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THEORETICAL STUDIES ON THE CONFORMATIONS OF ALDOHEXOPYRANOSE PENTAACETATES*

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ABSTRACT

The net charges on various atoms of aldohexopyranose pentaacetates were computed by using the MO-LCAO method of Del Re for σ-charges and the Hückel MO method for π-charges. The potential and free energies of sixteen aldohexopyranose pentaacetates in the *C1*(D) and *1C*(D) conformations were estimated. Minimization of the energies of these conformations was studied by suitably tilting the axial C–C and C–O bonds. As with the free sugars, considerable release of strain is achieved when tilts of 4.5 and 2° are given to the axial CH_2OAc and the axial OAc groups, respectively, involved in the Hassel–Ottar effect in the *1C*(D) conformations. In the case of *C1*(D) conformations, the ideal models have the minimum energy even when the acetate groups are involved in *syn*-axial interactions, indicating that strain induced by axial acetate groups is less than that of axial hydroxyl groups. The calculated free-energies agree well with the experimental values after adding a value of 0.9 kcal.mole^{-1} for the anomeric effect of the acetoxyl group. The free-energy calculations also predict that α-D-idohexopyranose pentaacetate and α-D-altrose pentaacetate favour the *C1*(D) conformation and β-D-idose pentaacetate a $C1 \rightleftharpoons 1C$ equilibrium in solution, in agreement with n.m.r. studies.

INTRODUCTION

The favoured conformations of aldohexopyranose pentaacetates in solution have been studied by many workers[1–4] using n.m.r. spectroscopy. Lemieux and Chü[5,6] have also assigned energy values for various nonbonded interactions and for the anomeric effect of an acetoxyl group, from a consideration of the anomeric and conformational equilibria of aldopentopyranose tetraacetates. However, the scheme of Lemieux and Chü[6] predicts that, for α-D-idohexopyranose pentaacetate, substantial amounts of both the *C1*(D) and *1C*(D) conformations are present in solution. On the other hand, n.m.r. studies[4] show that this molecule exists in solution preponderantly in the *C1*(D) conformation.

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Recently, potential and free energies of aldohexopyranoses have been computed by using semi-empirical potential functions[7–10]. These theoretical results obtained on aldopyranoses[7,8] were in accord with the experimentally observed conformations in solution, and also predicted deviations of the order of 3.0–4.5° in bond angles when a conformation is involved in the Hassel–Ottar effect and about 1.5° when two *syn*-axial hydroxyl groups are present. Further, these calculations suggested that the anomeric effect of a hydroxyl group is only 0.4 kcal.mole^{-1}, and is independent of the orientation of the OH group at C-2 atom. However, no such data are available for acetylated sugars, and this report describes an attempt to determine the favoured conformations of aldohexopyranose pentaacetates in solution by computing their potential and free energies through use of semi-empirical functions. Incidentally, these studies also throw some light on the anomeric effect of an acetoxyl group, the effect of substituents on the pyranoid ring-conformation, and also the possible deviations in bond angles in different steric arrangements of side groups.

THEORETICAL TREATMENT

Expression for energy.—The potential energy of an aldohexopyranose pentaacetate molecule was computed by using the expression:

$$V = \sum_{i,j} V_{nb}(i,j) + \sum_{i,j} V_{es}(i,j) + \sum V_\theta \tag{1}$$

The first term gives the contribution from non-bonded interactions, the second term the contribution from electrostatic interactions, and the third term the strain energy due to distortions in single-bond angles θ. The expressions for $V_{nb}(i,j)$, $V_{es}(i,j)$, and V_θ, and the constants used are the same as those reported earlier[8,11]. A value of 3.5 was assigned for the effective dielectric constant[8], to take into account solvent effects in computing the electrostatic energy. As mentioned in the earlier paper[8], the variation in the value of the effective dielectric constant is very small, even though the actual dielectric constant of the solvent[12] varies from 5 to 100. As we are interested in the relative energies of various conformations, small changes in the effective dielectric constant do not seem to affect our results significantly. Making similar approximations as in the case of free sugars[7] (namely, $\Sigma N_i V_i \simeq V_{min}$), the free energy F of an aldohexopyranose pentaacetate molecule was computed by using the expression:

$$F = V_{min} - TS \tag{2}$$

where S is the conformational entropy of a molecule resulting from the various possible orientations of the side groups, and T is the absolute temperature.

