

Standard geometrical models for hexopyranoses

I. TVAROŠKA and J. GAJDOŠ

*Institute of Chemistry, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 38 Bratislava*

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Standard geometries for both anomers of eight hexopyranoses in 4C_1 chair form have been determined and given in the form of orthogonal coordinates. The structures of the pyranose ring correspond to averaged structures of rings determined by Sheldrick and Akrigg from 161 experimental structures. Geometrical parameters of ring substituents have been determined by the MM2CARB force-field method. The individual standard models of hexopyranoses are characterized by van der Waals surface and volume as well as by charge distribution, dipole moment, and ionization potential calculated by the semiempirical quantum-chemical PCILO method.

Определены и представлены в виде ортогональных координат стандартные геометрии обоих аномеров восьми гексапираноз в форме кресла 4C_1 . Строение пиранового кольца отвечает усредненной структуре колец, определенной Шелдриком и Акриггом, исходя из 161 экспериментальных структур. Геометрические параметры для заместителей в кольце были определены с помощью метода силового поля MM2CARB. Отдельные стандартные модели гексапираноз характеризуются ван дер Ваальсовыми поверхностью и объемом, а также распределением зарядов, дипольным моментом и потенциалом ионизации, рассчитанными с помощью полуэмпирического квантово-химического метода PCILO.

Conformational analysis of oligo- and polysaccharides as well as study of their structures by diffraction methods require explicitly Cartesian coordinates for all atoms. Since the problem studied is complicated, it is frequently necessary to take the monosaccharide unit for a rigid body, *i.e.* for a group where the interatomic distances and angles between vectors connecting the atoms remain invariant at rotation around arbitrary axis or translation in arbitrary direction. The use of experimental geometry of the given residue seems to be an obvious solution. However, statistical analysis of known structures of saccharides has shown that the structure of pyranose ring is sensitive to conformation at the glycosidic bond [1—3]. Likewise, investigation of influence of the geometry used [4, 5] on conformational energies of oligosaccharides revealed that application of geometry corresponding to a certain conformation affects the calculated abundance of conformers and the stability of this conformation is overesti-

mated. One of the ways avoiding this problem is the use of the so-called average geometry. *Arnott* and *Scott* [6] published the average geometry for α - and β -D-glucopyranose, determined from known experimental structures. Recently, *Sheldrick* and *Akrigg* [7] have calculated the geometry of average pyranose ring for eight hexopyranoses on the basis of 161 structures containing pyranose ring. However, geometrical parameters defining the positions of ring substituents were not determined. Therefore, the need of standard models of hexopyranoses which could be applied both to known and unknown structures of oligo- and polysaccharides is obvious.

In this report we present standard geometrical models for eight hexopyranoses in both anomeric forms calculated by the MM2CARB force-field method [5]. Our calculations were based on average geometries of pyranose ring published by *Sheldrick* and *Akrigg* [7]. The individual models of hexopyranoses are characterized by quantities, *e.g.* atomic charges, dipole moment, van der Waals surface and volume, which are frequently utilized in estimation of solvation energies.

Methods

Numbering of atoms in hexopyranose is illustrated in Fig. 1 and orientations of side groups for the individual hexopyranoses are presented in Table 1. In determination of geometry of the standard models the geometrical parameters determining the positions of all ring substituents, *i.e.* together 51 bond lengths, bond angles, and torsional angles, were optimized by the MM2CARB method [5]. This method is the MM2 force-field method [8] modified by the procedure according to *Jeffrey* and *Taylor* [9]. The structure of the ring corresponded to geometry determined by *Sheldrick* and *Akrigg* [7] and was invariant and the same for both anomers of the given hexopyranose. In calculation of Cartesian coordinates the atom C-1 was chosen for the origin of the coordinate system, *x*-axis was in the direction of the C-1—O-5 linkage and the *xy* plane was determined by the atoms C-1—O-5—C-5. For geometries obtained in such a way we calculated by the PCILO quantum-chemical method [10] electron distribution, dipole moment, and ionization potential. Van der Waals surface and van der Waals volume were calculated by using the *Herman* [11] and *Pavani* [12] programs, respectively.

Results and discussion

The calculated Cartesian coordinates together with atomic charges for all 16 hexopyranoses are presented in Tables 2—9. The distances between O-1 and other oxygen atoms are in Table 10, while Table 11 brings dipole moment, ionization potential, van der Waals surface, and van der Waals volume.

