Theor Chem Acc (1999) 101:215–222
DOI 10.007/s00214980m118

Theoretical
Chemistry Accounts

Regular article

Structure effects on isomerization pathways and vibrational spectra of epoxysaccharides: a numerical study*

Svetlana G. Kirillova, Victor M. Andrianov, Rostislav G. Zhbankov

B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, F. Skaryna Avenue 70, Minsk 220072, Belarus

Received: 24 March 1998 / Accepted: 3 September 1998 /

Abstract. Results of a comparative analysis of conformational possibilities of the hexopyranose ring of six epoxysaccharides differing from each other by the position of the oxirane ring within the limits of the hexapyranose ring and having different orientations of substituents and different positions of the oxirane ring with respect to the skeleton plane of the molecules are presented. Numerical simulations based on the Wiberg and Boyd method made it possible to determine all the stationary forms in which anhydropyranose rings can exist. The effect of various structural factors on the character of conformational transformations, heights of transition barriers, and the energy of stationary forms has been investigated. Normal vibrational modes of the stationary forms of the compounds were calculated using molecular mechanics. Based on results of our simulations, we predict a strong effect of steric factors on the vibrational spectra of sugar epoxides.

Key words: Conformational isomerism – Epoxysaccharides – Isomerization pathways – Normal vibrational modes

1 Introduction

Anhydro derivatives of carbohydrates occasionally occur in natural products [1]. Mainly, these compounds are of interest as key intermediates or substrates in the chemical synthesis of compounds of biological interest [1–3]. They are also used in the preparation of deuterated and tritiated compounds. As intermediates, sugar epoxides can also manifest biological activity [3]. Steric factors are known to play an important part in these reactions, since they can affect the rate, direction, final products of the chemical reaction, and parameters which determine the reaction mechanism [3]. Therefore, information on the conformational behavior of epoxysaccharides can be very important.

According to Reeves [4], the hexatomic pyranose ring usually adopts the chair conformation. However, strong interactions between substituents can deform the ring to the boat or skew conformation. Indeed, the skew form of the pyranose ring has been revealed for carbohydrates in conformational investigations [5, 6]. It is known [6] that the sofa and half-chair conformers are high-energy forms of these compounds. The oxirane ring has a strong effect on the conformational properties of the pyranose ring. The rigid oxirane ring in epoxides, as well as the double bond in unsaturated sugars, requires the coplanarity of four atoms. As a result, the ring adopts one of two possible half-chair forms [7]. In contrast to the hexatomic pyranose ring, epoxides of sugars are highly flexible due to the presence of the oxirane ring. In addition to the half-chair forms, X-ray studies have revealed the hybrid sofa + half-chair conformation [8–11]. In the process of chemical transformations, the epoxypyranose ring can also adopt the boat conformation [3]. These aspects allow epoxysaccharides to be regarded as model compounds for the investigation of conformational properties of carbohydrates [12].

However, not only ring conformations, but also configurations and conformations of substituents are of considerable interest. For example, the effect of orientations of the primary alcohol groups on the energy of α- and β-fructofuranose was investigated [13], and a comparative conformational analysis of α- and β-anomer pairs of eight hexoses has been carried out and anomeric ratios for these compounds have been estimated [6]. Therefore, the starting point of our investigations was our previous work [14] in which a comparative conformational analysis of two epoxysaccharide molecules with different orientations of substituent was carried out.

In computational studies of carbohydrates, ab initio methods [15, 16] and semi-empirical techniques [16–18] are widely used; however, molecular mechanics is also useful for modeling various properties of carbohydrate molecules [6, 7, 13, 14].

---

*Contribution to the Proceedings of Computational Chemistry and the Living World, April 20–24, 1998, Chambery, France

Correspondence to: S.G. Kirillova

In a previous paper [19], we reported on a detailed investigation of isomerization pathways of six epoxysaccharides with different substituents and positions of the oxirane ring. We continue our molecular mechanics study of the conformational properties of these compounds. In the present communication, we propose a more convenient method for comparing isomerization pathways of epoxysaccharides with different localizations of the oxirane ring within the limits of the pyranose ring. Application of the method proposed makes it possible to find that the conformation space of epoxysaccharides limited by the coplanarity of four carbon atoms is predominantly determined by the localization of the oxirane ring, whereas other structural differences have only a minor effect on it. In addition to conformational investigations, we present the normal mode analysis of all stationary forms revealed during the conformational investigation of the molecules.

2 Subjects of investigation and method of calculation

Six epoxysaccharide molecules, namely, three molecules with epoxypyranose rings [2, 3], methyl 2,3-anhydro-2,3,4-trideoxy-*β*-*d*-lyxo-hexapyranoside (referred to in what follows as βL), methyl 2,3-anhydro-4-deoxy-*α*-*d,l*-ribo- and -*α*-*d,l*-lyxo-hexapyranosides (R and αL, respectively), and three molecules with epoxypyranose rings [3, 4], methyl 2,6-di-O–acetyl-3,4-anhydro-*α*-*d,l*-(6,6-$^2H_2$) derivatives of talopyranoside (T) and galactopyranoside (G), and methyl 3,4-anhydro-*α*-*d,l*-allopyranoside (A), where chosen as the subjects of the investigation. The 2,3-epoxysaccharides and the molecules T and G are configurational isomers. As is evident from Fig. 1, the molecules differ from one another by

1. The position of the oxirane ring within the limits of the hexapyranose ring.
2. Different orientations of substituents.
3. Different positions of the oxirane ring with respect to the skeleton plane of the molecules.
4. The molecules T and G have bulky acetogroups at the C2 and C5 atoms of the skeleton.