Calculation of σ- and π-charges.—In order to calculate the electrostatic energy, the fractional charges on the atoms of the aldohexopyranose pentaacetate molecule were computed by treating the molecular fragment as consisting of a σ-system, and a separate π-system of bonds over the σ-skeleton. In effect, the π-charges due to the mobile electron-density at each atom in the conjugated parts (acetate groups) and

σ-charges on the saturated singlebond framework were evaluated separately. The MO-LCAO method of Del Re[13] was used to evaluate the σ-charges. For the calculation of π-charges, the usual Hückel[14] LCAO-MO method was employed.

The values of the parameters used in the σ-charge calculation were those reported by Berthod and Pullman[15]. To obtain the net charge on each atom, the σ- and π-charges were totalled (Fig. 1).

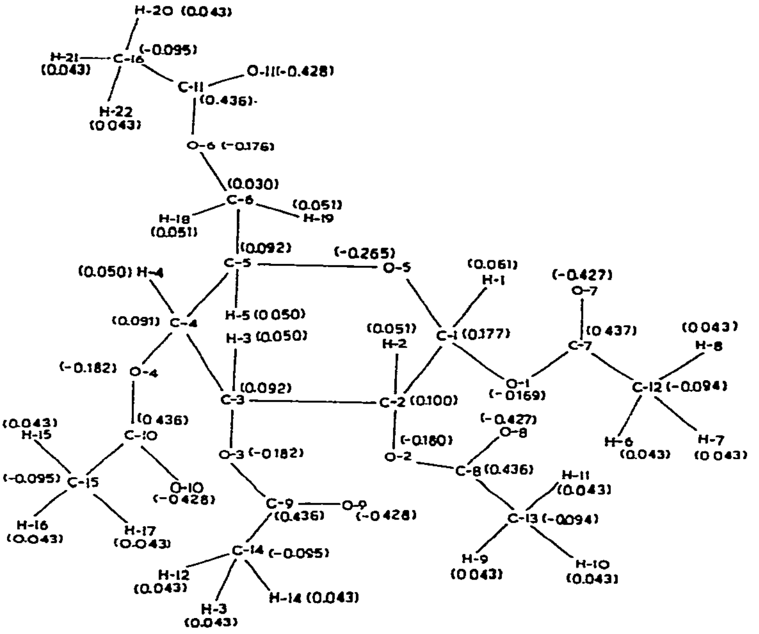

Fig. 1. Charge distribution in an aldohexopyranose pentaacetate (in fractions of an electronic charge)

Bond-length and bond-angle distortion at C-1.—It has been found from crystal-structure studies of glycopyranosides[16] that there is a preferential shortening of the anomeric C–O bond when it is equatorially oriented (1.39 Å) compared with when it is axially disposed (1.41 Å). The O-5–C-1–O-1 bond angle is about 107° in the equatorial anomer and 111.4° in the axial anomer. In the absence of any available crystallographic data on acetylated sugars, data on glycopyranosides were used to fix the O-1 atom in acetylated sugars. In the case of the axial C-1–O-1 bond, deviations from 111.4° were considered for the O-5–C-1–O-1 bond angle whenever the group attached to the C-1 atom is involved in the Hassel–Ottar effect[17], or in *syn*-diaxial interactions.

The energy V_l due to bond-length distortion of the C-1–O-1 bond was computed separately by using the expression:

$$V_l = k_l(l - 1.43)^2. \qquad (3)$$

The constant[18] k_l (in kcal·mole^{-1}·Å^{-2}) was taken to be 324.