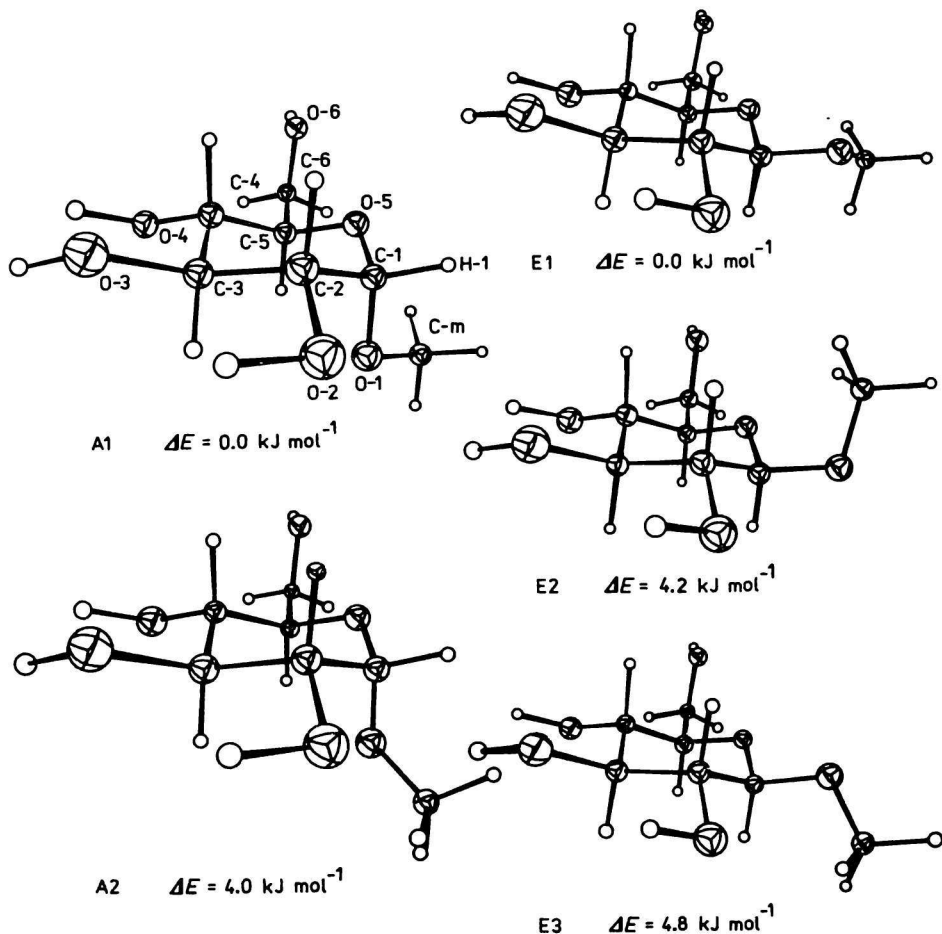


Fig. 1. Numbering scheme of atoms in hexopyranoses.

The standard models calculated in this way represent minima on the energetic surface for the given average ring structure. The average pyranose rings were obtained from different numbers of known structures available for eight hexopyranoses. The structures of glucopyranose, mannopyranose, and galactopyranose were obtained from more than 3 known structures. Thus, average geometries of the pyranose ring correspond to present available information and might be improved in the future. When there are sufficient experimental data, it will be necessary to distinguish also the average geometries of the ring for both anomers. Since the geometries of average rings were discussed in the original work [7], here we focus only on some geometrical parameters characterizing the substituents.

Table 1

Pendant groups orientations for 4C_1 chair ring form in D-hexopyranoses

Hexopyranose	Anomer	Carbon atom				
		1	2	3	4	5
Glucopyranose	α	a	e	e	e	e
	β	e	e	e	e	e
Mannopyranose	α	a	a	e	e	e
	β	e	a	e	e	e
Allopyranose	α	a	e	a	e	e
	β	e	e	a	e	e
Galactopyranose	α	a	e	e	a	e
	β	e	e	e	a	e
Talopyranose	α	a	a	e	a	e
	β	e	a	e	a	e
Altropyranose	α	a	a	a	e	e
	β	e	a	a	e	e
Gulopyranose	α	a	e	a	a	e
	β	e	e	a	a	e
Idopyranose	α	a	a	a	a	e
	β	e	a	a	a	e

a — axial, e — equatorial.