Molecular mechanics was used for the calculations. The particular form of the potential function of the molecular mechanics method was proposed by Dachevskii [20]. It includes potentials for bond stretching, bending, torsional potentials, and van der Waals interactions. Its parametrization for conformational and spectroscopic investigations of carbohydrates was proposed by Andrianov et al. [21].

One of the standard methods with "dihedral drivers" due to Wiberg and Boyd [22] was used to calculate interconversion pathways. In order to determine the conformations on the pathway from a starting point to the enantiomer, the method described in Ref. [14] was used. It consists of changing a separate endocyclic torsional angle with a step of 5°. On each step the other five endocyclic torsional angles are varied alternately, and the molecular conformation with the lowest energy is determined. Cartesian coordinates revealed in X-ray studies [8–11, 23] were used as the zero approximation. Structural parameters of the crystalline forms of the molecules are presented in Tables 1 and 2.

The normal mode analysis of all stationary forms revealed during conformational investigation of these compounds was carried out using molecular mechanics. Molecular mechanics is known to be a more convenient approach to account for nonbonding interactions compared to the conventional valence force field method [24, 25], since in the former method second derivatives over independent (Cartesian) coordinates forming the matrix of dynamic coefficients (force constants) are changed automatically upon variations in the conformation or configuration of the molecule.

Two parameters are usually used for the description of conformations of rings with four coplanar atoms [7]. However, the Cremer–Pople diagram (based on three parameters: Q, ϕ and Θ) was used in the present investigation for presentation of interconversion pathways of the molecules [26]. The sphere proposed by Cremer and Pople on which the conformations of six-membered rings can be mapped (for a constant Q) is indicated in Fig. 2. The necessity of using three parameters instead of two stems from the fact that the dihedral angles of the oxirane ring deform substantially (up to 10°) in the process of conformational transformations, and the above-mentioned four bonded atoms may lose their coplanarity.

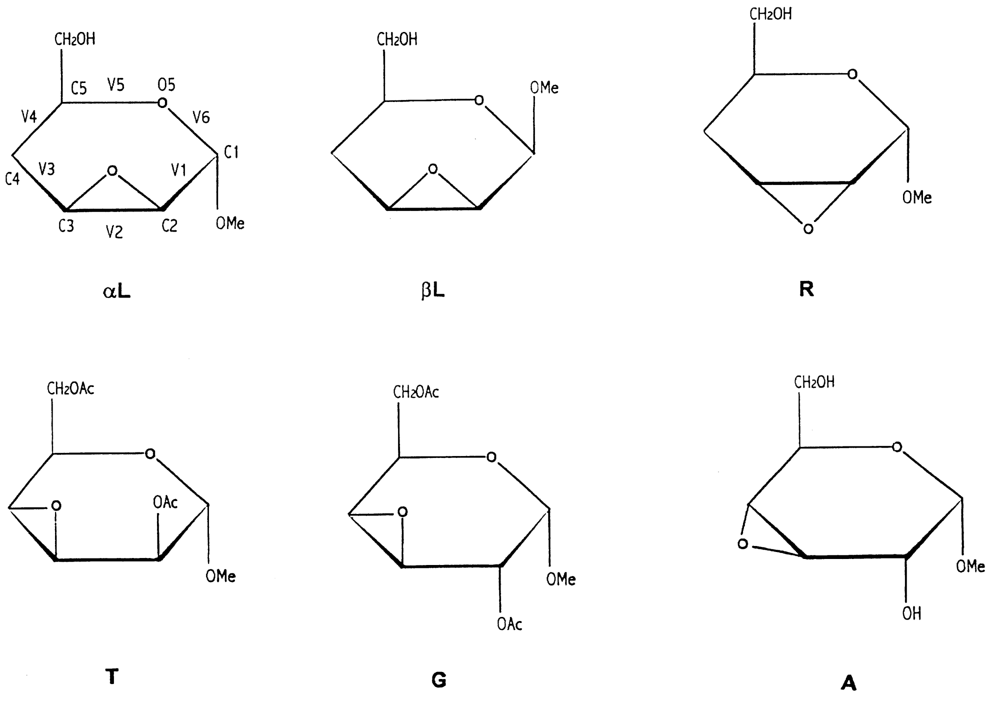

Fig. 1. Schematic presentation of the molecules under investigation with identification of atoms and notation of the torsional angles

Table 1. Structural and energy parameters of stationary and crystalline forms of the molecules αL, βL and R

