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THEORETICAL ANALYSIS OF HYDROGEN BONDS IN CARBOHYDRATE CRYSTALS

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ABSTRACT

The rotational states of hydroxyl groups and the structure of hydrogen bonds in crystals of α-D-glucopyranose, β-D-glucopyranose, α-D-galactopyranose, β-D-galactopyranose, methyl α-D-altropyranoside,and methyl β-D-galactopyranoside are predicted by using the atom–atom potential method. Good agreement is observed between theoretical and neutron-diffraction data on the geometry of the hydrogen bond.

INTRODUCTION

Hydrogen bonds in carbohydrates have been studied extensively[1–23], and they play an important role in structure and reactivity. The hydrogen bond is a weak interaction, and its investigation by experimental and theoretical methods is difficult. Despite the unique nature of hydrogen bonding and its importance in the regulation of biological function, knowledge of hydrogen bonds in carbohydrate molecules is rather limited. The presence of several hydroxyl groups in carbohydrate molecules allows various possibilities for hydrogen bonding. The carbon and oxygen atoms are rigidly fixed in the carbohydrate molecule, whereas the hydrogen atoms of hydroxyl groups have a higher freedom of motion; rotation about the C-O bonds is hindered mainly by hydrogen bonding. Intermolecular hydrogen-bonds are the determining factor in the crystal packing of carbohydrate molecules. The geometry of hydrogen bonds in a crystal is usually studied by X-ray and neutron-diffraction methods. The X-ray method, although more widely used, gives a less precise spatial location of hydrogen atoms than neutron diffraction. In some cases, this has led to erroneous conclusions concerning the geometry of hydrogen bonds in crystals[12]. The method of atom–atom potentials has proved to be very useful in the theoretical analysis of hydrogen bonds in crystals, and has considerable predictive power[2,24]. However, determination of the optimal arrangement of molecules in a crystal requires large amounts of computer time. The location of hydrogen-bonded hydrogen atoms is much easier when X-ray structural data on molecular packing are used. The strategy of establishing a hydrogen-bond framework for a given packing involves the determination of minimum energy structures. Tactically, it is better to start with a theoreti-

cal analysis of the distances between atoms participating in hydrogen bonding and then to minimise the potential energies of the selected structures having the highest number of relatively short hydrogen-bonds. The number of such structures will depend on the complexity of the hydrogen-bond system.

We now report on the determination of the hydrogen-bond geometry in crystals of α-D-glucopyranose, β-D-glucopyranose, α-D-galactopyranose, β-D-galactopyranose, methyl α-D-altropyranoside, and methyl β-D-galactopyranoside by the atom–atom potential method.

CALCULATIONS

The analysis of hydroxyl-group rotamers and hydrogen bonds in the foregoing crystals was performed by using our programme "Kristall", on the basis of known co-ordinates of the atoms C, O, and H in CH groups. Local systems of co-ordinates characterised by triplets of mutually orthogonal vectors $\vec{\alpha}$, $\vec{\beta}$, $\vec{\gamma}$ were assigned to C-1–C-4 and C-6 in D-aldopyranoses, and to C-2, C-3, C-4, and C-6 in methyl D-aldopyranosides: the triplet of vectors $\vec{i}$, $\vec{j}$, $\vec{k}$ determined a reference co-ordinate system (see Fig. 1) The system of coordinates $\vec{\alpha}$, $\vec{\beta}$, $\vec{\gamma}$ was located in space through co-ordinates of O-5, C-1, O-1, C-i, C-i+1, O-i+1 (i = 1, 2, 3), C-5, C-6, and O-6. The co-ordinates of hydroxyl hydrogen atoms were calculated from the angles φ and χ and the C-O and O-H bond-lengths by using standard matrix treatment[25] Conversion into the reference co-ordinate system was carried out by using cosines of angles between vectors $\vec{\alpha}$, $\vec{\beta}$, and $\vec{\gamma}$, and unit vectors $\vec{i}$, $\vec{j}$, and $\vec{k}$, of the reference co-ordinate system. The lattice cell was generated by "multiplication" of co-ordinates of the initial molecule on the basis of the number of molecules in the cell (Z) and its space group. Thus, for the group $P2_12_12_1$, Z = 4 (observed for all the compounds studied), the atomic co-ordinates were calculated from the expressions