As some investigators[16] have considered the distortions at C-1 just mentioned as part of the anomeric effect, the difference of about 0.4 kcal.mole^{-1} between the α- and β-anomers that arises through these deviations alone, was incorporated in the anomeric effect separately.

Potential energy calculations. — The atoms in the ring and the atoms bonded directly to the ring (except at C-1), were fixed in the *C1*(D) and *1C*(D) conformations, by using the bond lengths and bond angles reported earlier[9]. The O-1 atom was, however, fixed depending upon the orientation of the C-1–O-1 bond having the bond length and bond angle given in the previous section. The atoms of the acetoxy group were fixed by taking the different bond-lengths as C–C = 1.53, C–O = 1.36, C=O = 1.22, and C–H = 1.1 Å, and the bond angles at the tetrahedral carbon atom as 109.47°, the angle at the divalent oxygen atom as 118°, and that at the sp^2-hybridized carbon atom as 120°. The acetate groups were taken to be planar in view of the partial double-bond character of the carbonyl carbon–hydroxyl-oxygen bond, because of resonance. Hence, no free rotation was assumed about the carbonyl carbon–hydroxyl-oxygen bond. As examination of models revealed that the orientation of the -CH_3 group is not influenced by the orientation of the acetate group (of which it is a part), the -CH_3 group was fixed such that one of the C–H bonds is cis to the C=O bond.

However, in order to fix an acetate group in the pyranoid ring, we required, in addition to the bond lengths and bond angles, an additional parameter χ the dihedral

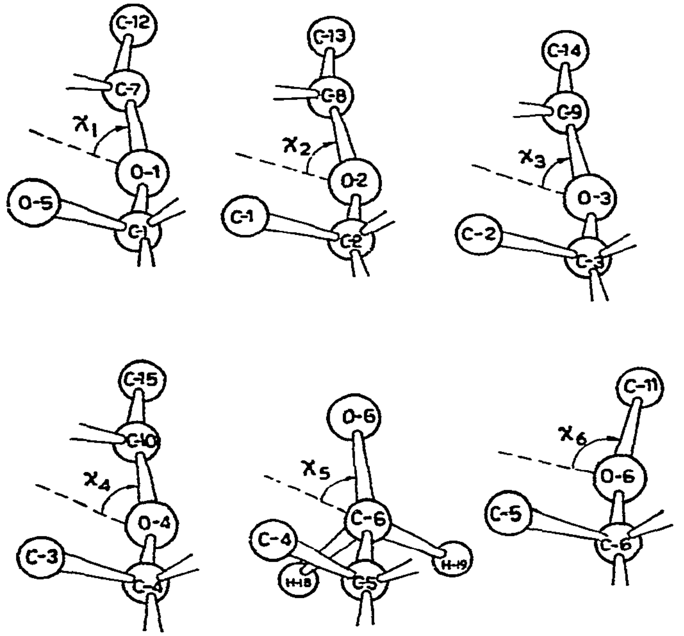

Fig. 2. Schematic representation of dihedral angles of rotations of OAc and CH_2OAc groups in aldohexopyranose pentaacetates. The dashed line denotes the position of the bond for $\chi = 0$ (numbering of atoms is the same as in Fig. 1).

angle of rotation about the neighbouring single-bond (see Fig. 2). The acetate groups were fixed by using χ in the position of minimum energy, by an iterative process similar to that described for free sugars[8,10]. To fix the acetate groups in the minimum-energy positions, each acetate group was rotated as a unit about the corresponding ring carbon–hydroxyl-oxygen bond from 0 to 360° in intervals of 10°.