Conformation[a]	Torsion angle (deg)						Puckering coordinate			OMe substituent at Cl atom		CH$_2$OH substituent at C5 atom		ΔU kcal/mol
	V1	V2	V3	V4	V5	V6	Q, A	ϕ (deg)	Θ (deg)	Orientation[b]	Configuration of substituent and oxirane ring	Orientation[b]	Configuration of substituent and oxirane ring	
^{0}E + ^{0}H$_5$ (βL$_{cr}$)	23	0	9	−40	69	−59	0.498	104	128	e	*cis*	e	*cis*	–
^{0}E + ^{0}H$_5$ (βL0)	26	−6	15	−44	69	59	0.500	101	134	e	*cis*	e	*cis*	1.6
^{5}E + ^{5}H$_0$ (βL1)	−9	−2	−18	47	−61	42	0.457	258	53	a	*cis*	a	*cis*	2.6
B$_{4,1def}$ (βL2)	48	0	−41	34	13	−55	0.612	175	95	e	*cis*	a	*cis*	4.5
^{1,4}B$_{def}$ (βL3)	−48	−2	46	−40	−9	55	0.662	356	88	a	*cis*	e	*cis*	4.7
^{5}S$_4$ + ^{2}T$_4$ (βL4)	28	−3	−34	49	−28	−11	0.480	204	76	e	*cis*	a	*cis*	6.1
^{4}S$_{5def}$ (βL5)	−29	2	41	−62	39	7	0.582	26	107	a	*cis*	e	*cis*	6.7
^{0}S$_1$ + ^{3}T$_1$ (βL6)	46	0	−29	12	35	−65	0.568	160	106	e	*cis*	a	*cis*	4.8
^{5}E + ^{5}H$_0$ (R$_{cr}$)	−8	−2	−20	53	−68	43	0.506	256	53	a	*cis*	e	*trans*	–
^{5}E + ^{5}H$_0$ (R0)	−15	2	−19	50	−68	49	0.497	264	49	a	*cis*	e	*trans*	0.0
^{0}H$_{5def}$ (R1)	18	−2	15	−45	65	−50	0.469	91	131	e	*cis*	a	*trans*	1.1
B$_{4,1def}$ (R2)	45	2	−41	36	11	−51	0.601	175	93	e	*cis*	e	*trans*	4.1
^{1,4}B (R3)	−49	0	46	−45	−3	49	0.660	0	90	a	*cis*	a	*trans*	5.0
B$_{4,1}$ + ^{2}T$_4$ (R4)	34	−1	−41	52	−20	−22	0.547	194	79	e	*cis*	e	*trans*	3.8
^{4}S$_{5def}$ (R5)	−34	4	41	−59	31	14	0.579	21	104	a	*cis*	a	*trans*	5.7
^{1}S$_0$ + ^{1}T$_3$ (R6)	−43	−4	31	−10	−38	65	0.577	338	75	a	*cis*	a	*trans*	6.0
^{5}H$_{0def}$ (αL$_{cr}$)	−17	−2	−12	45	−68	52	0.491	273	52	a	*trans*	e	*cis*	–
^{5}H$_{0def}$ (αL0)	−21	2	−14	44	−68	54	0.493	276	49	a	*trans*	e	*cis*	0.1
^{0}H$_{5def}$ (αL1)	20	−4	13	−40	60	−49	0.426	96	132	e	*trans*	a	*cis*	2.7
B$_{4,1def}$ (αL2)	50	0	−46	42	8	−54	0.671	177	92	e	*trans*	e	*cis*	4.9
^{1,4}B + ^{1}T$_3$ (αL3)	−44	−2	36	−23	−23	58	0.571	345	81	a	*trans*	a	*cis*	3.5
^{5}S$_4$ + ^{2}T$_4$ (αL4)	35	−5	−41	60	−32	−14	0.595	202	76	e	*trans*	e	*cis*	5.8
^{4}S$_{5def}$ (αL5)	−21	−1	33	−45	25	7	0.418	21	108	a	*trans*	a	*cis*	6.1

[a] "cr" indicates the conformations of the crystalline forms of the molecules

[b] "e" represents a pseudo-equatorial orientation and "a" represents a pseudo-axial orientation

Table 2. Structural and energy parameters of stationary and crystalline forms of the molecules T, G and A

