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CRYSTAL AND MOLECULAR STRUCTURE OF 1,2:3,4-DI-*O*-ISOPROPYLIDENE-6-*O*-TOLUENE-*p*-SULFONYL-α-D-GALACTOPYRANOSE: RING CONFORMATIONS IN DI-*O*-ISOPROPYLIDENEGALACTOPYRANOSE SYSTEMS

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ABSTRACT

1,2:3,4-Di-*O*-isopropylidene-6-*O*-toluene-*p*-sulfonyl-α-D-galactopyranose has been investigated by X-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$ ($Z = 4$) with cell dimensions $a = 15.210(2)$, $b = 15.658(2)$, and $c = 8.858(1)$ Å. The structure was solved by direct methods and the atomic parameters were refined anisotropically against 1030 observed reflections by a full-matrix, least-squares procedure giving R 0.039. The pyranoid ring has a twist ($^{o}T_2$) conformation. The 1,2- and 3,4-dioxolane rings were assigned the ^{3}E and $^{2}T_1$ conformations, respectively. Models of the di-*O*-isopropylidenegalactopyranose system with minimised strain energy were compared conformationally with several experimental structures containing the above ring systems.

INTRODUCTION

High-resolution ^{1}H-n.m.r. investigations[1] for 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose derivatives variously substituted at C-6 established twist-boat (T) conformations of galactopyranose rings fused to two 2,2-dimethyl-1,3-dioxolane rings in accord with earlier reports[2]. The pyranoid ring was found to be rigid and independent of the polarity of the solvent over a wide range of temperatures.

However, recent X-ray structural investigations of 1(*S*)-acetoxy-3-[6(*R*)-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl]-1-(methyl 2,3,4-tri-*O*-benzyl-6-deoxy-β-D-galactopyranosid-6-yl)propyne[3] (**2**) and 6-*C*-(2-furyl)-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-hexopyranose[4] (**3**) showed that the galactopyranose rings in the above fused systems may adopt different conformations (*i.e.*, $^{o}S_5 + {}^{o}T_2$ in **2**, and $^{o}T_2 + B_{2,5}$ in **3**) in the crystalline state. Therefore, it

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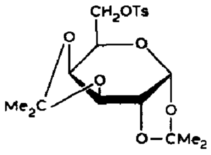

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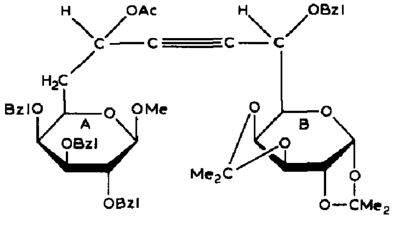

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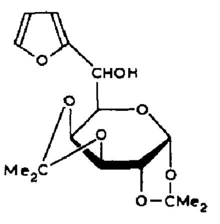

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seems that the conformation of the ring in these compounds may be influenced by structural factors causing considerable lability.

In order to investigate this phenomenon on other simple derivatives, an X-ray study of 1,2:3,4-di-*O*-isopropylidene-6-*O*-toluene-*p*-sulfonyl-α-D-galactopyranose (**1**) was undertaken.

EXPERIMENTAL

Colourless crystals of **1**, obtained according to Schmidt[5], had m.p. 103° after recrystallisation from light petroleum–ether. A well-shaped crystal (0.45 × 0.32 × 0.24 mm) was chosen for X-ray diffraction measurements (CuKα radiation, $\lambda = 1.54178$ Å) using a Siemens AED single-crystal automated diffractometer. Cell dimensions were calculated and refined during the alignment of the crystal, using the angular values of 20 reflections.

Crystal data for **1** ($C_{19}H_{26}O_8S$): orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 15.210(2)$, $b = 15.658(2)$, and $c = 8.858(1)$ Å, $V = 2109.6(4)$ Å^3, $M_r = 414.46$, $F(000) = 880$, $D_c = 1.26$ Mg.m^{-3}, μ(CuKα) = 16.689 cm^{-1}.