$$x_2 = a/2 - x_1, \quad x_3 = a/2 + x_1, \quad x_4 = -x_1,$$
$$y_2 = -y_1, \quad y_3 = b/2 - y_1, \quad y_4 = b/2 + y_1,$$
$$z_2 = c/2 + z_1, \quad z_3 = -z_1, \text{ and } \quad z_4 = c/2 - z_1,$$

where a, b, and c are unit-cell parameters, and x_1, y_1, and z_1 are atomic co-ordinates of the initial molecule in the reference system. The unit cell thus obtained, by translation along crystallographic axes a, b, and c, was surrounded with twenty-six similar cells. In order to save computer time, only the interactions of atoms encountered in a

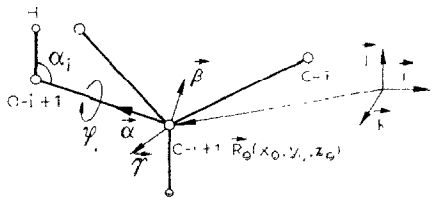

Fig. 1. The scheme of local co-ordinate systems.

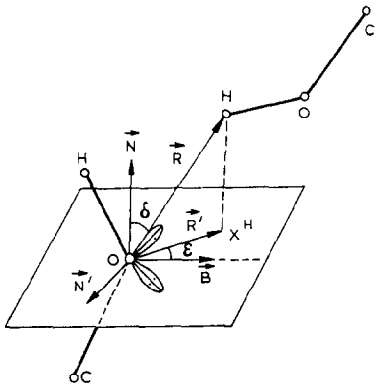

Fig. 2. Hydrogen-bond parameters: δ, the angle between the normal $\vec{N}$ to the acceptor plane containing the oxygen acceptor-atom and two orbitals of lone pairs of electrons and the hydrogen-bond vector $\vec{R}$; ε, the angle between vector $\vec{R}'$ (projection of vector $\vec{R}$ onto the acceptor plane) and vector $\vec{B}$, directed along the bisector of the angle between lone-pair orbitals.

sphere of radius 0.6 nm around each hydroxyl oxygen atom of all molecules in the crystallographic cell were taken into account. Such a cut-off enables the energy of pair-wise interaction of hydrogen atoms with all surrounding atoms to be estimated with reasonable accuracy.

When searching for hydrogen bonds in the crystals, it was taken into account that bonds are formed at certain mutual orientations of the orbitals of lone pairs of electrons on each oxygen acceptor and the direction of the straight line connecting the potential acceptor and donor. Fig. 2 shows the angles of orientation of the straight line O···H in respect to oxygen-acceptor orbitals. The angle δ characterises the deviation of the hydrogen-bond direction from the acceptor plane, and ε that from

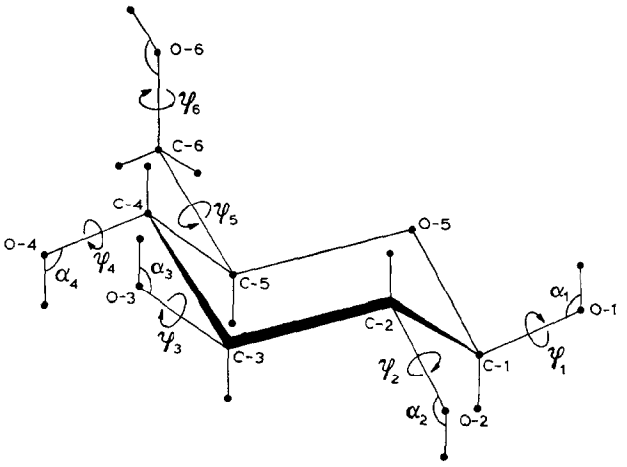

Fig. 3. β-D-Glucopyranose molecule. Hydrogen atoms are not indicated.

the direction of the bisector of the angle between the orbitals. The plane of the orbitals is normal[3] to the plane formed by atoms C, O, and H. Vectors B, N, N', R, and R' are introduced for calculation of the angles δ and ε. The vectors are determined from the co-ordinates of the corresponding C, H, and O atoms in the reference system. The search for hydrogen bonds consisted in determination of hydroxyl-group orientations at which the distance L (H-i–O-k) = 0.25 nm, and the angles δ and ε fall within the range of angles typical of hydrogen bonding[3].