The C-O bond lengths vary in the interval of 140.9–141.6 pm and do not differ much from the standard C-O bond length 143 pm [13]. The only exception is the C-1—O-1 bond which is substantially shorter and, according to the anomeric form, falls into two intervals of magnitudes which differ significantly. The magnitude of this bond length is influenced by the anomeric effect. Due to delocalization interactions of lone pairs of oxygens, the C-1—O-1 bond is shorter than the standard C-O length and is longer in α anomers than in β anomers of saccharides [14]. This has also been observed. In α anomeric forms the C-1—O-1 bond is in the interval of 139.2–139.4 pm, while in β anomers this interval is 138.1–138.4 pm. The anomeric effect manifests itself also in differences of the bond angle O-5—C-1—O-1. In α anomer the values for the O-5—C-1—O-1 angle are in the interval of 108.1°–109.4°, while in β anomer in the interval of 103.5°–105.9°. Orientation of the hydroxymethyl group is *gauche-gauche* in all cases. However, the values of the torsion angle O-5—C-5—C-6—O-6 vary from case to case in the interval of -55° — -72° .

In conformational analysis and X-ray determinations of structure the so-called virtual bond length is an important parameter. Virtual bond is a vector connecting successive glycosidic oxygens and its use is very advantageous in many cases of model analysis of fibre polysaccharides [15]. The magnitude of

Table 2

Average coordinates and PCILO calculated net atomic charges for α -D-glucopyranose and β -D-glucopyranose

Atom	α				β			
	x/pm	y/pm	z/pm	<u>Net charge</u> e	x/pm	y/pm	z/pm	<u>Net charge</u> e
C-1	0.0	0.0	0.0	0.2289	0.0	0.0	0.0	0.2382
O-5	142.1	0.0	0.0	-0.1906	142.1	0.0	0.0	-0.1872
C-5	199.2	131.8	0.0	0.1090	199.2	131.8	0.0	0.1072
C-4	157.2	205.0	127.6	0.0867	157.2	205.0	127.6	0.0850
C-3	5.4	208.2	138.5	0.0966	5.4	208.2	138.5	0.0917
C-2	-51.0	67.3	127.0	0.0816	-51.0	67.3	127.0	0.0737
C-6	351.7	121.3	-17.6	0.1127	351.7	121.3	-17.8	0.1146
O-6	410.7	72.0	100.5	-0.1722	410.7	72.0	100.3	-0.1715
O-1	-44.1	64.0	-115.5	-0.2054	-32.4	-134.5	-4.6	-0.2019
O-4	208.4	336.5	126.1	-0.1938	208.0	336.7	125.4	-0.1942
O-3	-31.6	263.0	263.3	-0.1959	-31.8	263.1	263.2	-0.1923
O-2	-191.9	69.8	127.8	-0.1826	-191.7	74.4	122.7	-0.1832
H-1	-31.0	-105.3	-9.9	-0.0382	-32.9	43.8	-95.6	-0.0548
H-O1	1.2	23.0	-190.8	0.1176	43.2	-180.3	-44.6	0.1283
H-5	156.6	181.3	-90.8	-0.0192	156.4	181.2	-90.7	-0.0317
H-61	376.2	51.3	-101.0	-0.0201	376.1	51.2	-101.2	-0.0190
H-62	397.2	221.0	-38.7	-0.0275	397.3	220.9	-39.0	-0.0273
H-O6	501.4	43.8	80.7	0.1051	501.3	43.8	80.7	0.1063
H-4	198.5	153.1	217.3	-0.0082	198.7	153.4	217.4	-0.0042
H-O4	299.1	333.6	160.4	0.1126	298.2	334.44	161.0	0.1138
H-3	-38.1	273.2	58.6	-0.0118	-37.6	273.3	58.5	-0.0211
H-O3	2.3	353.9	265.4	0.1166	2.7	353.7	266.2	0.1171
H-2	-18.0	5.6	214.1	-0.0219	-21.2	4.5	214.5	-0.0061
H-O2	-219.7	117.1	207.7	0.1198	-221.5	109.9	207.9	0.1187

Table 3

Average coordinates and PCILO calculated net atomic charges for α -D-mannopyranose and β -D-mannopyranose