Intensities were collected at room temperature using the $\omega/2\theta$ scan mode in the range up to $2\theta_{max}$ 150°. The stability of the intensities was controlled on two reflections at 50 reflection intervals (no considerable decay). Of 2293 unique reflections, only 1030 were of $I > 2\sigma_I$, which were then used for structure refinement. The Lorentz and polarisation, but no absorption, correction was applied. The phase problem for **1** was solved by direct methods using the SHELX-78 programme[6].

The refinement of atomic positional and thermal parameters, initially isotropic and then anisotropic, was performed by a full-matrix, least-squares procedure with complex atomic scattering factors implemented in SHELX-78. The positions of hydrogen atoms were found from $\Delta\rho$ maps (except the phenyl hydrogen atoms which were calculated geometrically). The final refinement step involved all atomic positional and thermal parameters except the hydrogen temperature factors (fixed as equal to B_{eq} of the adjacent atom + 1 Å^2). The final reliability factor was $R = 0.039$ [$R_w = 0.040$, $w = (\sigma_F^2 + 0.007F^2)^{-1}$] at the Δ/σ value <0.08. The maximum residual electron densities checked on final $\Delta\rho$ maps were <0.5 e.Å^{-3} and found to be localised exclusively around the sulfur atom, probably due to some absorption effects. The refined fractional co-ordinates and the B_{eq} values for non-hydrogen atoms of **1** are given in Table I.

TABLE I

FRACTIONAL CO-ORDINATES ($\times 10^4$)[a] AND EQUIVALENT, ISOTROPIC TEMPERATURE FACTORS ($Å^2$)[b]

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
C-1	9415(4)	5497(4)	8269(7)	4.2(2)
C-2	9367(4)	5491(4)	9972(6)	4.3(2)
C-3	9665(4)	6337(4)	10685(6)	4.2(2)
C-4	9376(4)	7137(4)	9846(7)	4.2(2)
C-5	9004(3)	6947(3)	8297(6)	3.6(2)
C-6	9025(4)	7716(4)	7323(7)	4.1(1)
C-7	8129(4)	4868(4)	9093(7)	4.2(2)
C-8	7188(4)	5084(5)	8884(8)	6.1(3)
C-9	8252(5)	3932(4)	9471(10)	6.8(3)
C-10	10847(4)	7226(4)	10528(8)	4.9(2)
C-11	11681(5)	7273(6)	9622(10)	7.5(3)
C-12	10921(5)	7632(5)	12051(7)	5.6(2)
C-13	7676(4)	8829(3)	5008(6)	3.8(2)
C-14	6850(4)	8532(3)	4605(7)	4.0(2)
C-15	6133(4)	9020(4)	4917(8)	5.3(2)
C-16	6182(4)	9805(4)	5610(7)	5.1(2)
C-17	7015(5)	10081(4)	6013(9)	6.2(3)
C-18	7733(4)	9611(4)	5710(9)	5.8(3)
C-19	5418(5)	10333(5)	6037(11)	8.0(3)
S	8596(1)	8200(1)	4615(2)	4.47(4)
O-1	8626(3)	5104(3)	7815(4)	4.7(1)
O-2	8462(2)	5388(2)	10273(4)	4.5(1)
O-3	10600(3)	6353(2)	10639(5)	4.9(1)
O-4	10172(3)	7609(3)	9685(5)	5.2(1)
O-5	9507(2)	6293(2)	7587(4)	4.1(1)
O-6	8595(3)	7506(2)	5900(4)	4.4(1)
O-7	9370(2)	8706(2)	4738(5)	5.5(1)
O-8	8433(3)	7727(3)	3275(4)	6.0(2)

[a]Estimated standard deviations in parentheses. [b]$B_{eq} = 8\pi^2 \cdot D_u^{1/3}$, where D_u is the determinant of the U matrix.

RESULTS AND DISCUSSION

Tables II and III give the bond lengths and valence angles, respectively, for **1**, the steric projection of which is shown in Fig. 1.