Conformation[a]	Torsion angle (deg)						Puckering coordinate			Substituent at C1 atom		Substituent at C2 atom		Substituent at C5 atom		ΔU
	V1	V2	V3	V4	V5	V6	Q, A	ϕ (deg)	Θ (deg)	Orientation[b]	Configuration of substituent and oxirane ring	Orientation[b]	Configuration of substituent and oxirane ring	Orientation[b]	Configuration of substituent and oxirane ring	kcal/mol
$E_0 + {}^1H_0$ (T_{cr})	−39	9	−1	22	−54	64	0.460	317	51	a	*trans*	a	*cis*	e	*cis*	–
${}^1H_{0def}$ (T0)	−47	16	−2	18	−51	68	0.493	329	49	a	*trans*	a	*cis*	e	*cis*	0.0
${}^0H_{1def}$ (T1)	51	−19	0	−12	46	−68	0.501	160	130	e	*trans*	e	*cis*	a	*cis*	0.2
${}^{2,5}B_{def}$ (T2)	39	−42	1	45	−48	7	0.601	243	89	e	*trans*	e	*cis*	e	*cis*	4.3
${}^{2,5}B + {}^2T_4$ (T3)	51	−41	−1	36	−25	−18	0.558	227	99	e	*trans*	e	*cis*	e	*cis*	4.5
$B_{2,5} + {}^0T_2$ (T4)	−24	36	−2	−42	55	−21	0.562	72	98	a	*trans*	a	*cis*	a	*cis*	6.5
${}^1H_{0def}$ (G_{cr})	−51	19	−1	14	−49	70	0.504	337	50	a	*trans*	e	*trans*	e	*cis*	–
${}^1H_{0def}$ (G0)	−49	18	−2	17	50	68	0.497	333	48	a	*trans*	e	*trans*	e	*cis*	1.0
${}^0H_{1def}$ (G1)	55	−25	2	−8	40	−65	0.496	171	130	e	*trans*	a	*trans*	a	*cis*	1.0
${}^{2,5}B_{def}$ (G2)	46	−44	1	43	−41	−3	0.608	238	93	e	*trans*	a	*trans*	e	*cis*	3.9
${}^{2,5}B + {}^2T_4$ (G3)	54	−43	0	34	−22	−22	0.565	226	101	e	*trans*	a	*trans*	e	*cis*	3.9
${}^1E + {}^1H_0$ (A_{cr})	−50	23	−3	10	−41	62	0.448	347	49	a	*cis*	e	*cis*	e	*trans*	–
${}^1H_{0def}$ (A0)	−51	21	−3	14	−46	66	0.487	340	48	a	*cis*	e	*cis*	e	*trans*	0.0
${}^0H_{1def}$ (A1)	48	−18	1	−13	46	−65	0.471	157	130	e	*cis*	a	*cis*	a	*trans*	1.0
${}^{2,5}B_{def}$ (A2)	49	−45	−2	49	−44	−4	0.657	236	92	e	*cis*	a	*cis*	e	*trans*	5.0
${}^2S_1 + {}^2T_4$ (A3)	61	−41	−6	37	−17	−31	0.606	219	102	e	*cis*	a	*cis*	e	*trans*	5.3
$B_{2,5} + {}^0T_2$ (A4)	−20	32	−3	−37	50	−21	0.496	75	98	a	*cis*	e	*cis*	a	*trans*	4.5

[a] "cr" indicates the conformations of the crystalline forms of the molecules

[b] "e" represents a pseudo-equatorial orientation and "a" represents a pseudo-axial orientation

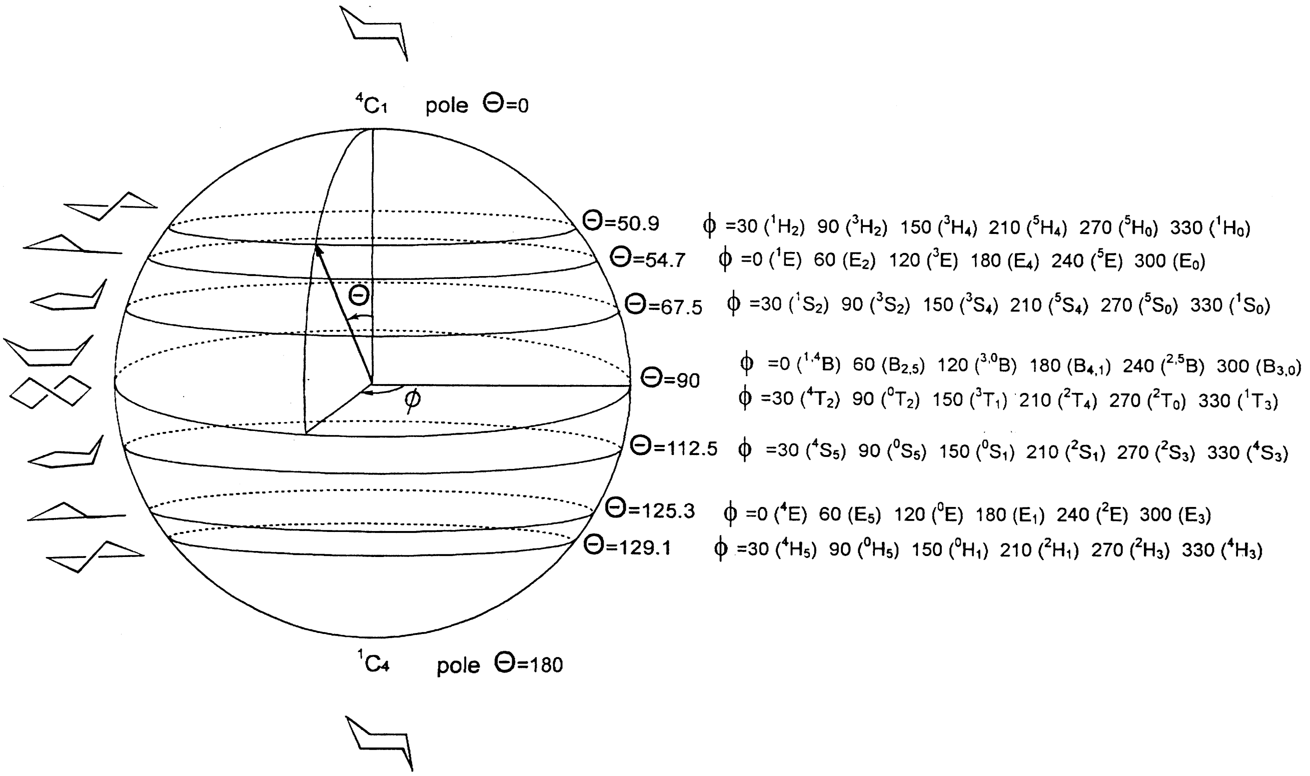

Fig. 2. The sphere proposed by Cremer and Pople on which conformations of six-membered rings can be mapped (at a constant Q). Values of angles ϕ and Θ determining special conformations are indicated in degrees