Atom	α				β			
	x/pm	y/pm	z/pm	Net charge e	x/pm	y/pm	z/pm	Net charge e
C-1	0.0	0.0	0.0	0.2177	0.0	0.0	0.0	0.2285
O-5	141.0	0.0	0.0	-0.1853	141.0	0.0	0.0	-0.1799
C-5	201.3	131.6	0.0	0.1197	201.3	131.6	0.0	0.1094
C-4	154.9	210.3	121.2	0.0888	154.9	210.3	121.2	0.0899
C-3	4.7	218.0	124.8	0.0914	4.7	218.0	124.8	0.1120
C-2	-55.7	77.8	118.9	0.0735	-55.7	77.8	118.9	0.0710
C-6	354.0	114.3	-7.4	0.1153	354.1	117.6	-11.4	0.1153
O-6	400.1	49.3	109.1	-0.1683	407.6	70.1	110.1	-0.1693
O-1	-44.0	56.6	-119.3	-0.2197	-36.7	-133.3	3.8	-0.2120
O-4	207.3	341.5	114.8	-0.1960	209.3	340.5	114.7	-0.1974
O-3	-38.4	287.2	240.2	-0.1866	-40.4	287.3	239.2	-0.1831
O-2	-20.9	3.3	233.8	-0.1893	-20.1	4.3	234.1	-0.1753
H-1	-31.7	-105.6	-4.0	-0.0370	-31.4	38.5	-98.4	-0.0651
H-O1	6.0	14.9	-191.0	0.1219	45.1	-183.6	-10.3	0.1360
H-5	165.1	178.7	-94.7	-0.0216	163.3	178.0	-94.3	-0.0342
H-61	381.3	50.5	-94.9	-0.0257	380.4	44.9	-91.9	-0.0205
H-62	406.9	212.2	-15.6	-0.0220	402.6	215.7	-33.3	-0.0272
H-O6	494.8	30.7	98.7	0.1031	499.1	41.7	95.4	0.1054
H-4	193.8	163.3	214.6	-0.0054	191.8	163.0	215.3	0.0066
H-O4	212.3	375.1	205.6	0.1134	295.1	338.6	160.0	0.1130
H-3	-32.8	275.5	36.5	-0.0195	-31.9	275.9	36.4	-0.0381
H-O3	-42.8	382.0	219.6	0.1094	2.0	374.6	239.8	0.1159
H-2	-167.3	81.7	113.3	0.0034	-167.3	80.7	114.1	-0.0201
H-O2	73.2	-20.4	231.3	0.1188	-57.5	-84.7	225.3	0.1193

Table 4

Average coordinates and PCILO calculated net atomic charges for α -D-allopyranose and β -D-allopyranose

Atom	α				β			
	x/pm	y/pm	z/pm	<u>Net charge</u> e	x/pm	y/pm	z/pm	<u>Net charge</u> e
C-1	0.0	0.0	0.0	0.2382	0.0	0.0	0.0	0.2333
O-5	139.6	0.0	0.0	-0.1865	139.6	0.0	0.0	-0.1867
C-5	204.6	128.8	0.0	0.1133	204.6	128.8	0.0	0.1268
C-4	160.6	206.2	123.0	0.0920	160.6	206.2	123.0	0.1014
C-3	9.3	221.0	124.1	0.0854	9.3	221.0	124.1	0.0972
C-2	-56.4	83.7	114.1	0.0738	-56.4	83.7	114.1	0.0627
C-6	356.7	106.7	-8.2	0.1149	356.7	106.8	-7.9	0.1163
O-6	401.2	35.8	105.4	-0.1669	404.2	36.5	106.1	-0.1673
O-1	-40.3	51.4	-123.1	-0.2109	-40.0	-131.8	10.2	-0.2125
O-4	220.9	334.0	125.3	-0.1982	223.2	332.9	123.8	-0.1854
O-3	-29.9	300.4	13.5	-0.2016	-32.3	297.8	13.1	-0.1882
O-2	-196.6	94.7	105.0	-0.1773	-196.4	94.2	102.1	-0.1870
H-1	-32.7	-105.3	-0.1	-0.0409	-30.4	34.7	-100.1	-0.0559
H-O1	12.4	6.3	-190.9	0.1191	32.6	-184.8	-26.0	0.1314
H-5	170.3	177.6	-94.4	-0.0165	170.5	177.6	-94.6	-0.0196
H-61	382.1	45.5	-98.0	-0.0274	382.3	45.4	-97.5	-0.0274
H-62	412.5	203.2	-12.9	-0.0218	412.3	203.5	-12.8	-0.0201
H-O6	497.1	22.9	98.4	0.1023	496.9	22.9	98.4	0.1019
H-4	193.2	152.3	215.3	-0.0016	192.6	153.0	215.8	-0.0205
H-O4	173.9	391.2	62.6	0.1221	173.9	393.5	181.0	0.1113
H-3	-25.0	274.0	216.3	-0.0272	-25.4	274.6	215.9	-0.0315
H-O3	-100.8	255.8	-35.1	0.1349	-129.1	304.6	16.3	0.1198
H-2	-34.3	27.2	208.0	-0.0302	-35.2	26.9	208.0	-0.0204
H-O2	-231.7	135.2	185.8	0.1111	-231.4	3.8	98.6	0.1203

Table 5

Average coordinates and PCILO calculated net atomic charges for α -D-galactopyranose and β -D-galactopyranose