In the pyranoid ring of **1**, bond-elongation and an increase in the values of the valence angles involving C-2,3,4 were observed. A similar situation was found for **2** (ring B) and for **3**. The angles at C-2 and C-3 in **1** [113.0(5)° and 115.1(5)°, respectively] deviated significantly from those in a cyclohexane chair.

Conformation of the pyranose ring in **1**. — It may be expected that, as in **2** (ring B) and **3**, the conformation of the α-D-galactopyranose ring in **1** differs greatly from a chair (*C*) form. Analysis of the torsion angles (Table IV), asymmetry[7] parameters, and puckering[8] parameters (Table V) indicates that the α-D-galactopyranose ring in **1** approximates to a twist-boat (*T*) more than do the pyranose rings in **2** or **3**. This conclusion is supported by an analysis of the deviations of the

TABLE II

BOND DISTANCES (Å)[a] FOR **1**

C-1–C-2	1.510(8)	C-10–C-11	1.416(4)
C-2–C-3	1.536(9)	C-10–C-12	1.496(10)
C-3–C-4	1.521(9)	C-5–C-6	1.482(8)
C-4–C-5	1.514(8)	C-6–O-6	1.458(7)
C-5–O-5	1.425(6)	O-6–S	1.574(4)
O-5–C-1	1.392(7)	S–O-7	1.423(3)
C-1–O-1	1.407(8)	S–O-8	1.421(4)
O-1–C-7	1.411(7)	S–C-13	1.746(6)
C-7–O-2	1.418(7)	C-13–C-14	1.386(8)
O-2–C-2	1.411(7)	C-14–C-15	1.360(8)
C-7–C-8	1.482(9)	C-15–C-16	1.376(9)
C-7–C-9	1.515(9)	C-16–C-17	1.385(10)
C-3–O-3	1.423(8)	C-17–C-18	1.344(10)
O-3–C-10	1.421(7)	C-18–C-13	1.376(8)
C-10–O-4	1.404(8)	C-16–C-19	1.475(10)
O-4–C-4	1.426(8)		

[a] Estimated standard deviations in parentheses.

TABLE III

BOND ANGLES (DEGREES)[a] FOR **1**

O-5–C-1–C-2	116.4(5)	O-4–C-10–C-11	108.2(6)
C-1–C-2–C-3	113.0(5)	O-4–C-10–C-12	110.7(5)
C-2–C-3–C-4	115.1(5)	C-11–C-10–C-12	113.4(6)
C-3–C-4–C-5	112.9(5)	C-4–C-5–C-6	111.1(5)
C-4–C-5–O-5	109.9(4)	O-5–C-5–C-6	108.4(4)
C-5–O-5–C-1	113.5(4)	C-5–C-6–O-6	108.1(5)
C-2–C-1–O-1	104.0(5)	O-6–S–O-7	109.3(3)
C-1–O-1–C-7	110.0(4)	O-6–S–O-8	104.1(2)
O-1–C-7–O-2	104.5(5)	O-7–S–O-8	119.9(3)
C-7–O-2–C-2	105.9(4)	O-6–S–C-13	104.2(2)
O-2–C-2–C-1	103.7(4)	O-7–S–C-13	109.5(2)
O-1–C-7–C-8	110.9(5)	O-8–S–C-13	108.7(3)
O-1–C-7–C-9	111.4(5)	S–C-13–C-14	119.1(4)
O-2–C-7–C-8	107.8(5)	C-13–C-14–C-15	119.1(5)
O-2–C-7–C-9	110.4(5)	C-14–C-15–C-16	123.3(6)
C-8–C-7–C-9	111.6(6)	C-15–C-16–C-17	116.3(6)
C-4–C-3–O-3	105.1(5)	C-16–C-17–C-18	121.4(6)
C-3–O-3–C-10	106.4(4)	C-17–C-18–C-13	121.8(6)
O-3–C-10–O-4	104.7(5)	C-18–C-13–C-14	118.2(5)
C-10–O-4–C-4	110.3(5)	C-18–C-13–S	122.8(5)
O-4–C-4–C-3	103.3(5)	C-15–C-16–C-19	124.9(6)
O-3–C-10–C-11	107.9(6)	C-17–C-16–C-19	118.6(6)
O-3–C-10–C-12	111.5(6)		

[a] Estimated standard deviations in parentheses.

