Conformation of a Seven-membered-ring Sugar: 1,2:3,4-Di-O-Isopropylidene-5-O-Chloroacetyl-α-D-Glucoseptanose

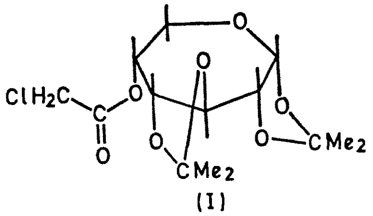
By J. JACKOBS† and M. SANDARALINGAM*‡

(*Department of Chemistry, Case Western Reserve University, Cleveland, Ohio and Department of Biochemistry, University of Wisconsin, Madison, Wisconsin* 53706)

Summary The *X*-ray structure of 1,2 : 3,4-di-*O*-isopropylidene-5-*O*-chloroacetyl-α-D-glucoseptanose shows that the seven-membered septanose ring adopts a conformation which lies between the chair and twist-chair forms.

WE here report the crystal structure and conformation of the septanose derivative 1,2 : 3,4-di-*O*-isopropylidene-5-*O*-chloroacetyl-α-D-glucoseptanose (I).[1] This crystal structure represents the first example of a sugar with a seven-membered ring.

Excellent single crystals of the compound were kindly supplied to us by Dr. J. D. Stevens who is pursuing the n.m.r. studies on (I) and related seven-membered-ring sugars with the intention of understanding their conformational characteristics in solution.[1] The colourless crystals belong to the orthorhombic system, space group $P2_12_12_1$



(I)

---

† Present address: Department of Physics, Heidelberg College, Tiffin, Ohio 44883.

‡ Present address: Department of Biochemistry, University of Wisconsin, Madison, Wisconsin 53706.

with $a = 27{\cdot}750 \pm 0{\cdot}002$, $b = 10{\cdot}714 \pm 0{\cdot}001$, $c = 5{\cdot}702 \pm 0{\cdot}001$ Å, $Z = 4$, $D_m = 1{\cdot}25$ g.cm.$^{-3}$ (by flotation in KI–H_2O solution at 25°), $D_c = 1{\cdot}21$ g.cm.$^{-3}$.

The structure analysis was based on 1234 independent reflections recorded on a four-circle Picker automatic diffractometer, using Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å) to a 2θ limit of 126°. The structure was essentially solved by the heavy-atom technique. Phases for the 395 strongest planes, based on the chlorine positions, were refined using the tangent formula.[2] An E-map calculated from the refined phases unequivocally established the structure. The final discrepancy factor R after full-matrix least-squares refinement was 0·066, and the estimated standard deviations in the atomic positions are about 0·008 Å.

The molecule viewed down the c axis is shown in perspective in the Figure. Of particular interest to us is the conformation of the septanose ring. The torsional angles about the ring bonds for the seven-membered ring and the two dioxalan rings are given in the Figure. It is of interest to compare these values with those predicted for the preferred chair and twist–chair conformations of cycloheptane by Hendrickson based on energy calculations[3] (see Table). In cycloheptane the twist–chair was predicted to be slightly more stable than the chair. However, our solid state study reveals that the septanose ring lies between the chair and the twist–chair conformations. The intermediate conformation may be influenced by the rigidity imposed on the septanose ring by the dioxalan rings and the presence of the ring oxygen atom. The n.m.r. data of Dr. Stevens point to a chair conformation for the septanose ring in solution.[1]

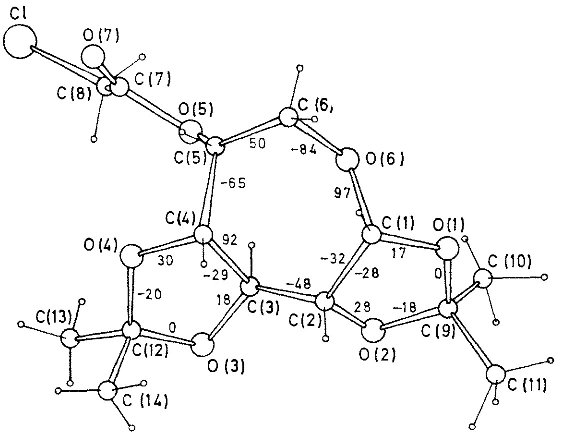


FIGURE.

Comparison of the torsional angles in the septanose with those of the chair and twist–chair conformations in cycloheptane.

Bond	Septanose[b]	Cycloheptane[3]	
		Chair[a]	Twist–chair
C(1)–C(2)	−32	0	−53
C(2)–C(3)	−48	−71	76
C(3)–C(4)	92	92	−97
C(4)–C(5)	−65	−70	41
C(5)–C(6)	50	70	41
C(6)–O(6)	−84	−92	−97
O(6)–C(1)	97	71	76

[a] It should be pointed out that this is only one of the chair forms of cycloheptane which it passes through in its pseudorotation itinerary.

[b] The estimated standard deviation in the torsional angles is about 1·2°.

The conformations of the two isopropylidene rings are nearly identical and occur in a perfect envelope (**E**) conformation. In the 1,2-*O*-isopropylidene ring atom C(2) is displaced from the remaining four ring atoms, while in the 3,4-*O*-isopropylidene ring atom C(4) is displaced. The envelope conformation appears to be the rule rather than the exception for the isopropylidene rings having a fused C–C bond.[4]

We thank Dr. J. D. Stevens for supplying the crystals and Dr. Martin A. Reno for collecting the data. Financial assistance from the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

(*Received, November 25th*, 1969; *Com.* 1790.)

---

[1] J. D. Stevens, *Chem. Comm.*, 1969, **1140**, and personal communication.

[2] J. Karle and H. Hauptman, *Acta Cryst.*, 1956, **9**, 635.

[3] J. B. Henrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537.

[4] M. Sundaralingam, unpublished results.