The energy minimization was also studied by suitably tilting the axially oriented C–O or C–C bonds, as described for free sugars[7,8]. With the *1C*(D) conformations of aldohexopyranose pentaacetates, in order to reduce the computer time required for calculating energies, the calculations were first performed for α-D-idopyranose pentaacetate, which has only the acetoxymethyl group in axial orientation. There was a considerable release of strain energy (about 4 kcal.mole^{-1}) when this group was tilted by 4.5° from the tetrahedral angle. The total potential energy, made up of the non-bonded, the electrostatic, and the bond-angle-strain contributions, passes through a minimum at a tilt angle of 4.5° for the CH_2OAc group, corresponding to a value of 114° for the C-4–C-5–C-6 and O-5–C-5–C-6 bond angles. For the other molecules in the *1C*(D) conformation, the CH_2OAc group was fixed with this value of 114° for the foregoing bond angles and the energy calculations were performed by varying the bond angles at other axially oriented acetoxyl groups. In this manner, a conformation of overall minimum energy was determined for the *1C*(D) conformations. The minimum-energy conformations were determined also for the *C1*(D) conformations by suitably tilting the axial acetoxyl groups. The angles that deviate from the ideal values in these minimum-energy conformations are shown in Table I.

Conformational entropy calculations.—The conformational entropy resulting from the various possible orientations of the acetoxyl groups around the ring-carbon-hydroxyl oxygen bonds were estimated to a first approximation by determining from contact-distance criteria the allowed rotational positions for each acetate group. In determining these allowed regions, small changes of the order of about 2° in the bond angles given in the preceeding section were also considered; these changes are within experimental limits. The allowed regions thus determined for the acetate groups of β-D-glucopyranose pentaacetate in the *C1*(D) conformation are shown in Fig. 3; there are three small regions A, B, and C allowed for each acetate group. However, it was found from contact-distance criteria that an equatorial acetate group can take up all three positions only when both of the ring-carbon-hydroxyl-oxygen bonds on either side of the acetate group are also equatorially disposed (Fig. 4a). On the other hand, even if one of the adjacent OAc groups is axially oriented, then the equatorially oriented acetate group, when in position C, would interact with the axially oriented adjacent OAc group; in such cases only two regions are allowed (Fig. 4b and 4c). An axially oriented acetate group appears to take up only two positions, independent of the orientation of the adjacent groups. As in the calculation of entropy, the acetoxymethyl group was treated as a single unit by considering only its possible orientations around the C-5–C-6 bond. It can adopt all three dispositions when the C-5–C-6 bond is equatorially oriented and two dispositions when it is axially oriented. Thus *P*, the number of possible acetate-group orientations for β-D-glucopyranose pentaacetate in

TABLE I

BOND ANGLES AT THE RING ATOM HAVING AN AXIAL SUBSTITUENT IN THE MINIMUM-ENERGY CONFORMATION*

Aldohexopyranose pentaacetate	*Bond-angle deviations from initial values in the minimum-energy conformation (in degrees)*	
	1C *Conformation Bond angle*	*Value*
α-D-*allo*	O-5–C-5–C-6 C-4–C-5–C-6	114
β-D-*allo*	O-5–C-5–C-6 C-4–C-5–C-6	114
α-D-*altro*	O-5–C-5–C-6 C-4–C-5–C-6	114
β-D-*altro*	O-5–C-5–C-6 C-4–C-5–C-6	114
	O-5–C-1–O-1 C-2–C-1–O-1	112
α-D-*galacto*	O-5–C-5–C-6 C-4–C-5–C-6	114
	C-2–C-3–O-3 C-4–C-3–O-3	112
β-D-*galacto*	O-5–C-5–C-6 C-4–C-5–C-6	114
	O-5–C-1–O-1 C-2–C-1–O-1	113
	C-2–C-3–O-3 C-4–C-3–O-3	113
α-D-*gluco*	O-5–C-5–C-6 C-4–C-5–C-6	114
	C-1–C-2–O-2 C-3–C-2–O-2	111
	C-2–C-3–O-3 C-4–C-3–O-3	111
	C-3–C-4–O-4 C-5–C-4–O-4	111
β-D-*gluco*	O-5–C-5–C-6 C-4–C-5–C-6	114
	O-5–C-1–O-1 C-2–C-1–O-1	111
	C-1–C-2–O-2 C-3–C-2–O-2	111
	C-2–C-3–O-3 C-4–C-3–O-3	111
β-D-*gluco*	C-3–C-4–O-4 C-5–C-4–O-4	111
α-D-*gulo*	O-5–C-5–C-6 C-4–C-5–C-6	114
β-D-*gulo*	O-5–C-5–C-6 C-4–C-5–C-6	114
	O-5–C-1–O-1 C-2–C-1–O-1	112
α-D-*ido*	O-5–C-5–C-6 C-4–C-5–C-6	114
β-D-*ido*	O-5–C-5–C-6 C-4–C-5–C-6	114
	O-5–C-1–O-1 C-2–C-1–O-1	112
α-D-*manno*	O-5–C-5–C-6 C-4–C-5–C-6	114
	C-2–C-3–O-3 C-4–C-3–O-3	111
β-D-*manno*	O-5–C-5–C-6 C-4–C-5–C-6	114
	O-5–C-1–O-1 C-2–C-1–O-1	113
	C-2–C-3–O-3 C-4–C-3–O-3	113
α-D-*talo*	O-5–C-5–C-6 C-4–C-5–C-6	114
	C-2–C-3–O-3 C-4–C-3–O-3	112
β-D-*talo*	O-5–C-5–C-6 C-4–C-5–C-6	114
	O-5–C-1–O-1 C-2–C-1–O-1	112
	C-2–C-3–O-3 C-4–C-3–O-3	112