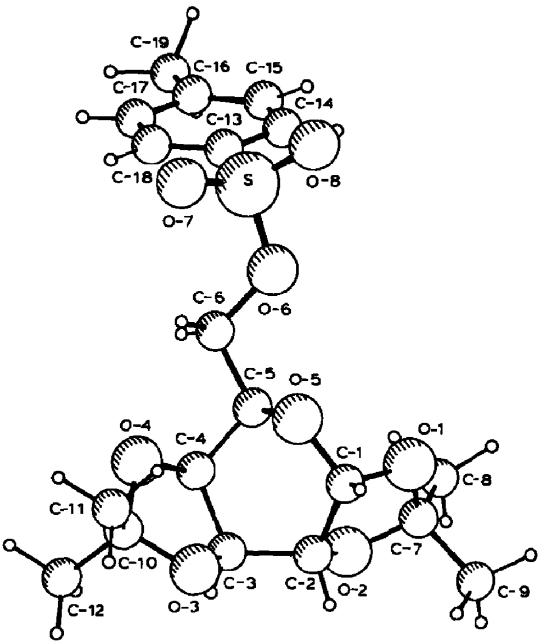

Fig. 1. Parallel projection of **1**, oriented to give an optimal view of the molecule, with crystallographic labelling of atoms.

ring atoms from a least-squares plane defined by all of these atoms (Table V). Thus, the conformation of the α-D-galactopyranose ring in **1** may be defined as $^{\mathrm{O}}T_2$, slightly deformed towards a half-chair.

The recent and present X-ray structural investigations of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose derivatives (**1**–**3**) indicate that, in the crystalline state, there is a considerable conformational lability of the galactopyranose rings which is limited by three extreme conformations, namely, skew-boat (*S*), twist-boat (*T*), and boat (*B*).

Conformations of the dioxolane rings. — Table VI contains the results of conformational calculations for the dioxolane rings in **1**–**3**. The dioxolane rings in **1** and **3** are similar. Each 1,2-ring has an envelope (*E*) conformation, whereas the 3,4-ring is *T* in **1** and *T* + *E* in **3**. This difference is due to a strong intermolecular hydrogen-bond in **3**, involving O-3 in the 3,4-*O*-isopropylidene residue. The conformational lability of dioxolane rings fused with a furanose ring has been discussed[9]. The conformations of the dioxolane rings in the complex molecule of **2**, where the situation is the opposite of that in **1**, may be explained on this basis (Table VI).

Semi-empirical strain-energy calculations. — In order to investigate the possible steric influence of dioxolane rings on the conformation of the pyranose ring in **1**–**3**, Cartesian molecular models of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**3**, less the furyl ring) and of a C_{15} compound (**2**, less the benzyl

TABLE IV

COMPARISON OF SOME TORSIONAL ANGLES (DEGREES) FOR **1**, **2**, AND **3**[a]