Atom	α				β			
	x/pm	y/pm	z/pm	Net charge e	x/pm	y/pm	z/pm	Net charge e
C-1	0.0	0.0	0.0	0.2251	0.0	0.0	0.0	0.2320
O-5	143.7	0.0	0.0	-0.1780	143.7	0.0	0.0	-0.1732
C-5	199.1	132.5	0.0	0.1255	199.1	132.5	0.0	0.1244
C-4	158.0	206.3	127.3	0.0879	158.0	206.3	127.3	0.0863
C-3	5.7	208.4	136.5	0.0902	5.7	208.4	136.5	0.0863
C-2	-50.9	67.9	125.8	0.0851	-50.9	67.9	125.8	0.0701
C-6	350.6	125.9	-27.3	0.1171	350.6	125.8	-27.6	0.1186
O-6	417.4	46.2	67.9	-0.1536	416.9	44.4	66.4	-0.1526
O-1	-43.3	63.3	-116.3	-0.2066	-30.9	-134.9	-2.4	-0.2085
O-4	209.8	140.8	241.0	-0.1741	209.6	140.2	240.8	-0.1720
O-3	-35.1	268.8	257.8	-0.1930	-35.1	268.6	257.9	-0.1903
O-2	-191.8	71.6	125.1	-0.1842	-191.6	75.8	120.6	-0.1852
H-1	-30.6	-105.4	-9.5	-0.0363	-33.2	42.8	-96.0	-0.0435
H-O1	2.8	21.1	-190.4	0.1176	51.3	-181.7	19.5	0.1343
H-5	153.1	182.5	-88.7	-0.0319	152.6	182.4	-88.6	-0.0449
H-61	369.0	79.5	-127.1	-0.0278	368.8	80.7	-128.1	-0.0264
H-62	396.5	227.6	-25.4	-0.0344	396.8	227.3	-24.3	-0.0342
H-O6	509.2	31.8	39.7	0.1007	509.3	32.3	39.4	0.1014
H-4	198.7	310.4	127.6	-0.0378	198.9	310.3	127.9	-0.0366
H-O4	172.5	180.3	321.3	0.1155	173.2	180.0	321.3	0.1167
H-3	-36.2	270.8	53.7	-0.0195	-35.7	271.0	53.7	-0.0285
H-O3	-33.6	365.2	247.3	0.1075	-38.6	364.9	246.7	0.1086
H-2	-19.7	6.5	213.8	-0.0120	-22.4	5.4	213.8	0.0008
H-O2	-220.6	110.9	209.0	0.1169	-222.7	102.1	208.6	0.1166

Table 6

Average coordinates and PCIO calculated net atomic charges for α -D-altropyranose and β -D-altropyranose

Atom	α				β			
	x/pm	y/pm	z/pm	<u>Net charge</u> e	x/pm	y/pm	z/pm	<u>Net charge</u> e
C-1	0.0	0.0	0.0	0.2194	0.0	0.0	0.0	0.2331
O-5	140.9	0.0	0.0	-0.1870	140.9	0.0	0.0	-0.1840
C-5	199.4	131.5	0.0	0.1226	199.4	131.5	0.0	0.1117
C-4	158.5	204.2	126.9	0.0865	158.5	204.2	126.9	0.0932
C-3	7.1	213.0	138.8	0.0864	7.1	213.0	138.8	0.1079
C-2	-57.3	76.6	118.6	0.0638	-57.3	76.6	118.6	0.0772
C-6	352.0	115.8	-14.3	0.1155	351.8	119.2	-18.0	0.1139
O-6	402.7	42.6	95.2	-0.1675	411.0	69.6	100.0	-0.1707
O-1	-43.2	56.6	-119.7	-0.2176	-37.5	-133.1	0.8	-0.2087
O-4	215.5	333.7	126.2	-0.1901	215.2	333.6	129.6	-0.1963
O-3	-44.5	303.5	43.3	-0.2017	-40.8	297.1	35.8	-0.1987
O-2	-30.7	-2.2	233.0	-0.1956	-32.2	-0.2	234.5	-0.1896
H-1	-31.9	-105.4	-4.9	-0.0368	-30.7	39.7	-98.1	-0.0609
H-O1	2.7	10.2	-191.3	0.1227	35.7	-181.7	-40.1	0.1308
H-5	159.5	181.6	-91.5	-0.0195	157.9	180.8	-91.3	-0.0254
H-61	376.4	58.8	-107.1	-0.0282	375.3	48.6	-101.2	-0.0209
H-62	403.9	214.5	-17.3	-0.0194	398.4	218.2	-39.7	-0.0279
H-O6	498.7	33.9	84.5	0.1024	501.7	415.6	80.2	0.1045
H-4	198.9	151.0	216.4	-0.0162	197.1	149.3	216.1	-0.0050
H-O4	155.7	395.6	170.6	0.1168	304.0	326.0	168.0	0.1132
H-3	-21.3	254.4	238.8	-0.0074	-24.4	259.1	235.7	-0.0210
H-O3	-50.5	262.4	-44.1	0.1244	0.8	383.8	48.1	0.1196
H-2	-168.3	84.7	109.2	0.0071	-168.4	83.8	108.8	-0.0196
H-O2	61.7	-32.1	232.2	0.1192	-63.8	-90.2	217.5	0.1237