*When the axial substituents were tilted, the hydrogen atoms attached to these ring-carbon atoms were re-fixed by following Hendrickson's[22] method to minimise the total energy of angle strain in the five angles involved. These bond angles are not shown in the table.

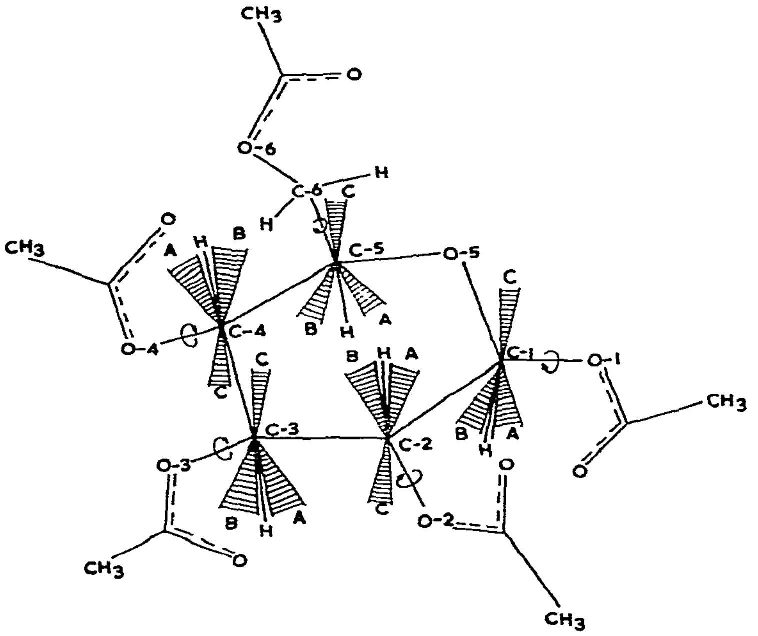

Fig. 3. Schematic representation showing the allowed rotational positions of the acetate groups (shaded areas) of β-D-glucose pentaacetate in the *C1*(D) conformation. The shaded areas are the projections of space that are swept by the planar acetate groups in their rotations about C–O bonds and the CH_2OAc group about the C–C bond.

