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Note

Theoretical studies on the conformations of aldopentopyranose tetraacetates*

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In previous papers we reported energy calculations on aldopyranoses[1–3], cyclitols[4], methyl glycopyranosides[5], and aldohexose pentaacetates[6] These calculations have now been extended to aldopentopyranose tetraacetates to afford more information about the stereochemistry of six-membered rings

The atoms in the ring (Fig 1) and the atoms bonded directly to the ring were fixed in the *C1*(D) and *1C*(D) conformations by using the bond lengths and bond angles reported earlier[1–3 5 6] The acetate groups were also fixed in the minimum-energy positions by an iterative process[6] To calculate the electrostatic contribution to the total energy, the fractional charges on various atoms were assigned by a molecular-orbital method[7,8] The π charges arising from the mobile electron-density at each atom in the conjugated regions (namely, the acetate groups), and σ charges on the saturated single-bond framework, were evaluated separately and the net charges obtained by summing the π- and σ-charge contributions The net charges so obtained on the atoms of the aldopyranose tetraacetate molecule are shown in Fig 1 The expressions used, and the procedure followed to obtain the minimum potential- and free energies of these molecules in the *C1*(D) and *1C*(D) conformations, are the same as those reported earlier[6].

RESULTS AND DISCUSSION

The results of the energy calculations on aldopentopyranose tetraacetates are shown in Table I The potential energies of the minimum-energy conformations are given in columns 2 and 3 and the free energies in columns 4 and 5 of Table I The

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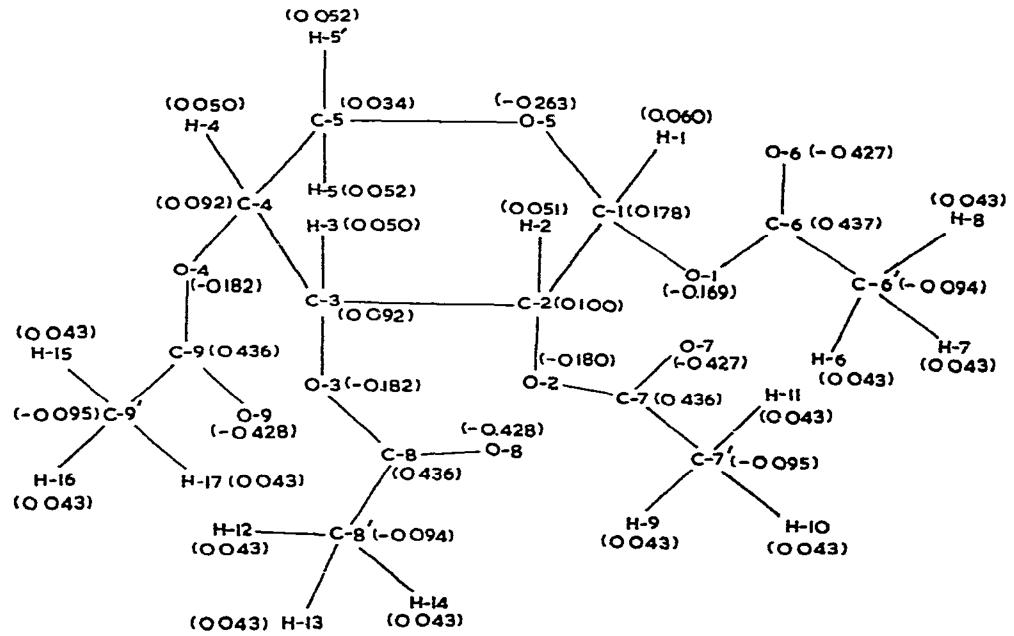

Fig 1 Charge distribution in aldopentopyranose tetraacetates (in fractions of an electronic charge)

TABLE I

CONFORMATIONAL ENERGIES OF ALDOPENTOPYRANOSE TETRAACETATES[a] (IN KCAL MOLE^{-1})

Aldopento-pyranose tetraacetate	*Calculated potential energies*		*Calculated free energies*		*Free energies corrected for the anomeric effect*		*Free energy difference ΔG*	*ΔG from[b] n m r for*
	C1	1C	C1	1C	C1	1C	C1−1C	C1–1C
α-D-*arabino*	−0.36	−0.07	+0.61	+0.42	−0.09	+0.42	−0.51	+0.81±0.34
β-D-*arabino*	+0.11	−0.05	+1.08	+0.92	+1.08	+0.22	+0.86	+1.9±1.0
α-D-*lyxo*	−0.12	−0.22	+0.61	+0.51	−0.09	+0.51	−0.60	−0.55±0.30
β-D-*lyxo*	−0.01	−0.35	+0.72	+0.62	+0.72	−0.08	+0.80	+0.28±0.27
α-D-*ribo*	−0.05	−0.56	+0.92	+0.41	+0.22	+0.41	−0.19	−0.74±0.33
β-D-*ribo*	−0.16	−0.63	+0.57	+0.34	+0.57	−0.36	+0.93	+0.18±0.26
α-D-*xylo*	−0.12	−0.27	+0.37	+0.70	−0.33	+0.70	−1.03	<−2.4
β-D-*xylo*	+0.00	−0.65	+0.00	+0.32	+0.00	−0.38	+0.38	−0.58±0.30

[a] The excess energy of a particular conformation in each set, over that of β-D-xylopyranose tetraacetate in the *C1* conformation in that set, is given [b] Data taken from ref 9.

calculated free-energy difference (ΔG) between the *C1*(D) and *1C*(D) conformations agree fairly well with the experimental values of Durette and Horton[9] (columns 8 and 9) after adding a value of 0.7 kcal mole^{-1} (without considering the nature of the solvent) to the conformations having an equatorial C-1–O bond to account for the observed preferential shortening[5,6,10,11] and the exo-anomeric effect[12]; the former may contribute about 0.4 kcal mole^{-1} and the latter about 0.2–0.4 kcal mole^{-1}. This value probably depends to a small extent on the nature of the solvent. Some investigators have considered the shortening of the C-1–O bond as part of the anomeric effect[10]. Columns 8 and 9 of Table I show that the signs of the calculated ΔG values are in agreement with experimental values for all of the molecules, except for α-D-arabinose and β-D-xylose tetraacetates. However, the low calculated ΔG values in these two cases indicate that they exist to an appreciable extent in both *C1* and *1C* conformations in solution, in agreement with experimental evidence (Table II).

TABLE II

CONFORMATIONAL EQUILIBRIA OF D-ALDOPENTOPYRANOSE TETRAACETATES

Compound	*Calculated* (%)		*Equilibrium data*[a] (%)	
	C1	1C	C1	1C
α-D-*arabino*	70	30	21	79
β-D-*arabino*	19	81	4	96
α-D-*lyxo*	73	27	71	29
β-D-*lyxo*	21	79	39	61
α-D-*ribo*	58	42	77	23
β-D-*ribo*	17	83	43	57
α-D-*xylo*	85	15	>98	<2
β-D-*xylo*	34.5	65.5	72	28

[a] Taken from ref. 9.

It is also interesting that for both the *C1*(D) and the *1C*(D) conformations of the aldopentopyranose tetraacetates, the overall potential energies were found to be at a minimum for the ideal (initial) models, in contrast to the results obtained for the free sugars. This observation indicates that the strain introduced by *syn*-diaxial acetate groups is less than that of similarly disposed hydroxyl groups[3], in agreement with the results obtained for aldohexopyranose pentaacetates[6].

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