

1, 6-Anhydropyranose 의 분자구조의 역학적응용

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Application of Molecular Mechanics to the Structure of 1, 6-Anhydropyranoses

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요 약. Empirical force-field method 를 단결정 회절방법으로 구조가 연구된 여덟개의 1,6-anhydropyranose 분자구조^{13~21}에 적용하였다. 이론적 계산에서도 분자들간의 pyranose 고리 conformation 의 1C_4 와 E_0 사이의 차이는 실험치와 비슷하게 얻어졌다. Five-membered anhydro 고리의 분자들간의 작은 conformation 차이는 잘 예측되지 않았다. C-C 결합 길이의 계산치는 실험치와 0.012 Å 내에서, C-O 결합 길이는 0.027 Å 내에서, non-hydrogen atom 의 결합각은 1.9° 이내에서 일치되고 있다.

ABSTRACTS. Empirical force-field calculations have been applied to eight 1,6-anhydropyranoses, the crystal structures^{13~21} of which have been studied by single crystal X-ray or neutron diffraction analysis. The theoretical calculations reproduce closely the variations in conformation between 1C_4 and E_0 , which are observed in the pyranose rings. The smaller conformational differences in the five-membered anhydro ring are not so well predicted. The calculated C—C bond lengths agree with those observed within 0.012 Å with one exception. The C—O bond lengths show a larger deviation, 0.027 Å. The non-hydrogen atom valence angles agree within 1.9°.

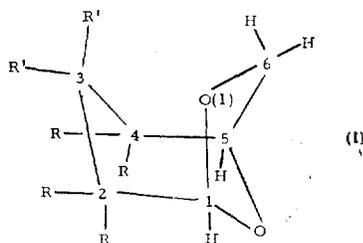
INTRODUCTION

Empirical force-field methods or "molecular mechanics" have been shown to predict the dimensions of alkanes and non-conjugated alkenes to within the experimental limits of error of gas-phase and crystal X-ray diffraction methods^{1,2}. The application of these methods to

carbohydrates is more uncertain because of difficulties associated with the anisotropy of the electronic distribution about ring and glycosidic oxygen atoms and hydroxyl groups. However, a force field calculation on α - and β -glucopyranose did give a value for the energy difference between the two anomers which was consistent with experiment³. In that work, the

empirical parameters were adjusted to give a good fit with the structure of α -D-glucopyranose, as observed by neutron diffraction⁴, and a good agreement was obtained for the bond lengths and valence angles.

In this study, we are testing the predictability for carbohydrates of a general purpose mechanics program⁵ against the molecular structural data provided by eight crystal structure determinations of molecules of the type I, where R is H, OH, or OAc, and R' is H, OH, NH₂ or NH₃⁺. These also include a molecule with a 2,3-oxirane ring and a 3,4-dioxalane ring.



1. MOLECULAR MECHANICS CALCULATIONS

The program used was Allinger's MMI/MMPI^{6,7}, adapted for use on a DEC 1099 computer. The starting atomic parameters for the energy minimization were those from the crystal structure determination⁸. Because of the "false minima", there is no certainty that the structure corresponding to the energy minimization is that of lowest possible energy, nor can we say that a minimization starting from any other set of atomic coordinates would converge on the same structure.

RESULTS

The experimental data set is given in the key to Fig. 1 which shows the overall comparison in calculated and observed conformations of the pyranose rings. The agreement is excellent.

The average differences in the Q , θ , and ϕ pyranose ring puckering parameters⁹ are 0.011 Å, 3.73°, and 6.17°, respectively. Particularly noteworthy are the two experimental points for molecule VIII, which correspond to two symmetry-independent molecules in the crystal structure. The difference between theory and experiment is clearly the same order of magnitude as the conformational differences between the two molecules due to crystal field forces.

In contrast, the conformational differences of the five-membered anhydro rings in these eight molecules show little correlation between theory and experiment, as shown in Table 1. This could be the consequence of two approximations. One is that no distinction was made in the empirical force-field parameters between the C—O bonds, although they are known from X-ray structural data and ab-initio calculations^{10,11} to have different bond lengths, valence angles, and torsion angle potentials. The second is that the potential for conformational changes in the anhydro ring is pseudo-rotational in character, and very susceptible to the crystal field forces, which were omitted from consideration.

The agreement between the experimental and theoretical bond lengths and valence angles is summarized in Table 2. Omitted from this summary is the C-2—C-3 bond in VIII. The shortening to 1.457 Å, 1.463 Å (1.467, 1.473 Å corrected for thermal motion) due to the oxirane ring was not reproduced by the theoretical calculations which gave a normal value of 1.527 Å. Otherwise, the overall agreement for the C—C bond lengths was very good. That for the C—O bond lengths was less good, the theoretical values tending to be shorter than the experimental (the thermal motion corrections increase these discrepancies, since they lengthen the observed values). The agreement in the valence angles is reasonably good with no ob-