TABLE II

CONFORMATIONAL ENTROPIES OF ALDOHEXOPYRANOSE PENTAACETATES RESULTING FROM VARIOUS POSSIBLE ORIENTATIONS OF THE OAc GROUPS AND CH_2OAc GROUP

Aldohexopyranose pentaacetate	P		*Conformational entropy in cal.mole^{-1}.deg^{-1}*	
	C1	1C		
α-D-*allo*	48	32	7.70	6.89
β-D-*allo*	72	32	8.50	6.89
α-D-*altro*	48	72	7.70	8.50
β-D-*altro*	48	32	7.70	6.89
α-D-*galacto*	48	32	7.70	6.89
β-D-*galacto*	108	32	9.31	6.89
α-D-*gluco*	108	32	9.31	6.89
β-D-*gluco*	243	32	10.92	6.89
α-D-*gulo*	48	32	7.70	6.89
β-D-*gulo*	72	32	8.50	6.89
α-D-*ido*	48	108	7.70	9.31
β-D-*ido*	48	48	7.70	7.70
α-D-*manno*	72	48	8.50	7.70
β-D-*manno*	72	32	8.50	6.89
α-D-*talo*	48	48	7.70	7.70
β-D-*talo*	48	32	7.70	6.89

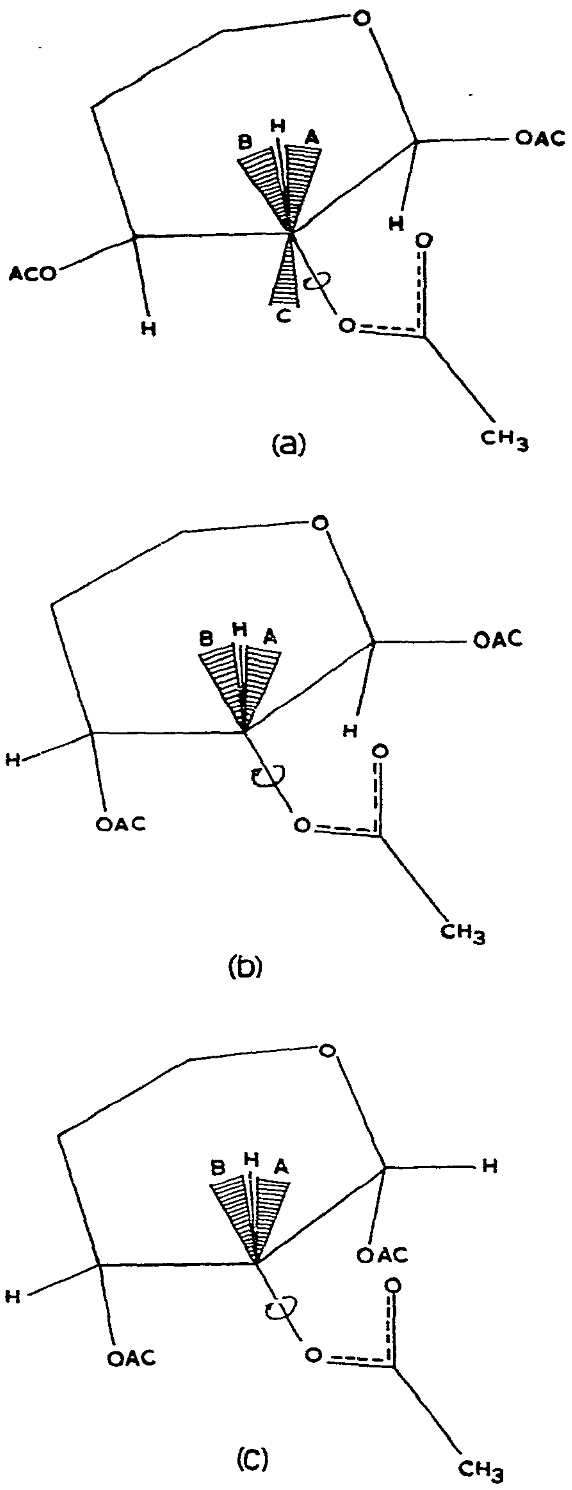

Fig. 4. Schematic representation showing the allowed regions (shaded areas) of the equatorial acetate group (*a*) when both of the adjacent acetate groups are equatorially disposed (*b*) when one of the adjacent acetate groups is axially disposed, and (*c*) when both of the adjacent acetate groups are axially disposed. The shaded areas are the projections of the space swept by the planar acetate group in its rotation about the C–O bond.

the *C*1(D) conformation, is 243, whereas in the *1C*(D) conformation there are 32 possible orientations. The values of *P* thus obtained for the sixteen aldohexopyranose pentaacetates are given in columns 2 and 3 of Table II. From these values, the conformational entropies were computed according to the expression:

$$S = 2.3 R \log P, \qquad (4)$$

where *R* is the universal gas constant.