	1	**2**[b]	**3**	*A*[c]	*B*[c]	*C*[d]
Galactopyranose ring						
O-5–C-1–C-2–C-3	−14.9(7)	−8.6(5)	−17.7(8)	−11.9	−17.2	−31.1
C-1–C-2–C-3–C-4	39.3(7)	29.2(5)	37.3(7)	38.4	39.3	64.5
C-2–C-3–C-4–C-5	−11.6(7)	−2.0(5)	−5.5(7)	−11.4	−7.6	−31.1
C-3–C-4–C-5–O-5	−40.0(6)	−45.3(5)	−45.6(6)	−41.4	−46.0	−31.1
C-4–C-5–O-5–C-1	68.6(5)	70.6(4)	70.6(5)	73.1	73.1	64.5
C-5–O-5–C-1–C-2	−39.0(6)	−41.4(5)	−36.1(6)	−44.1	−38.6	−31.1
1,2-Dioxolane ring						
C-2–C-1–O-1–C-7	−0.3(6)	−9.6(4)	2.7(7)	−11.6	0.8	—
C-1–O-1–C-7–O-2	20.6(6)	27.2(4)	17.7(8)	32.3	18.1	—
O-1–C-7–O-2–C-2	−33.9(5)	−34.5(4)	−31.9(7)	−41.2	−32.0	—
C-7–O-2–C-2–C-1	33.4(6)	28.4(4)	32.8(6)	31.8	31.6	—
O-2–C-2–C-1–O-1	−22.2(6)	−11.6(4)	−21.1(6)	−12.5	−19.8	—
3,4-Dioxolane ring						
C-4–C-3–O-3–C-10	27.3(6)	23.4(4)	23.7(6)	29.7	23.3	—
C-3–O-3–C-10–O-4	−32.8(6)	−34.9(4)	−31.3(6)	−40.5	−31.6	—
C-3–C-10–O-4–C-4	25.6(6)	33.2(4)	27.0(7)	34.1	27.0	—
C-10–O-4–C-4–C-3	−8.6(6)	−18.2(4)	−12.3(6)	−14.5	−12.8	—
O-4–C-4–C-3–O-3	−11.5(6)	−3.1(4)	−7.1(6)	−9.5	−6.5	—
Other angles						
C-3–C-4–C-5–C-6	−159.9(5)	−162.9(3)	−165.9(5)	−159.7	−166.5	—
C-1–O-5–C-5–C-6	−169.8(4)	−167.7(3)	−166.1(4)	−166.2	−164.7	—
C-4–C-5–C-6–O-6	−175.5(4)	−56.6(4)	−59.7(6)	−47.4	−60.9	—
O-5–C-5–C-6–O-6	63.6(5)	−176.4(3)	178.8(4)	−166.9	178.2	—

[a] Estimated standard deviations in parentheses. [b] Ring B of **2**. [c] Models of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose obtained by MM calculations (see text) (A, without coordinate restrictions; B, *O*-isopropylidene atomic coordinates restricted to maintain the original conformation of dioxolane rings). [d] For cyclohexane model.

rings) were made by a strain-energy minimisation process (program MM1[10], with parametrisation based on 1975 force field).

For the first model, two modes of strain-energy minimisation were performed (Fig. 2; *a*, without restrictions of co-ordinate shifts; *b*, *O*-isopropylidene atoms fixed). The torsion angles as well as the asymmetry and puckering parameters of the model optimised in the *a*-mode are close to those of **1** (Tables IV and V). The resulting conformation of the galactopyranose ring, when compared with an ideal ${}^{6}T_{2}$ conformation of cyclohexane, exhibits considerable flattening of the fragment C-1/C-4 (diminishing of the values of the torsion angles and of the puckering parameter q_2) reflecting the presence of the ring oxygen.

The *b*-mode of strain-energy minimisation (Fig. 2) involved some restrictions in the movement of the co-ordinates in order to keep the dioxolane conformations unchanged. The minimisation stopped at the energy level which was higher by