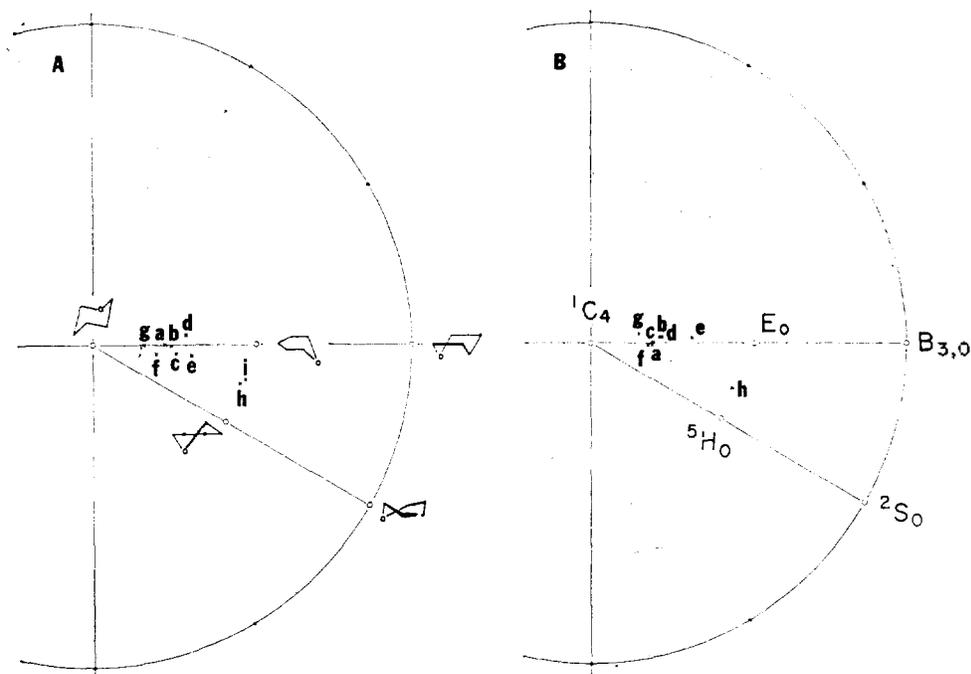


Fig. 1. Stereograms¹² of the θ and ϕ puckering parameters⁹ for 1,6-anhydropyranoses; (A) experimental values, (B) theoretical values.

Key		Q_{exp} 0.01 Å	Q_{theory} 0.01 Å
a	I 1,6-anhydro- β -D-glucopyranose ^{13,14}	61.0	63.0
b	II 3-amino-1,6-anhydro-3-deoxy- β -D-glucopyranose ¹⁵	61.5	62.6
c	III 1,6-anhydro-2,3,4-triacetyl glucose ¹⁶	61.7	62.7
d	IV 3-ammonio-1,6-anhydro-3-deoxy- β -D-glucopyranose chloride monohydrate ¹⁷	61.6	61.4
e	V 1,6-anhydro-3,4-O-isopropylidene- β -D-talopyranose ¹⁸	63.0	61.5
f	VI 2,3-di-O-acetyl-1,6-anhydro- β -D-galactopyranose ¹⁹	62.4	63.3
g	VII 2,7-anhydro-D-altrioheptulose ²⁰	64.4	63.5
h	VIII 1,6:2,3-dianhydro- β -D-gulopyranose ²¹	62.9 63.1	62.2

vious distinction between those between C—C bonds and C—C and C—O bonds.

In general, the agreement between the calculations and the experimental data was remarkably good, taking into account the fact that theoretical method used makes no distinction between ring and glycosidic oxygen atoms, hydroxyl oxygen atoms, and carbonyl oxygen atoms, and no corrections were made

for the distortion due to crystal field forces.

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Table 1. Puckering parameters^a for the anhydro rings in 1,6-anhydropyranoses.

	q		φ	
	Experimental	Theoretical	Experimental	Theoretical
I ^b	41.9	43.6	41.39	39.97
II	42.3	44.4	49.99	49.35
III	35.5	44.0	36.60	46.73
IV	41.3	45.2	55.67	47.32
V	41.2	43.4	40.04	51.88
VI	42.1	44.2	43.89	42.69
VII	41.2	43.9	41.54	47.66
VIII	40.0 40.6	44.3	25.06 27.07	17.55

^aRef. 9. q are in 0.01 Å φ in degrees. The anhydro ring is numbered in the program so that C-1 is atom 1, O-5 is atom 2, proceeding clockwise around the ring when viewed from C-3.

^bThe key to the molecules is given in the caption to Fig. 1.

Table 2. Comparison of observed calculated bond lengths and valence angles in 1,6-anhydropyranoses.

	$\bar{\Delta}^a$	$ \bar{\Delta} ^b$
C-C	+0.3	1.2
C-O _r	-2.3	2.7
C-OH	-2.1	2.3
C-C-C	-0.3	1.9
C-C-OH	-0.4	1.7
C-O _r -C	-1.6	2.5
C-C-O _r	+0.9	1.7
O _r -C-O _r	+1.2	1.6

^a $\bar{\Delta}$ the mean deviation $\sum(b_{calc}-b_{obs})/n$, where n is the number of bonds or angles compared. Bond length deviations are in picometers, bond angles in degrees.

^b $|\bar{\Delta}|$ is the mean square root deviation $[\sum(b_{calc}-b_{obs})^2/n]^{1/2}$, where n is the number of bonds or angles compared.

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