaroška, *Theor Chim Acta*, 53 (1979) 9–19
8 G O Pierson and O A Runquist, *J Org Chem* 33 (1968) 2572–2578
9 C B Anderson and D T Sepp, *Tetrahedron*, 24 (1968) 1707–1716
10 E L Eliel and C A Giza *J Org Chem* 33 (1968) 3754–3758
11 A J de Hoog, H R Buys C Altona and E Havinga *Tetrahedron*, 25 (1969) 3365–3375
12 I Tvaroška and T Bleha, *Can J Chem* , 57 (1979) 424–435
13 G A Jeffrey and R Taylor, *J Comput Chem* 1 (1980) 99–109
14 I Tvaroška and T Kožar, *Chem Zvesti*, in press
15 A D French and V G Murphy *Carbohydr Res* , 27 (1973) 391–406
16 I Tvaroška and T Bleha *Biopolymers* 18 (1979) 2537–2548
17 R Perez and R H Marchessault *Carbohydr Res* 65 (1978) 114–120
18 I Tvaroška and T Bleha *Collect Czech Chem Commun* 45 (1980) 1883–1895
19 I Tvaroška and T Kožár *J Am Chem Soc* , 102 (1980) 6929–6936
20 S Arnott and W E Scott, *J Chem Soc* , *Perkin Trans 2*, (1972) 324–335
21 D A Brant and K D Goebel, *Macromolecules*, 8 (1975) 522–530