TABLE V

CONFORMATIONS OF THE GALACTOPYRANOSE RINGS IN **1**, **2**, AND **3**

	1	**2**[a]	**3**	*A*[b]	*B*[b]		*C*[c]
Atom deviations (Å)[d] *from six-atomic least-squares planes*							
C-1	−0.191(6)	−0.136(5)	−0.127(6)	−0.022	0.184	C-1	0.000
C-2	−0.321(6)	−0.244(5)	−0.310(6)	−0.260	−0.278	C-2	−0.388
C-3	0.335(6)	0.242(5)	0.271(6)	0.240	0.229	C-3	0.388
C-4	0.151(6)	0.116(5)	0.103(6)	0.036	0.071	C-4	0.000
C-5	−0.407(5)	−0.434(4)	−0.481(6)	−0.374	−0.399	C-5	−0.388
O-5	0.188(3)	0.220(3)	0.175(3)	0.379	0.359	C-6	0.388
Asymmetry parameters (°)[7]							
ΔC_2	2.5(6)	5.4(3)	11.2(6)	1.9	8.6		—
Puckering parameters[8]							
Q (Å)	0.628	0.592	0.632	0.643	0.652		0.777
Φ (°)	86.5	84.3	81.4	88.8	83.0		90.0
θ (°)	99.7	106.4	100.9	101.0	101.0		90.0
q_2 (Å)	0.619	0.568	0.621	0.623	0.639		0.777
Conformation							
	$^{O}T_2$	$^{O}S_5 + {}^{O}T_2$	$^{O}T_2 + B_{2,5}$	$^{O}T_2$	$^{O}T_2 + B_{2,5}$		$^{6}T_2$

[a] Ring B of **2**. [b] Models of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose obtained by MM calculations (see text) (A, without coordinate restrictions; B, *O*-isopropylidene atomic coordinates restricted to maintain the original conformation of the dioxolane rings). [c] For cyclohexene model. [d] Estimated standard deviations in parentheses.

TABLE VI

CONFORMATION OF DIOXOLANE RINGS IN **1**, **2**, AND **3**

	1		**2**		**3**	
	1,2-Dioxolane	*3,4-Dioxolane*	*1,2-Dioxolane*	*3,4-Dioxolane*	*1,2-Dioxolane*	*3,4-Dioxolane*
Asymmetry parameters (°)[a]						
ΔC_s	0.5(6)			3.9(4)	2.4(7)	8.6(6)
ΔC_2		2.3(6)	1.7(4)			4.4(6)
Puckering parameters						
q_2 (Å)	0.315	0.288	0.306	0.313	0.308	0.277
Φ (°)	253.1	13.9	237.1	30.5	257.4	22.2
Conformation[b]						
	^{3}E	$^{2}T_1$	$^{3}T_2$	^{2}E	^{3}E	$^{2}T_1 + {}^{2}E$

[a] Estimated standard deviations in parentheses. [b] The indexing conforms to that for cyclopentane.

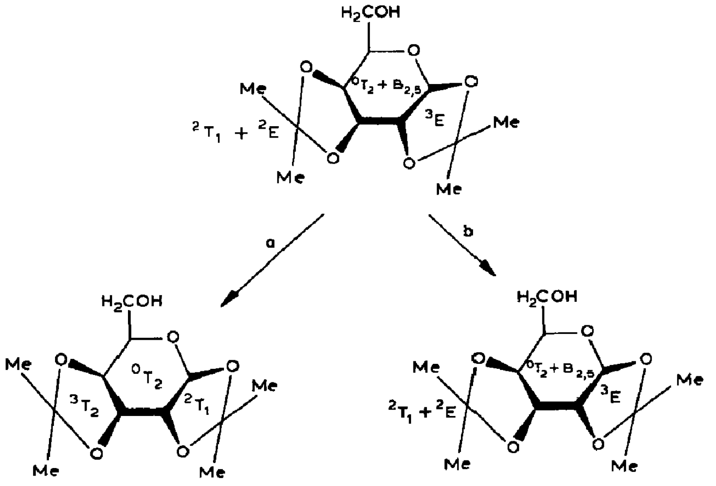

Fig. 2. Strain-energy minimisation scheme in a 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose model based on **3** (furyl ring removed). Starting and final conformations are given: *a*, all atomic positions optimised freely; *b*, dioxolane ring conformations fixed.