3 Results and discussion

3.1 *Interconversion pathways*

We calculated conformational parameters, the energy of stationary forms, and energies of conformational transitions of the epoxysaccharide molecules. Based on the calculations, Cremer–Pople diagrams for interconversion pathways of the molecules under investigation have been obtained. We have shown earlier [19] that interconversion pathways of all the molecules under investigation pass in the vicinity of certain canonical forms of the hexapyranose ring on the Cremer–Pople diagram [26]. The change in the localization of the oxirane ring from the position 2,3 to the position 3,4 can be understood as a 60° rotation of the oxirane ring within the limits of the pyranose ring. Since the oxirane ring plays an extremely important part in conformational transformations of the epoxysaccharides, it is suggested that this could be equivalent to a rotation of the Cremer–Pople diagram for interconversion pathways of 3,4–anhydropyranose rings by exactly the same angle with respect to the diagram for interconversion pathways of 2,3-anhydropyranose rings. Indeed, when the Cremer–Pople diagram of interconversion pathways of the molecules A, T, and G is rotated clockwise by an angle of 60° the presentations of interconversion pathways of all six molecules under investigation on the Cremer–Pople diagram become similar (Fig. 3). The two-dimensional polar projection of the spherical surface (Fig. 2), similar to a *pate carree* projection of the Earth's surface is represented in Fig. 3. Certain deviations of the interconversion pathways of different molecules from one another are observed within the sectors φ = 30–80°, 110–160°, 210–260°, and 280–330°. Thus, one can suggest that the structural regularities of epoxysaccharides discussed previously exert only a minute effect on the conformational properties of epoxysaccharides.

Points on the Cremer–Pople diagram correspond to steps of conformational transformations of the molecules. In most cases, torsion angles and the energy change insignificantly on each step of the conformational transformations (1–5° and 0.01–0.05 kcal mol^{-1}, respectively). However, sudden transitions are observed occasionally. In these cases, torsion angles can change by up to 67° and energy variations can be as high as 3 kcal mol^{-1}. As is evident from Fig. 3, transitions of this type are more characteristic for 2,3-anhydropyranose rings having a smaller number of substituents. The sudden transitions are observed, as a rule, on the final stage of the pathway from the original point to an enantiomer and from an enantiomer to the original point.

Conformational parameters of stationary forms revealed in the isomerization process along with their alphanumerical nomenclature are presented in Tables 1 and 2. The global minimum corresponding to the original conformation is labeled by the index 0, the corresponding enantiomer is labeled by the index 1, and local minima are labeled by indices 2 to 6. Most of them correspond to the boat (B) conformation, whereas the rest are hybrid forms: boat + twist (B + T), skew boat + twist (S + T). For 2,3-anhydropyranozides, the

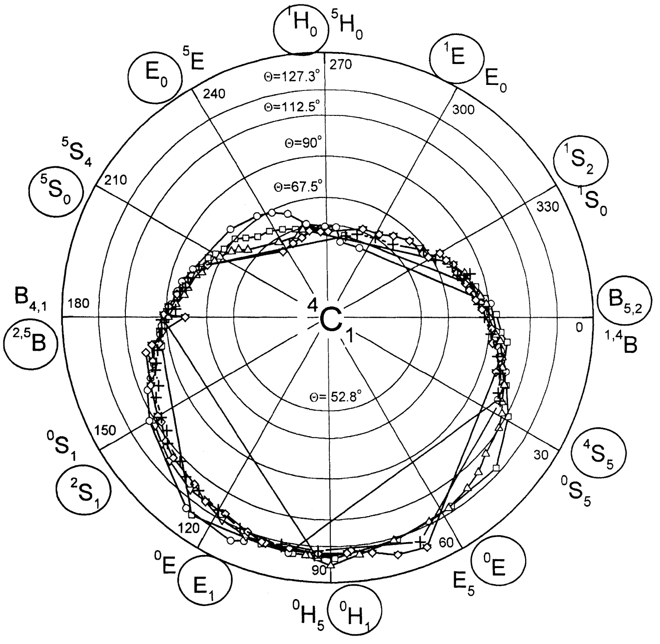

Fig. 3. Cremer–Pople diagram of interconversion pathways of the molecules under investigation: αL (■) βL (●) R (▲) T (▼) G (◆), and A (+). Canonical conformations occurring in the vicinity of the pathways are presented by alphanumerical nomenclature; symbols corresponding to the molecules A, T, and G are enclosed in *circles*. Notice that the interconversion pathways of the molecules A, T, and G are rotated clockwise by an angle of 60° with respect to their usual presentation. The interconversion pathways of the molecules A, T, G, and βL are directed clockwise, whereas the interconversion pathways of the molecules αL and R are directed counterclockwise

local minima in which the form of the skeleton is fairly close to the skew boat (S) are observed.