The torsional angles φ_1–φ_4, which describe the rotation of the hydroxyl groups at C-1 to C-4, and φ_6 (the same for the CH_2OH group) are counted clockwise in the direction of bonds O→C and C-6→C-5 in accordance with the notation proposed[26] for aldopyranoses and their derivatives. Zero values of the angles φ_1–φ_4 correspond to antiparallel or *trans* arrangements of C-H and O-H bonds, respectively, and the angles φ_5 and φ_6 to antiparallel arrangement of bonds C-5–H-5 and C-6–O-6, and C-5–C-6 and O-6–H-6 (Fig. 3). The torsional angle φ_5 was not varied, C-6 and O-6 being located according to diffraction data. For methyl α-D-altropyranoside and methyl β-D-galactopyranoside, the angle φ_1 was fixed, *i.e.*, the position of MeO-1 was not varied. The O-H bond-length was taken[5,6,14–23] as an average value of 0.097 nm, and the angle COH as 109.5 .

The potential energy of the crystal fragment included the potentials of non-bonded and electrostatic interactions, hydrogen-bond potentials, and torsional potentials. Torsional energies were calculated from the formula $U_{tors} = U_0/2(\cos 3\varphi + 1)$, with $U_0 = 4.184$ kJ.mol^{-1}. Pairwise, non-bonded interactions were described by the Lennard-Jones potential ($U_{nb} = A/r^6 + B/r^{12}$). Intramolecular interactions were calculated by using the Scott and Sheraga constants[27]. The parameters of non-bonded interactions of the type $CH_3\cdots CH_3$, $CH_3\cdots C$, $CH_3\cdots O$, and $CH_3\cdots H$ were taken from published data[28]. Intermolecular interactions of atoms in the crystal were calculated by using potentials that were chosen on the basis of data on the packing of a large number of organic molecules in their crystals[29]. The parameters A for cross interactions were calculated from the Slater–Kirkwood formula[30] by using atom polarisability data[31,32], and the parameters B according to the published method[29] from A and the equilibrium distances r_0 for the corresponding atomic pairs. Electrostatic interactions were calculated in the monopole approximation, using the net atomic charges and effective dielectric constant ($\varepsilon_{eff} = 2$) that were employed[4] in fitting the potential parameters for the intermolecular O-H···O hydrogen-bond. The energies of intra- and inter-molecular hydrogen-bonds were calculated as

$$U_{hb} = A/r_{OH}^{10} - B/r_{OH}^{12},$$

with A and B taken for intramolecular[33] and intermolecular interactions[4], respectively.

Minimisation of the crystal energy as a function of the torsional angles φ_1–φ_4 and φ_6 was carried out in two stages. In the first stage, the hydroxyl-group rotamers and possible hydrogen-bonds were analysed by varying the torsional angles φ_1–φ_4 and φ_6 at intervals of 5–10 . In doing so, the crystal energies, including the energies

of possible intra- and inter-molecular hydrogen-bonds, were calculated. From a selected set of crystal configurations thus obtained, the most probable spatial structure and the corresponding hydrogen-bond system were then established by minimisation of the crystal energy with respect to the torsional angles φ_1–φ_4 and φ_6. The minimisation was carried out by the Davidon–Fletcher–Powell method[2,24].