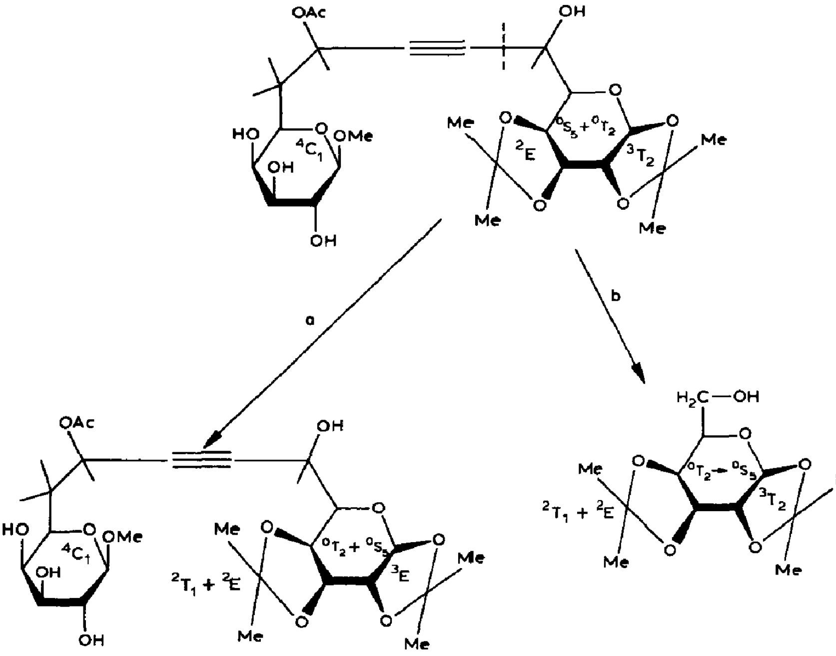

Fig. 3. Strain-energy minimisation scheme in a model derived from **2** (benzyl groups removed): *a*, C_{15} saccharide; *b*, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose isolated.

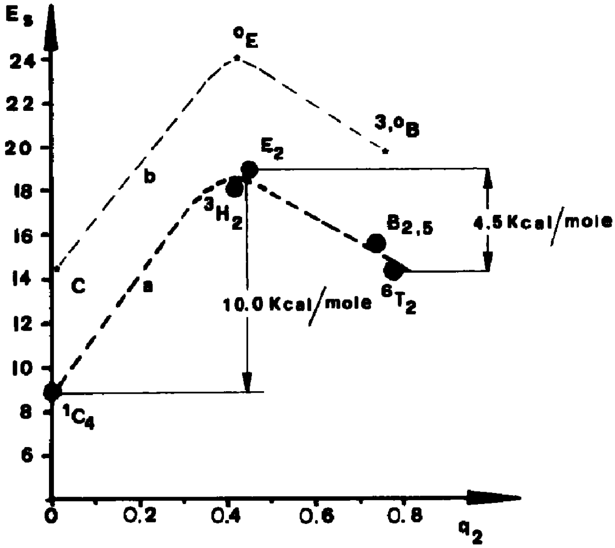

Fig. 4. Minimised strain energy (kcal/mole) plotted *vs.* puckering parameter $q_2 = Q \cdot \sin\theta$ (Å) for various basic conformations: *a*, cyclohexane; *b*, tetrahydropyran.

4 kcal/mole as in the *a*-mode. The final conformation of the pyranose ring was not changed markedly during optimisation.

The Cartesian model taken from **2** was subjected to a strain-energy minimisation process in order to assess the possible internal steric interactions in a complex molecule (Fig. 3a). Although, in general, the conformations of 1,2:3,4-di-*O*-isopropylidenegalactopyranose ring systems, when freed of intermolecular interactions, move to all-twist forms, the relatively large internal Van der Waals interactions and marked dipole–dipole energy increments (the sum is ~15 kcal/mole) result in conformational change during energy minimisation as shown in Fig. 3a.