Table 7

Average coordinates and PCILO calculated net atomic charges for α -D-talopyranose and β -D-talopyranose

Atom	α				β			
	x/pm	y/pm	z/pm	<u>Net charge</u> e	x/pm	y/pm	z/pm	<u>Net charge</u> e
C-1	0.0	0.0	0.0	0.2119	0.0	0.0	0.0	0.2207
O-5	142.9	0.0	0.0	-0.1770	142.9	0.0	0.0	-0.1722
C-5	200.8	132.3	0.0	0.1206	200.8	132.3	0.0	0.1194
C-4	157.2	204.1	128.2	0.0916	157.2	204.1	128.2	0.0901
C-3	4.1	208.7	134.4	0.0921	4.1	208.7	134.4	0.0886
C-2	-52.4	67.5	126.1	0.0808	-52.4	67.5	126.1	0.0736
C-6	352.7	123.2	-23.3	0.1179	352.6	122.5	-23.9	0.1197
O-6	413.9	37.5	70.5	-0.1528	413.2	35.0	68.5	-0.1517
O-1	-46.3	63.8	-114.7	-0.2164	-35.3	-133.5	-4.5	-0.2020
O-4	210.5	142.0	243.2	-0.1761	211.7	144.0	242.5	-0.1754
O-3	-38.8	274.8	251.7	-0.1845	-36.4	280.9	250.8	-0.1799
O-2	-13.2	-12.1	236.0	-0.1948	-11.0	-4.6	240.7	-0.1838
H-1	-30.7	-105.4	-9.9	-0.0362	-32.8	44.4	-95.4	-0.0621
H-O1	-0.7	23.5	-190.2	0.1212	43.9	-182.8	-31.0	0.1343
H-5	156.2	182.7	-89.2	-0.0318	156.2	182.5	-89.4	-0.0447
H-61	373.2	80.5	-124.4	-0.0291	372.7	80.9	-125.5	-0.0288
H-62	400.9	223.6	-15.5	-0.0321	401.6	222.4	-14.9	-0.0319
H-O6	508.1	28.4	49.4	0.1011	508.1	28.3	49.7	0.1018
H-4	196.8	308.6	127.4	-0.0420	199.6	310.3	125.4	-0.0409
H-O4	155.4	164.6	319.8	0.1250	153.4	160.9	318.1	0.1282
H-3	-35.3	268.4	48.6	-0.0271	-33.8	270.9	48.0	-0.0409
H-O3	-35.2	370.8	238.8	0.1065	-20.5	376.2	241.4	0.1075
H-2	-164.2	69.5	123.9	-0.0019	-163.3	72.9	127.3	-0.0037
H-O2	79.5	-38.6	224.7	0.1334	75.0	-45.3	221.2	0.1340

Table 8

Average coordinates and PCIO calculated net atomic charges for α -D-gulopyranose and β -D-gulopyranose