RESULTS AND DISCUSSION

The most accurate co-ordinates of hydroxyl hydrogen atoms are obtained by neutron diffraction. The crystal structures of α-D-glucopyranose[5,21] and methyl α-D-altropyranoside[6] were determined by this method. These compounds, with known hydrogen-bond geometry, were used to verify the predictive power of the

TABLE I

TORSIONAL ANGLES OF HYDROXYL GROUPS (ψ_i), AND TYPES, LENGTHS (L), AND ENERGIES OF HYDROGEN BONDS IN α-D-GLUCOPYRANOSE AND METHYL α-D-ALTROPYRANOSIDE CRYSTALS

Hydrogen bond HO-i···O-k	ψ_i *(degrees)*	*L (nm)*	$-U_{hb}$ *(kJ.mol^{-1})*
α-D-Glucopyranose			
HO-1···O-5	138[a]	0.191	—
	133[a]	0.193	9.4
HO-2···O-6	−37	0.182	—
	−40	0.181	13.2
HO-3···O-2	134	0.176	—
	138	0.175	14.6
HO-4···O-4	−164	0.182	—
	−163	0.183	12.5
HO-6···O-3	37	0.176	—
	39	0.176	14.4
Methyl α-D-altropyranoside			
HO-2···O-3	173	0.192	—
	175	0.191	9.9
HO-3···O-4	−78	0.214	—
	−83	0.219	3.7
Intramolecular			
HO-3···O-5	−78	0.219	—
	−83	0.227	2.8
HO-4···O-6	138	0.174	—
	141	0.176	14.4
HO-6···O-1	−110	0.209	—
	−115	0.205	6.2
HO-6···O-3	−110	0.214	—
	−115	0.221	3.5

[a]The upper figure is the value determined from neutron-diffraction experiments; the lower figure is the calculated value.

technique used for calculating the energy of intra- and inter-molecular interactions.

α-D-Glucopyranose. — The analysis of the crystal energy of α-D-glucopyranose gives the preferred structure with five intermolecular hydrogen-bonds, and the parameters are very close to those reported[5,21]. The packing of α-D-glucopyranose molecules observed in the neutron-diffraction experiment satisfies the minimum crystal energy as a function of the angles φ_1–φ_4 and φ_6. Crystal structures having other arrangements of hydroxyl groups are impossible, since their energy exceeds that of the optimal structure by more than 80 kJ.mol^{-1}. The types and energies of the hydrogen bonds, the torsional angles φ characterising the orientation of the hydroxyl groups, and the distances L between the hydrogen-bond donor (H-i) and acceptor (O-k) in the α-D-glucopyranose crystal are listed in Table I. Complete agreement is observed between the hydrogen-bond systems established[5,21] and that predicted on the basis of theoretical analysis of rotamers of hydroxyl groups in the α-D-glucopyranose crystal. The calculated data, as well as the diffraction data, indicate the absence of intramolecular hydrogen-bonds in crystalline α-D-glucopyranose. It should be noted that O-1 does not participate in hydrogen-bond formation. The anomeric hydroxyl (HO-1) exhibits more properties of a donor than of an acceptor. The experimental and calculated values for the corresponding torsional angles are similar (deviations $<5°$). The values of hydroxyl-group rotation-angles in the α-D-glucopyranose crystal do not correspond to orientations typical of an isolated molecule[26]. Intermolecular interactions, primarily intermolecular hydrogen-bonds, are responsible for the spatial arrangement of hydroxyl groups in the crystal. The agreement between experimental and calculated hydrogen-bond lengths suggests a considerable predictive power for the calculation technique.

Apart from the geometrical parameters, the hydrogen-bond energies were also calculated (see Table I), which are necessary for interpretation of the vibrational spectra of crystalline α-D-glucopyranose. As seen from Table I, in the α-D-glucopyranose crystal, there are two relatively strong hydrogen-bonds (HO-3···O-2 and HO-6···O-3), two slightly weaker (HO-4···O-4, HO-2···O-6), and one of moderate energy (HO-1···O-5). The energies of these hydrogen bonds differed by no more than 5.2 kJ.mol^{-1}.

Methyl α-D-altropyranoside. — According to neutron-diffraction data, the formation of one intramolecular and five intermolecular hydrogen-bonds is possible in the methyl α-D-altropyranoside crystal[6]. The hydrogen-bonding system calculated from an analysis of preferred orientations of hydroxyl groups is similar to that observed experimentally (see Table I). The minimum-energy crystal structure is characterised by a broad spectrum of hydrogen bonding; five intermolecular and one intramolecular bonds are observed. The calculated torsional angles φ_2, φ_3, φ_4, and φ_6 (MeO-1 was fixed according to ref. 6) are close to the experimental ones. Hydrogen-bond lengths are also in good agreement. The hydroxyl at C-3 may simultaneously participate in formation of a weak intramolecular (HO-3···O-4) and a weak intermolecular (HO-3···O-5) hydrogen bond.