RESULTS AND DISCUSSION

The charge distribution, evaluated as just described for aldohexopyranose pentaacetates, is shown in Fig. 1. There is a traceable pattern in the distribution of charges in different parts of the molecule. The anomeric carbon atom has a charge of about 0.18, whereas the other ring-carbon atoms have a charge of about 0.10. The ring-oxygen atom has a charge of about -0.27, but the net charge on other oxygen atoms directly linked to the ring-carbon atoms is about -0.18. The charge on hydrogen atom attached to the ring-carbon atom is about 0.05, whereas the hydrogen atoms of the acetate group possess charges of about 0.04. The net charge on a carbon atom in the sp^2 state is about 0.44. On the other hand, an sp^3-hybridized carbon atom linked to the foregoing carbon atom possesses a charge of -0.09. The carbonyl oxygen atom has a net charge of about -0.43.

It is noteworthy that the charges on the oxygen atoms directly linked to the ring-carbon atoms of the pentaacetate are less negative than the corresponding values observed for free sugars[8]. Also, the charges on the ring-carbon atoms are slightly less positive than the corresponding values in free sugars. Thus it seems that the replacement of the hydroxyl hydrogen atom by the acetate group affects the charges, not only at the site of replacement, but also the charges on the neighbours.

It can beseen from Table I that no distortion from the initial positions is required for energy minimization of the *C1*(D) conformations. In fact, the potential energy of the *C1*(D) conformations was found to increase when the axial acetate groups were given tilts, in contrast to the behavior found for free sugars[7,8]. These results indicate that the strain induced by axial acetoxyl groups is probably less than that of axial hydroxyl groups. Table I also shows that, in the 1*C*(D) conformations, the tilts of the axially disposed acetate groups involved in the Hassel–Ottar effect are about 1.5–2.5°. These tilts are about one degree less than those obtained for free sugars[8].

The potential energies of the minimum-energy conformations of sixteen aldohexopyranose pentaacetates are shown in columns 2 and 3 of Table III and their estimated free energies are given in columns 4 and 5 of Table III. The calculated free-energy differences of 2–4 kcal.mole^{-1} between the *C1*(D) and *1C*(D) conformations (columns 4 and 5 of Table III) of the pentaacetates of α- and β-glucose, and α- and β-mannose, clearly indicate that these molecules favour the *C1*(D) conformation in solution, in accordance with experimental observations[2]. However, the estimated free-energy difference between the *C1* conformations of the α- and β-anomers of D-mannose pentaacetate and D-glucose pentaacetate are -0.19 and 0.16 kcal.mole^{-1}, respectively, at variance with the corresponding experimental values[19] of −1.08 and −0.99 kcal.mole^{-1}, obtained from equilibrium data based on specific rotation of the isolated, anomerized products. This discrepancy between the theory and experiment may be due to the anomeric effect of the acetoxyl group, which was not taken into account in the present calculations. Hence, a value of 0.9 kcal.mole^{-1} was introduced for the anomeric effect of the acetoxyl groups. This value was added to the free energies given in columns 4 and 5 of Table III. The free energies, thus corrected for the anomeric effect, are shown in columns 6 and 7 of Table III.