Atom	α				β			
	x/pm	y/pm	z/pm	<u>Net charge</u> e	x/pm	y/pm	z/pm	<u>Net charge</u> e
C-1	0.0	0.0	0.0	0.2357	0.0	0.0	0.0	0.2300
O-5	141.4	0.0	0.0	-0.1838	141.4	0.0	0.0	-0.1808
C-5	202.9	130.1	0.0	0.1098	202.9	130.1	0.0	0.1104
C-4	157.9	208.8	121.7	0.0976	157.9	208.8	121.7	0.1033
C-3	6.2	217.1	128.4	0.1022	6.2	217.1	128.4	0.1118
C-2	-54.3	78.2	119.2	0.0761	-54.3	78.2	119.2	0.0634
C-6	354.9	118.1	-21.6	0.1123	355.0	117.5	-21.1	0.1137
O-6	417.8	52.2	86.1	-0.1679	417.1	50.2	86.1	-0.1668
O-1	-42.7	54.3	-121.0	-0.2079	-37.8	-132.8	6.7	-0.2168
O-4	200.7	146.2	240.8	-0.1974	201.1	146.4	240.8	-0.1939
O-3	-38.7	297.5	20.9	-0.2056	-39.4	293.6	18.8	-0.1992
O-2	-195.0	84.9	114.4	-0.1815	-194.9	84.7	110.4	-0.1906
H-1	-31.5	-105.6	-2.5	-0.0411	-31.4	37.3	-98.8	-0.0500
H-O1	6.6	9.1	-191.2	0.1177	43.6	-184.1	-4.5	0.1341
H-5	162.0	177.6	-92.5	-0.0188	162.6	177.7	-92.8	-0.0272
H-61	375.1	58.6	-113.8	-0.0203	375.2	58.8	-113.8	-0.0200
H-62	402.2	218.6	-32.0	-0.0313	402.8	217.9	-30.4	-0.0316
H-O6	500.7	13.0	54.7	0.1065	500.7	12.4	55.1	0.1066
H-4	202.9	311.2	120.9	-0.0296	202.7	311.3	120.6	-0.0307
H-O4	297.2	145.4	244.7	0.1257	297.5	146.2	245.0	0.1258
H-3	-27.0	267.9	222.5	-0.0257	-27.5	269.7	221.1	-0.0228
H-O3	-107.6	250.2	-28.2	0.1344	-135.9	299.9	26.9	0.1207
H-2	-28.2	19.7	210.7	-0.0171	-29.6	19.7	210.9	-0.0082
H-O2	-228.0	122.3	197.6	0.1098	-226.9	-6.9	106.6	0.1188

Table 9

Average coordinates and PCILO calculated net atomic charges for α -D-idopyranose and β -D-idopyranose

Atom	α				β			
	x/pm	y/pm	z/pm	<u>Net charge</u> e	x/pm	y/pm	z/pm	<u>Net charge</u> e
C-1	0.0	0.0	0.0	0.2224	0.0	0.0	0.0	0.2359
O-5	140.1	0.0	0.0	-0.1785	140.1	0.0	0.0	-0.1766
C-5	199.7	130.3	0.0	0.1279	199.7	130.3	0.0	0.1282
C-4	157.3	205.3	125.7	0.0933	157.3	205.3	125.7	0.1057
C-3	6.6	209.9	141.1	0.0844	6.6	209.9	141.1	0.0852
C-2	-55.2	71.4	122.6	0.0668	-55.2	71.4	122.6	0.0602
C-6	351.4	118.9	-24.1	0.1170	351.6	118.2	-23.2	0.1186
O-6	411.5	30.3	67.6	-0.1540	410.2	26.9	66.9	-0.1528
O-1	-45.6	59.4	-117.4	-0.2196	-35.9	-133.4	-4.9	-0.2072
O-4	213.9	146.8	241.1	-0.1744	213.3	144.7	240.3	-0.1717
O-3	-46.3	299.2	44.9	-0.2071	-45.8	294.1	40.4	-0.1966
O-2	-26.3	-8.8	235.3	-0.1979	-25.4	-4.9	237.8	-0.1919
H-1	-31.7	-105.4	-6.9	-0.0387	-31.6	43.2	-96.3	-0.0616
H-O1	-1.7	13.7	-190.7	0.1224	43.2	-182.1	-33.0	0.1328
H-5	156.0	180.7	-89.7	-0.0264	156.8	180.8	-90.1	-0.0333
H-61	370.6	77.6	-126.0	-0.0294	371.5	79.1	-125.8	-0.0297
H-62	401.6	218.2	-15.0	-0.0313	402.5	216.8	-11.3	-0.0318
H-O6	505.3	19.2	44.8	0.1005	505.2	20.0	48.1	0.1002
H-4	198.1	309.3	121.8	-0.0318	198.4	309.2	123.0	-0.0343
H-O4	190.5	199.1	319.3	0.1069	180.5	187.7	320.8	0.1072
H-3	-21.6	251.7	240.9	-0.0109	-23.2	255.3	238.9	-0.0231
H-O3	-82.1	251.5	-31.2	0.1264	-137.1	317.6	62.8	0.1097
H-2	-166.6	78.1	115.2	-0.0001	-166.7	77.3	115.8	-0.0071
H-O2	67.5	-33.1	233.6	0.1322	62.0	-45.0	225.5	0.1340