The primary hydroxyl-group forms intermolecular bonds with O-1 and O-3:

O-2 does not participate in hydrogen bonding. The strongest intermolecular bond is formed by HO-4 and O-6, the weakest by HO-3 and O-5.

The good predictive capacity of the method allows its use for obtaining sufficiently reliable information about the spatial orientation of hydroxyl groups, and possible hydrogen-bond systems and their parameters in crystals of D-aldopyranoses and their partially substituted derivatives, whose molecular structures have been determined by X-ray diffraction, but for which the locations of hydroxyl protons and therefore the hydrogen-bond geometry are either unknown or known with low accuracy. The crystal and molecular structures of β-D-glucopyranose[7], α-D-galactopyranose[8,9], β-D-galactopyranose[8,10], and methyl β-D-galactopyranoside[11] have been determined by X-ray diffraction analysis, but the types and geometrical parameters of hydrogen bonds proposed cannot be considered as sufficiently reliable because of the inaccuracy in the location of hydrogen atoms inherent in this method.

β-D-Glucopyranose. — The system of hydrogen bonds proposed[7] from an analysis of the distances between oxygen atoms includes four intermolecular hydrogen-bonds. According to our calculations, in addition to these bonds[7], the formation of a weak intermolecular-bond HO-4···O-2 is possible in the β-D-glucopyranose crystal. The angles of internal rotation of hydroxyl groups show considerable deviations from the "ideal" values corresponding to *trans* or *gauche* orientations[26]. The positions of hydroxyl groups in the β-D-glucopyranose crystal are thus determined by intermolecular interaction and, primarily, by intermolecular hydrogen-bonds.

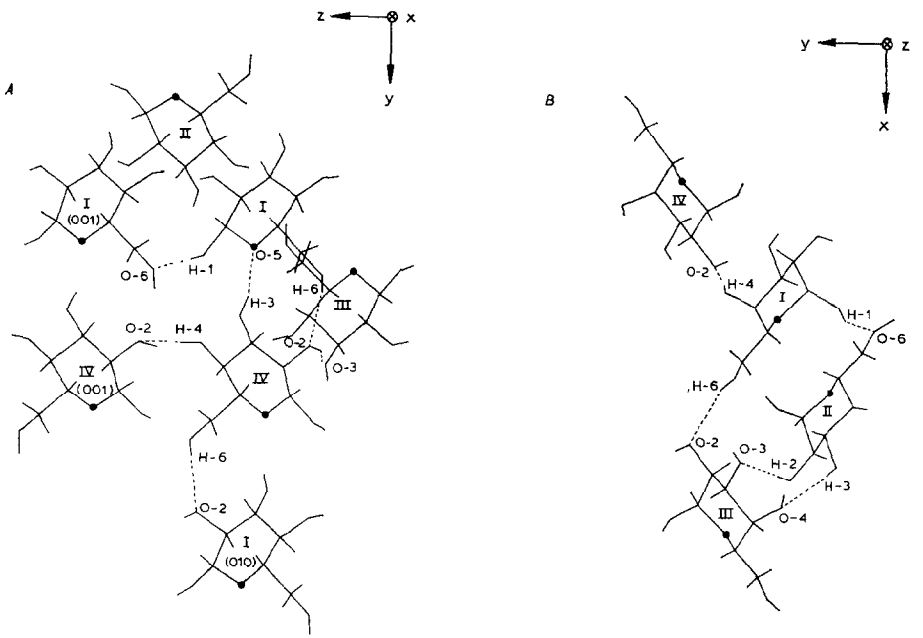

Fig. 4. Packing of molecules and hydrogen-bond schemes in *A*, β-D-glucopyranose; and *B*, α-D-galactopyranose crystals.

