

Short Communication

A Simplified Force Field for Glucopyranose

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In a former paper¹ we developed a force field for reproduction of the structures and the equilibrium distribution of α - and β -D-glucopyranoses through energy minimisation. The force field is simple and conventional: harmonic functions for bond and angle deformations, Pitzer terms for torsional motions, and Buckingham potentials for non-bonded interactions.

Some reflexions on the nature of torsional potentials (Ref. 2, p. 87) led us to the abandonment of this particular interaction. The rotation around single bonds in polyatomic molecules is truly hindered by a potential energy barrier, but only a very minor fraction of this barrier is a property of a bond which to a fair approximation is a sigma bond. The barrier arises from the interactions between charge clouds on atoms in vicinal positions to each other. Therefore a torsional term should simply not appear, leaving the hindered rotation around single bonds as the result of a pure non-bonded interaction.

The removal of torsional terms means a further simplification of our force field; yet, as we shall show, it achieves the same agreement with experimental observations. Because of technical difficulties in the complete removal of torsions, and because we wanted to keep the possibility of calculating torsional angles, the only change we made was in K_ϕ , where we use the value 0.02 kJ mol^{-1} or $0.005 \text{ kcal mol}^{-1}$. Otherwise the force field, called FF300, is identical to FF3 of the previous paper.¹ Minimisation in FF300 presents no problems.

In Table 1 we show deviations (calculated minus measured values) of bond lengths and angles. Comparison was made with neutron and X-ray diffraction structures of α - and β -D-glucopyranose^{3,4} and of methyl- α - and - β -D-glucopyranoside, which have

recently been published.^{5,6} For bonds we list the anomeric bond and the maximum, mean and mean square root deviations: there is no difference from one force field to the other. For valence angles, we list the maximum, mean and mean square root deviations, with the same conclusion. For torsions, the maximum and mean square root deviations are listed: the endocyclic and hybrid torsions show a slight improvement from FF3 to FF300.

Although none of the two force fields was selected to reproduce frequencies a comparison of calculated and measured vibrational spectra might be used to test the neglect of torsional potential terms. Our programme allows for a full normal coordinate calculation (Ref. 2, p. 162) of the minimised structure, which was carried out for the two anomers in both force fields.

As expected, any significant difference is seen in the range below 500 cm^{-1} . On the other hand, no experimental data, on basis of which a choice between the two force fields can be made, are available in this frequency range, because no assignments have yet been made.

The equilibrium distributions on anomers $\alpha:\beta$ are calculated to 0.39:0.61 in FF3 and 0.37:0.63 in FF300, based on the total energy as before.¹ Using a recent addition to our programme⁷ for evaluating statistical mechanical sums over the internal degrees of freedom, we find, based on the free enthalpy, the distributions 0.35:0.65 in FF3 and 0.31:0.69 in FF300. The calculations were done at 298 K and should be compared with measurements at 273 K (0.362:0.638),⁸ 273 K (0.374:0.626),⁸ 303 K (0.36:0.64)⁹ and 308 K (0.36:0.64).¹⁰ On this basis, FF3 is better than FF300. However, the validity of the statistical sums depends on the validity of the calculated frequencies, which, as mentioned above, cannot yet be checked.

Conclusion. The neglect of torsional potential terms leads to a very slight improvement in ring geometry and on the whole to no significant changes. In consequence, the simpler force field should be preferred in future work.

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Table 1. Deviations of calculated values from observed internal coordinates for -D-glucopyranoses.

	FF3				FF300			
	α -Neutron ³	Me- α -Neutron ⁵	β -X-ray ⁴	Me- β -X-ray ⁶	α -Neutron ³	Me- α -Neutron ⁵	β -X-ray ⁴	Me- β -X-ray ⁶
Bond lengths, Å								
anomeric	0.036	0.024	0.039	0.044	0.036	0.024	0.039	0.044
max, others	0.019	0.048	0.019	0.014	0.019	0.048	0.019	0.014
mean, all	0.003	0.006	0.006	0.006	0.003	0.006	0.006	0.006
mean sq.rt., all	0.011	0.014	0.014	0.015	0.011	0.014	0.015	0.015
Valence angles, °								
max	4.5	-3.7	-4.4	-2.8	4.5	-3.7	-4.5	-3.1
mean	0.2	0.1	0.2	0.2	0.2	0.0	0.2	0.2
mean sq.rt.	1.6	1.7	1.8	1.5	1.6	1.7	1.7	1.5
Endocyclic torsions, °								
max	4.2	2.4	4.5	5.8	2.0	2.5	3.6	5.0
mean sq.rt.	2.4	1.4	3.2	3.4	1.3	1.9	2.5	3.1
Hybrid torsions, °								
max	3.6	6.5	4.5	5.6	3.1	7.7	3.3	4.7
mean sq.rt.	2.1	4.0	3.2	4.1	1.7	4.2	2.5	3.7
Exocyclic torsions, °								
max	165	150	120	8	174	160	121	8
mean sq.rt.	114	107			114	112		

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Received October 17, 1977.