Earlier [19], we evaluated interconversion barriers for the six molecules under investigation. It should be noted they are not very large (from 4.3 to 6.2 kcal mol^{-1}), and the difference between levels of neighboring local minima of individual molecules does not exceed 2.6 kcal mol^{-1}, which bears witness to the high flexibility of these molecules. However, it has been found that the presence of bulky substituents leads to an increase in the energy of transitions from the original conformation to the enantiomer up to 7.2 and 8.5 kcal mol^{-1} (for molecules G and T, respectively) and thus somewhat reduces the flexibility of the molecules.

The orientation of substituents and the energy of stationary forms are presented in Tables 1 and 2. The energy was evaluated with respect to the global minimum with the lowest energy of the series of configurational isomers. These data make it possible to estimate the energy as a function of the substituent orientation, position of the oxirane ring with respect to the molecular plane, mutual disposition of substituents and the oxirane ring, and the conformation of the pyranose ring. In molecules αL, βL, and R, the orientation of the oxirane ring can change the energy of the molecule from 0.1 to 2.0 kcal mol^{-1}. The pseudo-axial position of the substituent at the C5 atom (CH_2OH) may lead to an increase in the energy of 2.6 kcal mol^{-1}, and vice versa, the pseudo-axial substituent orientation at the C1 atom (MeO) may lead to a decrease in the energy of the molecule of 1.5 kcal mol^{-1}. The *cis* position of the subsituents and the oxirane ring may correspond to an increase in energy of about 2.5 kcal mol^{-1}. Boat forms have, as a rule, a lower (by ~1–2 kcal mol^{-1}) energy compared to the skew conformation and hybrid skew + twist forms. Molecules T, A, and G have both a smaller number of stationary forms and a larger number of substituents, which complicates substantially elucidation of the above regularities. A notable increase of the steric energy observed for the conformer T4 (6.5 kcal mol^{-1}) can be explained by the pseudo-axial bulky substituents.

3.2 Normal mode analysis

To carry out the normal mode analysis of the compounds under investigation we calculated frequencies, potential energy distributions, and forms of normal vibrations for all stationary forms of the molecules using molecular mechanics.

It is evident that the assumption that a molecular vibration is localized in a particular group of atoms is the necessary condition for determination of spectrum-structure correlations. For carbohydrates, this approximation is not valid for vibrations lying in the region lower than 1500 cm^{-1}, except for the range 1200–700 cm^{-1} corresponding to vibrations of the groups of atoms peripheral to the pyranose or furanose rings of the sugar molecules known as the anomeric region [27]. Therefore, when investigating normal vibrations of the compounds, their localization was taken into account.

The presence of bands in IR spectra of carbohydrates in the region of about 1250 and 700–950 cm^{-1} bears witness to the presence of the oxirane ring [28, 29]. Our calculations have shown that vibrations more localized within the limits of the oxirane ring are situated in these frequency regions. Frequencies of vibrations of hydrogen-containing groups, i.e., C—C—H and O—C—H, coupled with stretching vibrations of C—C and C—O, are situated in the first region. Deformation vibrations of C—C—H and O—C—H, coupled with skeletal deformation vibrations of C—C—O, C—O—C, and C—C—C are situated in the second region. In the high-frequency region, frequencies of these vibrations vary within narrow ranges (several reciprocal centimeters). Therefore, we investigated only the low-frequency region where the scatter of frequencies is considerable (greater than 100 cm^{-1}).

The degree of localization of normal vibrations on particular C—C and C—O bonds forming the oxirane ring was evaluated as a sum of contributions of corresponding internal coordinates (angles at bonds under consideration) to the potential energy distributions of normal vibrations.

As is evident from Fig. 4, in the region 800–650 cm^{-1} when considerable localization of normal vibrations takes place on particular C—C and C—O bonds forming the oxirane ring, the frequency of the vibrations is dependent on the configuration and conformation of the molecules. The orientation of substituents with respect to the molecular plane and the configuration of the substituents and the oxirane ring of the molecules under investigation are presented in Tables 1 and 2. As is evident from Fig. 4, the conformers where the side groups at the C1 atom and the oxirane ring assume the *cis* configuration and where the side group has a psuedo-equatorial orientation (the molecules βL and R) have higher frequencies of normal vibrations localized preferentially in C2—C3 and C2—O2 bonds. The reverse situation is observed for the molecule αL, where the substituent at the C1 atom and the oxirane ring assume the *trans* configuration: higher frequencies of normal vibrations localized in C2—C3 and C2—O2 bonds are observed for conformers with the pseudo-axial conformation. Frequencies of normal vibrations localized preferentially in the C3—O3 bond are determined by the configuration and conformation of the side group at the C5 atom. Higher values of the frequencies are observed for conformers of the molecules αL and βL (*cis* configuration of the CH_2OH substituent at the C5 atom and the oxirane ring) when the substituent assumes the pseudo-axial orientation, and vice versa, the frequencies of the normal vibrations decrease in the case of the pseudo-axial orientation of the substituent in conformers of the molecule R (the *trans* configuration of the CH_2OH substituent at the C5 atom and the oxirane ring).