TABLE III

CONFORMATIONAL-ENERGY VALUES CALCULATED FOR ALDOHEXOPYRANOSE PENTAACETATES*
(IN kcal.mole^{-1})

Aldohexopyranose pentaacetate	*Calculated potential energies*		*Calculated free energies*		*Calculated free-energies after correcting for the anomeric effect*	
	C1	1C	C1	1C	C1	1C
α-D-*allo*	−0.38	1.26	0.59	2.47	−0.31	2.47
β-D-*allo*	−0.16	1.62	0.57	2.83	0.57	1.93
α-D-*altro*	−0.41	1.72	0.56	2.45	−0.34	2.45
β-D-*altro*	−0.18	2.04	0.79	3.25	0.79	2.35
α-D-*galacto*	−0.19	1.49	0.78	2.70	−0.12	2.70
β-D-*galacto*	−0.08	2.67	0.41	3.88	0.41	2.98
α-D-*gluco*	−0.33	1.72	0.16	2.93	−0.74	2.93
β-D-*gluco*	0.00	3.18	0.00	4.39	0.00	3.49
α-D-*gulo*	−0.20	1.52	0.77	2.73	−0.13	2.73
β-D-*gulo*	0.07	1.51	0.80	2.72	0.80	1.82
α-D-*ido*	−0.53	1.31	0.44	1.80	−0.46	1.80
β-D-*ido*	−0.14	1.43	0.83	2.20	0.83	1.30
α-D-*manno*	−0.27	1.43	0.46	2.40	−0.44	2.40
β-D-*manno*	−0.08	2.15	0.65	3.36	0.65	2.46
α-D-*talo*	0.43	1.22	1.40	2.19	0.50	2.19
β-D-*talo*	0.18	1.77	1.15	2.98	1.15	2.08

*The excess energy of a particular conformation in each set, over that of β-D-glucopyranose pentaacetate in the *C1*(D) conformation in that set, is given.

It can be seen from Table III that the free-energy differences between the *C1*(D) and *C1*(D) conformations of the pentaacetate molecules are decreased to 1.6–3.7 kcal.mole^{-1}. These differences are much smaller than those of 2–6 kcal.mole^{-1} obtained for free sugars[7,8].

Table III (columns 6 and 7) shows that the *C1*(D) conformations of most of the examples have lower free-energy than their *1C*(D) conformers. The calculated free-energy differences of about 2.8 and 2.3 kcal.mole^{-1} between the *C1* and *1C* conformations of α-D-altose pentaacetate and α-D-idose pentaacetate, respectively, indicate that these molecules exist in solution preponderantly in the *C1*(D) conformations, in agreement with n.m.r.-spectral evidence[3,4]. The free-energy calculations predict that the two chair forms of β-D-idopyranose pentaacetate differ by about 0.5 kcal.mole^{-1} in free energy, and should exist as a *C1*⇌*1C* conformational mixture in solution, the *C1*(D) conformation being the predominant (70%) form, in fairly good agreement with recent n.m.r. studies[20]. It is also noteworthy that, except for allose and gulose, the present calculations predict that α-anomer predominates in the equilibria between α- and β-anomers of the hexose pentaacetates, in agreement with experimental data[6].

The present study also reveals that the anomeric effect of the acetoxyl group in the pentaacetates is only about 0.9 kcal.mole^{-1}. (this value includes the bond-angle and bond-length strain energy of 0.4 kcal.mole^{-1} due to the distortions at the C-*1* atom, as explained earlier), which is much smaller than that of 1.5 kcal.mole^{-1} assigned by Lemieux and Chü[5,6]. However, this value is higher than the value of 0.4 kcal.mole^{-1} assigned for the anomeric effect of the hydroxyl group[7], as predicted by the earlier investigators[5].

It is also worthy of note that, although the free sugars α-D-altrose and α-D-idose favour the *C1*⇌*1C* equilibrium[7,21] and β-D-idose favours the *C1* conformation, the present calculations, as pointed out earlier, predict that the acetates of the former two molecules favour the *C1* conformation and the latter, the *C1*⇌*1C* equilibrium in solution. Thus, the present calculations also indicate, in conformity with earlier experimental results[4,6], that the pyranoid-ring conformation is influenced by the nature of the substituents.

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