TABLE II

HYDROGEN BONDS AND THEIR PARAMETERS IN CARBOHYDRATE CRYSTALS

Hydrogen bond HO-i···O-k	*L (nm)*	*$-U_{hb}$ (kJ.mol^{-1})*	*Hydrogen bond HO-i··· O-k*	*L (nm)*	*U_{hb} (kJ.mol^{-1})*
β-D-Glucopyranose			*β-D-Galactopyranose*		
HO-1· ·O-6	0.176	14.4	HO-1 O-6	0.172	15.1
HO-2·· O-3	0.180	13.4	HO-2·· O-4	0.188	11.0
HO-3···O-5	0.182	12.9	HO-3···O-1	0.206	6.0
HO-4···O-2	0.234	2.2	HO-4 · O-3	0.191	9.9
HO-6· ·O-2	0.174	14.9	HO-6···O-2	0.179	14.0
α-D-Galactopyranose			*Methyl β-D-galactopyranoside*		
HO-1···O-6	0.176	14.5	HO-2· ·O-4	0.180	13.3
HO-2···O-3	0.174	14.9	HO-3·· O-1	0.236	2.1
HO-3···O-4	0.196	8.4	HO-3 ··O-4[a]	0.235	2.1
HO-4···O-2	0.194	9.0	HO-4 ··O-6	0.179	13.6
HO-6 ··O-2	0.187	11.4	HO-6 ·O-2	0.188	10.8

[a]Intramolecular hydrogen-bond

Fig. 4 shows the packing of β-D-glucopyranose molecules in the crystal, with an indication of the hydrogen bonds that satisfy the overall minimum of the crystal energy. The types, lengths, and energies of hydrogen bonds in the β-D-glucopyranose crystal are listed in Table II. According to the magnitude of the energy, the intermolecular hydrogen-bonds may be divided into three groups, namely, strong bonds (HO-6···O-2 and HO-1···O-6), moderate bonds (HO-2· ·O-3 and HO-3···O-5), and weak bonds (HO-4·· O-2); O-1 and O-4 do not participate in the formation of hydrogen bonds.

α-D-*Galactopyranose*. — Two independent studies of molecule packing in α-D-

TABLE III

TORSIONAL ANGLES (φ_1) AND HYDROGEN BONDS IN α-D-GALACTOPYRANOSE CRYSTAL

Experiment				*Theory*	
8		*9*			
φ_1 (degrees)	*Hydrogen bond*	*φ_1 (degrees)*	*Hydrogen bond*	*φ_1 (degrees)*	*Hydrogen bond*
−76	HO-1· ·O-3	110	HO-1···O-6	136	HO-1 ··O-6
−155	HO-2· ·O-6	11	HO-2·· O-3	2	HO-2·· O-3
−145	HO-3 · O-4	123	HO-3· ·O-4	133	HO-3 O-4
0	HO-4···O-2	61	HO-4···O-2	3	HO-4 · O-2
138	HO-6·· O-1	10	HO-6 ··O-2	−7	HO-6·· O-2

galactopyranose crystals[8,9] suggest two different schemes of hydrogen bonding, although the locations of O and C atoms in each structure are practically coincident. Using the co-ordinates of atoms C, O, and H (CH groups) from ref. 8, the locations of hydroxyl groups, and the types, lengths, and energies of hydrogen bonds were determined by searching for the minimum of crystal energy with respect to the angles φ_1–φ_4 and φ_6. The values of the torsional angles of hydroxyl groups and hydrogen-bond types reported[8,9], and those calculated in this work, are listed in Table III. The calculations give preference to the reported[9] hydrogen-bond scheme. Other calculated crystal-structures possess an excess of energy exceeding 80 kJ.mol^{-1}. Only intermolecular hydrogen-bonds are formed upon packing of α-D-galactopyranose molecules. The oxygen of HO-1 does not participate in donor–acceptor interactions with protons of other hydroxyl groups; a similar situation was reported in ref. 9. In the hydrogen-bond scheme proposed[8], the HO-1 group behaves as a proton acceptor, which does not agree with the calculation results. The torsional angles of stable hydroxyl-group orientations at C-1–C-4 and C-6, determined from atomic co-ordinates[9], are relatively close to the calculated angles (deviations do not exceed 25°). The angle φ_4, however, correlates better with other data[8]. The location of the hydrogen atom in HO-4 requires experimental verification, as noted by others[9]. The calculated values of the angles φ_1–φ_4 and φ_6 are within the range typical of *gauche* and *trans* orientations of hydroxyl groups in an isolated α-D-galactopyranose molecule[26]. The calculated crystal-packing of α-D-galactopyranose is shown in Fig. 4, together with an indication of the hydrogen bonds. Hydrogen bonds and their parameters in the α-D-galactopyranose csystal are listed in Table II. With respect to energy, the hydrogen bonds may be divided into two groups: strong (HO-1···O-6 and HO-2···O-3) and moderate (HO-6···O-2, HO-3···O-4, and HO-4···O-2); O-1 and O-5 do not form hydrogen bonds.