Since the molecules A, T, and G have more substituents than the above-mentioned molecules, one cannot easily reveal which of the substituents determines the frequency of vibrations localized preferentially in the C3—C4 bond (Fig. 5); however, regularities similar to those discussed previously were found for vibrations localized in C3—O3 and C4—O3 bonds. Higher frequencies of the normal vibrations localized in the C3—O3 bond are characteristic of conformers of the molecules A and T (where the side groups at the C2 atom and the oxirane ring assume the *cis* configuration) when the side group at the C2 atom assumes the pseudo-

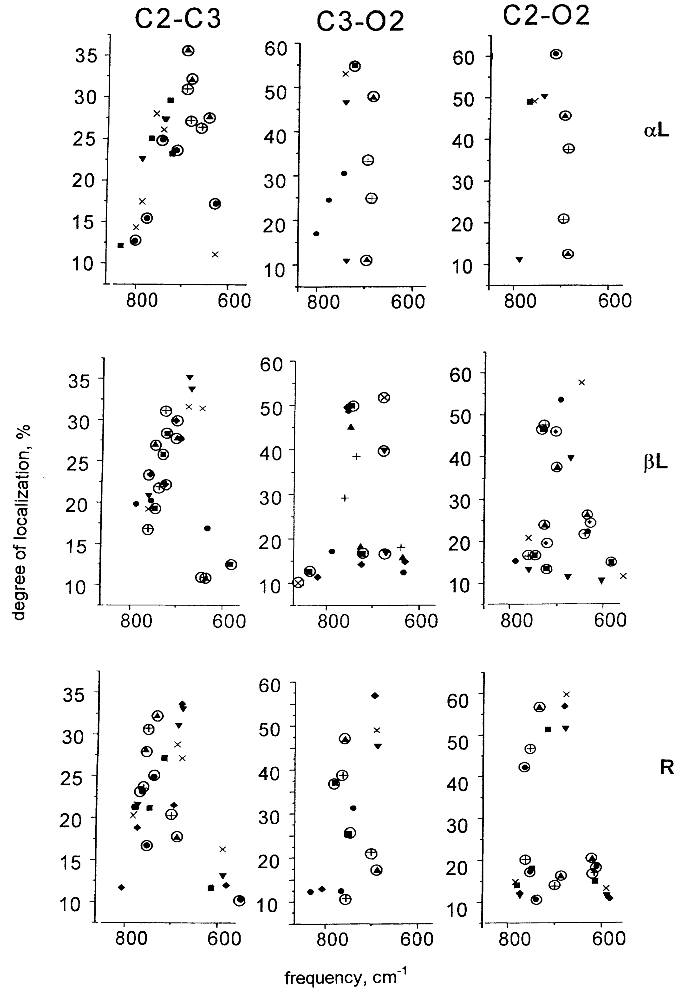

Fig. 4. Degree of localization of vibrations in particular C—C and C—O bonds forming the oxirane ring as a function of the frequency of normal vibrations of the αL, βL, and *R* molecules under investigation: αL0, βL0, R0 (■), αL1, βL1, R1 (●), αL2, βL2, R2 (▲) αL3, βL3, R3 (▼), αL4, βL4, R4 (+), αL5, βL5, R5 (×), L6, R6 (◆). Symbols enclosed in *circles* correspond to pseudo-equatorial or equatorial positions of substituents

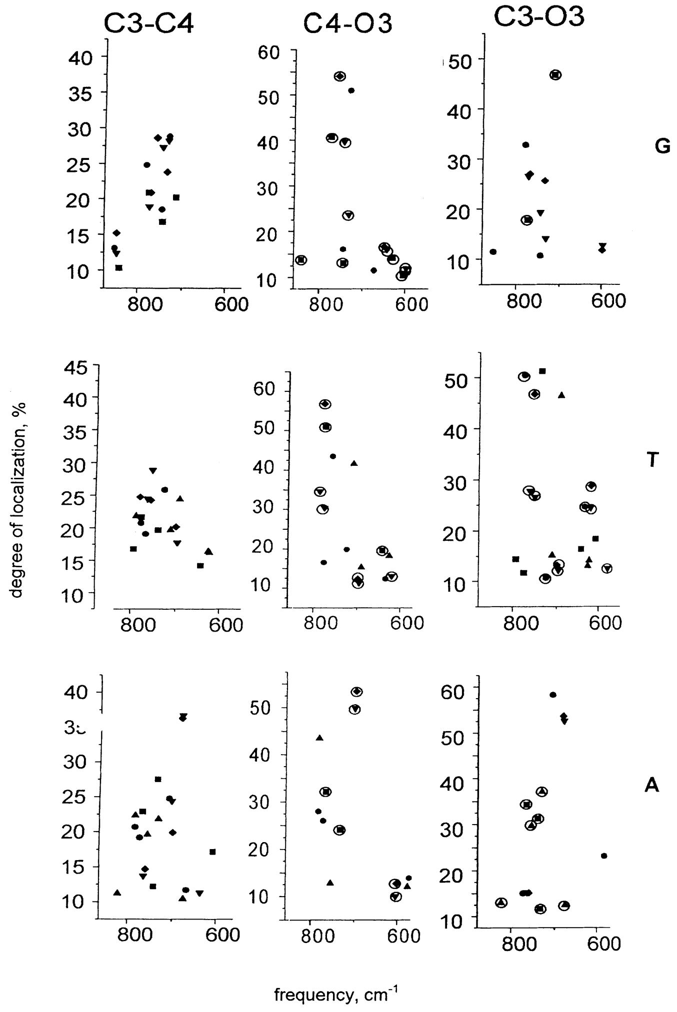

Fig. 5. Degree of localization of vibrations in particular C—C and C—O bonds forming the oxirane ring as a function of the frequency of normal vibrations of the *G*, *T*, and *A* molecules under investigation: T0, G0, A0 (■), T1, G1, A1(●), T2, G2, A2 (▼), T3, G3, A3 (◆), T4, A4 (▲). Symbols enclosed in *circles* correspond to pseudo-equatorial or equatorial positions of substituents