Table 10

Calculated oxygen—oxygen distances (*d*) in average structures of hexopyranoses

Hexopyranose	Anomer	<i>d</i> /pm			
		O-1—O-2	O-1—O-3	O-1—O-4	O-1—O-6
Glucopyranose	α	284.7	428.1	443.2	503.6
	β	291.9	479.3	544.6	499.9
Mannopyranose	α	357.9	427.1	446.2	499.5
	β	268.8	482.0	545.3	500.0
Allopyranose	α	279.9	284.2	458.1	497.5
	β	289.8	429.7	546.1	481.9
Galactopyranose	α	283.5	426.9	444.7	496.5
	β	292.2	480.2	439.0	487.2
Altropyranose	α	357.8	295.8	451.9	495.2
	β	268.9	431.7	546.1	502.1
Talopyranose	α	360.3	422.8	447.3	496.7
	β	278.0	486.8	446.1	484.6
Gulopyranose	α	282.1	281.6	445.7	504.9
	β	287.6	426.6	436.0	496.7
Idopyranose	α	359.7	289.6	451.1	494.1
	β	274.8	430.0	446.7	479.3

virtual bond for individual types of glycosidic linkages is given by the distance between O-1 and the respective oxygen atom according to the type of the glycosidic linkage. So the distance O-1—O-4 in β -glucose characterizes the virtual bond for model 1-4- β -glucan constructed on the basis of β -D-glucopyranose. The values in Table 10 show that virtual bond may be taken for an index in which variations in geometry of the monosaccharide residue are cumulated and its magnitude in the individual types of glycosidic linkages differs in dependence on the type of the monosaccharide residue. For example, for a polysaccharide where glucopyranose, mannopyranose, galactopyranose or talopyranose are the monomeric components linked by β -(1-3) glycosidic linkages, the virtual bond is 499.9 pm, 500.0 pm, 487.2 pm, and 484.6 pm, respectively.

Comparison of the calculated van der Waals surfaces (Table 11) shows that, except mannopyranose, the surface of α anomers is greater than that of β anomer. The differences vary from $1 \times 10^{-20} \text{ m}^2$ to $4 \times 10^{-20} \text{ m}^2$. On the other hand, correlation between surface and number of axially or equatorially oriented hydroxyl groups on the pyranose ring has not been observed: Similar situation is in the case of van der Waals volumes. The differences in volumes of α and β anomers are, however, very small. The differences in experimental values of partial molal volumes for glucopyranose, mannopyranose, and galactopyra-

Table 11

Calculated dipole moment (μ), molecular van der Waals surface (S) and volume (V), and ionization potential I for standard structures of hexopyranoses

Hexopyranose	Anomer	$\mu \cdot 10^{30} / (\text{A m s})$	$S \cdot 10^{20} / \text{m}^2$	$V \cdot 10^3 / \text{m}^3$	I / eV
Glucopyranose	α	14.5	194.8	159.9	16.817
	β	17.5	195.9	160.0	16.833
Mannopyranose	α	13.0	195.0	159.9	16.774
	β	15.1	194.8	159.9	16.692
Allopyranose	α	3.2	191.6	160.0	16.690
	β	1.7	195.2	160.4	16.673
Galactopyranose	α	13.5	195.0	159.8	16.565
	β	18.6	196.0	159.9	16.626
Altropyranose	α	9.5	190.0	160.0	16.712
	β	11.8	193.3	160.0	16.775
Talopyranose	α	17.8	190.7	159.9	16.584
	β	21.7	191.8	160.6	16.553
Gulopyranose	α	9.6	189.7	159.6	16.703
	β	11.1	191.9	159.6	16.788
Idopyranose	α	11.0	189.8	159.8	16.585
	β	13.4	193.6	160.4	16.562

nose are also small and close to experimental errors [16]. Electron structures of the standard models of the individual hexopyranoses are described by charges on the individual atoms (Tables 1—9), dipole moments, and ionization potentials (Table 11), calculated by the PCILO quantum-chemical method. The differences in atomic charges of the hemiacetal segment O-1, C-1, O-5, H-1 between α and β anomers are another manifestation of the anomeric effect. The dipole moment of β anomers is, except allopyranose, higher than that of α anomers.

The presented models of 16 standard hexopyranoses and some of their characteristics allow consistent and uniform investigation of conformational properties of oligo- and polysaccharides, both of known and unknown structures. Deviations from these geometries, determined theoretically or experimentally, are rooted in variations of electron structure and can be discussed with regard to these "reference" or "average" values. However, it should be realized that they are based on current information about the structure of the pyranose ring and molecular force-field of carbohydrates. Similarly, the presence of six torsion angles in the hexopyranose molecule, characterizing the orientation of pendant groups, points to existence of large number of local minima on the energetic surface of hexopyranoses. Population of the individual minima will be influenced by chemical structure of the saccharide as well as by the medium. When considering three minima for each rotating group, 729 conformers may be formed for each hexopyranose, while the other geometrical parameters are constant. Though many of these conformers are energetically not advantageous due to steric reasons, it is necessary to use statistical thermodynamics in quantitative studies of the entire shape of hexopyranoses in solution and in solid state to determine their orientation by considering puckering forces.

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