The energy minimisation of an isolated three-ring system (as in Fig. 2) was repeated with the model taken from **2** (Fig. 3b). The final energy level was close to that obtained previously (difference, +0.6 kcal/mole); the resulting conformations differed slightly, deviating a little from a "pure" twist form. This finding confirmed that the conformations of the 1,2:3,4-di-*O*-isopropylidenegalactopyranose system are rather labile, oscillating around the twist form.

In order to determine the relationship of the optimised strain energy to various conformations of six-membered rings, several conformations [*C* (chair), *E* (sofa), *H* (half-chair), *B* (boat), and *T* (twist-boat)] of cyclohexane and tetrahydropyran were subjected to strain-energy minimisation processes with all possible symmetry restrictions deriving from point groups of each model. For tetrahydropyran (conformations *C*, *E*, and *B*), the oxygen was always placed on a symmetry plane. The geometry of the optimised rings was then analysed conformationally (Table VII). Fig. 4 contains diagrams of minimised strain energies

TABLE VII

CONFORMATIONAL PARAMETERS FOR ENERGETICALLY OPTIMISED RINGS OF CYCLOHEXANE AND TETRAHYDROPYRAN

Cyclohexane	$^{1}C_{4}$	$^{5}H_{6}$	E_{4}	$^{1,4}B$	$^{6}T_{2}$
Torsion angles (°)					
C-6–C-1–C-2–C-3	−56.0	−17.1	0	−52.4	−31.1
C-1–C-2–C-3–C-4	56.0	0	31.4	0	64.5
C-2–C-3–C-4–C-5	−56.0	−17.1	−63.3	52.4	−31.1
C-3–C-4–C-5–C-6	56.0	50.8	63.3	−52.4	−31.1
C-4–C-5–C-6–C-1	−56.0	−68.4	−31.4	0	64.5
C-5–C-6–C-1–C-2	56.0	50.8	0	52.4	−31.1
Puckering parameters					
Q (Å)	0.577	0.541	0.548	0.736	0.777
Φ (°)	0	270.0	180.0	0	90.0
θ (°)	0	50.9	54.8	90.0	90.0
q_2 (Å)	0	0.423	0.448	0.736	0.777

Tetrahydropyran[a]	$^{O}C_{3}$	^{O}E	$^{3,O}B$
Torsion angles (°)			
O-5–C-1–C-2–C-3	−57.6	32.3	1.9
C-1–C-2–C-3–C-4	52.8	0	52.4
C-2–C-3–C-4–C-5	−52.8	0	−52.4
C-3–C-4–C-5–O-5	57.6	−32.3	1.9
C-4–C-5–O-5–C-1	−61.6	67.6	59.9
C-5–O-5–C-1–C-2	61.6	−67.6	−59.9
Puckering parameters			
Q (Å)	0.577	0.529	0.753
Φ (°)	0	120.0	120.0
θ (°)	1.5	124.8	89.2
q_2 (Å)	0.015	0.434	0.753

[a] Atom numbering as in pyranose rings.

for both compounds *vs.* the puckering parameter q_2 calculated for particular conformations. The curves have a shape similar to that for tetrahydropyran shifted with respect to that for cyclohexane by ~ +5 kcal/mole. The *H* and *T* conformations of tetrahydropyran, which cannot be optimised energetically by the above method, may be placed on the diagram, by analogy to cyclohexane, close to the *E* and *B* conformations, respectively. The strain energy levels for the *H* and *E* conformations, as well as those for the *B* and *T* conformations differ for cyclohexane by 1–2 kcal/mole. Thus, the barriers between these conformations cannot be high. Therefore, even for small inter- or intra-molecular effects, there is a strong probability of hybridisation of these conformations. This makes understandable the frequent occurrence in various sugar compounds[11] of hybrids of pyranose conformations of the types $H + E$ or $T + B$. The hybrid conformation $^{o}S_5 + {}^{o}T_2$ found in **2**, taking into account the fact that the *S* conformation is energetically close to the *H* or *E* conformations, although the energy difference may be of the order of 3 kcal/mole. Thus, conformations that are sterically forced to be different from a chair form are energetically labile.

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