equatorial orientation. In the molecule G, where the AcO substituent and the oxirane ring are in the *trans* configuration, higher frequencies of the normal vibrations are observed in the case of the axial position of the substituent. The frequency of the normal vibrations localized preferentially in the C4—O3 bond is determined by the configuration and conformation of substituents at the C5 atom: when the substituent and the oxirane ring assume the *cis* configuration (molecules T and G), higher frequencies are observed with the pseudo-equatorial substituent orientation; in the case of the *trans* configuration (molecule A) higher vibration frequencies are observed for the pseudo-axial orientation of the substituent.

Conclusions

The comparative conformational analysis of the six epoxysaccharide molecules differing in the position of the oxirane ring within the pyranose ring, configuration of substituents and the oxirane ring, and the presence of bulky substituents made it possible to draw the following conclusions:

1. The struczxtural differences almost do not affect interconversion pathways of the molecules investigated.
2. Canonical conformations lying in the vicinity of the interconversion pathways in the Cremer–Pople diagram are determined by the position of the oxirane ring within the pyranose ring.
3. The presence of bulky substituents leads to a loss of the flexibility of the epoxysaccharide molecules investigated.
4. In the region 800–650 cm^{-1}, frequencies of normal vibrations localized preferentially in particular C—C or C—O bonds forming the oxirane ring depend on the configuration of the molecules and on the conformation of the pyranose ring.

References

1. Pigman WW, Goeff RM (1948) Chemistry of carbohydrates. Academic Press, New York, p 345
2. Schuerch C (1981) Adv Carbohydr Chem Biochem 39:157
3. Buchanan JG, Sable HZ (1972) In: Thyagarajan BS (ed) Selective organic transformations. Wiley, New York, p 2
4. Reeves RE (1958) Annu Rev Biochem 27:15
5. Ferro DR, Provasoli A, Ragazzi M, Casu B, Torri G, Bossennec V, Perly B, Sinay P, Petitou M, Choay J (1990) Carbohydr Res 195:157
6. Dowd MK, French AD, Reilly PJ (1994) Carbohydr Res 264:1
7. French AD, Brady JW (1990) In: French AD, Brady JW (eds) Computer modeling of carbohydrate molecules. ACS, Washington, DC, p 1
8. Krajewski JW, Gluzinski P, Urbanczyk-Lipkowska Z, Banaszek A, Parkanyi L, Kalman A (1985) Carbohydr Res 144:13
9. Krajewski JW, Gluzinski P, Banaszek A (1990) Carbohydr Res 203:195
10. Krajewski JW, Urbanczyk-Lipkowska Z, Gluzinski P, Banaszek A (1990) Carbohydr Res, 194:31
11. Krajewski JW, Gluzinski P, Banaszek A, Galitskii NM, Yasnitskii GA, Golikov AE, Verenich AJ (1988) Carbohydr Res 173:145
12. Prihodchenko LK, Kolosova TE, Zhbankov RG, Ratajczak H, Marchewka MK (1996) In: Carmona P, Navarro R, Hernanz A (eds) Spectroscopy of biological molecules: modern trends, Annex. UNED, Madrid, Spain p 49
13. French AD, Tran V (1990) Biopolymers 29:1599
14. Andrianov VM, Zhbankov RG (1993) Zh Strukt Khim (in Russian) 34:112
15. Polavarapu PL, Ewig CS (1992) J Comput Chem 13:1255
16. Cramer CJ, Truhlar DG (1993) J Am Chem Soc 115:5745
17. Saran A, Govil G (1971) Indian J Chem 9:1095
18. Tvaroska I, Kozar T (1986) Theor Chim Acta 70:99
19. Andrianov VM, Kirillova SG, Zhbankov RG (1997) J Mol Struct 412:103
20. Dachevskii VG (1970) Zh Strukt Khim (in Russian) 11:912
21. Andrianov VM, Zhbankov RG, Dachevskii VG (1980) Zh Strukt Khim (in Russian) 21:35
22. Wiberg KB, Boyd RH (1972) J Am Chem Soc 94:8426
23. Krajewski JW, Gluzinski P, Banaszek A, Argay G, Kalman A (1987) Carbohydr Res 166:13
24. Pietila L (1989) J Mol Struct 195:111
25. Sundius T, Rasmussen K (1980) J Mol Struct 65:215
26. Cremer D, Pople JA (1975) J Am Chem Soc 97:1354
27. Mathlouthi M, Koenig JL (1986) Adv Carbohydr Chem Biochem 44:7
28. Williams NR (1970) Adv Carbohydr Chem Biochem 25:109
29. Panov VP, Zhbankov RG (1975) Chem Conformations of sugars (in Russian). Nauka i Tekhnika, Minsk, p 142