β-D-Galactopyranose. — X-Ray structural studies of crystalline β-D-galactopyranose[8,10] gave identical schemes of hydrogen bonding. However, hydrogen-atom locations were determined with insufficient accuracy. The theoretical analysis of rotamers of hydroxyl groups and hydrogen bonds (using data[8,10] on crystal packing and on pyranoid-ring geometry) allowed the geometrical parameters to be refined and the bond energies to be calculated. The calculated scheme of hydrogen bonds coincides with that proposed[8,10]. Only intermolecular hydrogen-bonds are observed in the β-D-galactopyranose crystal. Two torsional angles φ_1 and φ_2 have values corresponding to *gauche* orientations of hydroxyl groups. The oxygen of HO-1 participates in hydrogen-bond formation. The types, lengths, and energies of the hydrogen bonds are listed in Table II. With respect to energy, the hydrogen bonds may be classified as strong (HO-1···O-6 and HO-6···O-2), moderate (HO-2···O-4 and HO-4···O-3), and relatively weak (HO-3···O-1), O-5 does not participate in hydrogen-bond formation.

Methyl β-D-galactopyranoside. — The analysis of the positions of hydroxyl groups and hydrogen bonds in the methyl β-D-galactopyranoside crystal showed that the hydrogen-bond system corresponding to the overall minimum of crystal

energy with respect to angles φ_2, φ_3, φ_4, and φ_6 (φ_1 was fixed at the experimental value) is similar to the scheme proposed[11] on the basis of an X-ray structural study. The calculations do not exclude a very weak, intramolecular hydrogen-bond of the type HO-3···O-4. The values of torsional angles of stable hydroxyl-group positions show considerable deviations from "ideal" orientations[20]. The types, lengths, and energies of the hydrogen bonds in the methyl β-D-galactopyranoside crystal are listed in Table II. With respect to energy, the hydrogen bonds may be classified as strong (HO-2···O-4 and HO-4···O-6), moderate (HO-6···O-2), and very weak (HO-3···O-1) intermolecular hydrogen-bonds, and a very weak intramolecular bond (HO-3···O-4); O-3 and O-5 do not participate in hydrogen-bond formation.

According to calculations, HO-1 in β-D-glucopyranose, α-D-galactopyranose, and β-D-galactopyranose crystals form the same type of intermolecular hydrogen-bond, HO-1···O-6, and the highest energy value corresponds to this type of hydrogen bond. All hydroxyl groups in the carbohydrate crystals considered are involved in hydrogen bonds, and all hydrogen atoms and the majority of hydroxyl oxygen atoms participate in their formation. The energies of hydrogen bonds, however, differ considerably. The length of some bonds is close to the critical distance of hydrogen bonding established by statistical treatment of structural data for a large number of organic compounds[33,34]. At the same time, the i.r. spectra of crystalline monosaccharides do not exhibit absorption bands typical of free hydroxyl groups[32]. It is intermolecular hydrogen-bonding that determines the orientation of hydroxyl groups and the crystal packing of D-aldopyranose molecules. Of the compounds studied here, D-aldopyranose molecules form stronger hydrogen-bonds than their methyl glycosides.

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