Carbohydrate Research, 219 (1991) 9–13
Elsevier Science Publishers B.V., Amsterdam

Crystal structure of ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*-hexopyranoside

Zbigniew Ciunik,
Instytut Chemii, Uniwersytet Wrocławski, 50-383 Wrocław (Poland)

Roman Szweda, and Zygfryd Smiatacz
Instytut Chemii, Uniwersytet Gdański, 80-952 Gdańsk (Poland)

(Received October 4th, 1990; accepted for publication, February 14th, 1991)

ABSTRACT

The crystals of the title compound, $C_{14}H_{21}NO_9$ (M_r 347.4), are orthorhombic, space group $P2_12_12_1$ with $a = 8.998(2)$, $b = 13.641(2)$, $c = 14.027(3)$ Å, $V = 1721.7(6)$ Å^3, and $Z = 4$; $D_c = 1.34$ g.cm^{-3}. The pyranoid ring has the distorted $^4C_1$ conformation and the hydroxyimino group has the *Z* conformation.

INTRODUCTION

2-Deoxy-2-oxyiminopyranosides (with one sp^2-hybridised carbon atom in the ring) have a distorted chair conformation, and the N(oxime) atom is in a pseudo-equatorial position[1,2]. The pyranoid rings of these compounds have different distortions of the chair conformation, whereas the exocyclic substituents are similar. Moreover, the same chemical, but symmetry-independent molecules have quite different endocyclic torsion angles (the maximum difference for the angle C-1–C-2–C-3–C-4 is 15.1°). The results now reported are part of a study of the structures of pyranosides having one sp^2-hybridised carbon atom in the ring.

EXPERIMENTAL

The title compound, prepared and recrystallised as described[3], had m.p. 139–140° and $[\alpha]_{589}^{20}$ +76° (*c* 0.5, chloroform).

*X-Ray structure determination**. — The space group was determined from oscillation and Weissenberg photographs. All measurements for a crystal 0.80 × 0.55 × 0.55 mm were made on a Syntex $P2_1$ diffractometer, using Mo-*Kα* radiation ($\lambda = 0.71069$ Å). The cell parameters were determined from a least-squares refinement of the setting angles of 15 reflections. Intensities of 2275 independent reflections were measured in the

* Lists of the observed and calculated structure factors, anisotropic thermal parameters, and fractional atomic co-ordinates have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/471/*Carbohydr. Res.*, 219 (1991) 9–13.

0008-6215/91/$ 03.50

2θ range 4–55° with the $\omega/2\theta$ scan technique, and h from 0 to 11, k from 0 to 17, and l from 0 to 18. The scan rate varied from 2.0 to 29.3°/min, depending on the intensity. Two standard reflections monitored periodically exhibited no significant variations in intensity during the period of data collection, and 1704 reflections with $I > 1.96\sigma(I)$ were used in the analysis. The intensities were not corrected for absorption.

The structure was solved by direct methods. Heavy atoms were refined by the block diagonal least-squares routine with isotropic and, subsequently, a full-matrix program with anisotropic temperature factors. The methyl and hydroxyl hydrogens were found from ΔF syntheses, and the positions of the remaining hydrogens were calculated based on the geometry of the molecule. The refinement of all non-H atom parameters yielded final R and R_w indexes of 0.051. The function minimised was Σ $w(|F_O| - |F_C|)^2$ with $w = \sigma^{-2}(F_o)$, where $\sigma(F_o)$ was taken from the counting statistics. During the last cycle of refinement, no parameter shifted more than 25% of its standard deviation. A final ΔF synthesis showed maximum and minimum electron densities of ± 0.22 eÅ^{-3}. Neutral-atom scattering factors were those listed[4]. The anomalous dispersion was included for O atoms. Calculations were performed using the following programs: MULTAN[5], Syntex XTL/XTLE[6], PUCK 2[7], and ORTEP[8].

RESULTS AND DISCUSSION

The numbering scheme, overall conformation, and molecular packing diagram of the title compound are shown in Figs. 1 and 2. Tables I and II list the bond lengths and angles, and selected torsion angles, respectively.

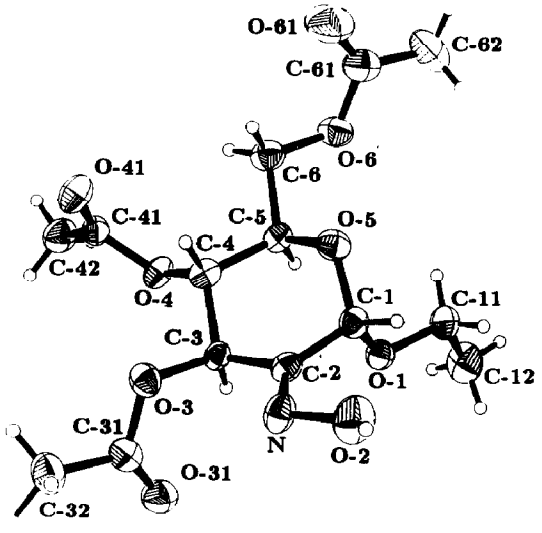

Fig. 1. ORTEP drawing showing atom numbering. The non-hydrogen atoms are represented by 30% probability ellipsoids, and the hydrogen atoms are drawn as spheres of arbitrary size.

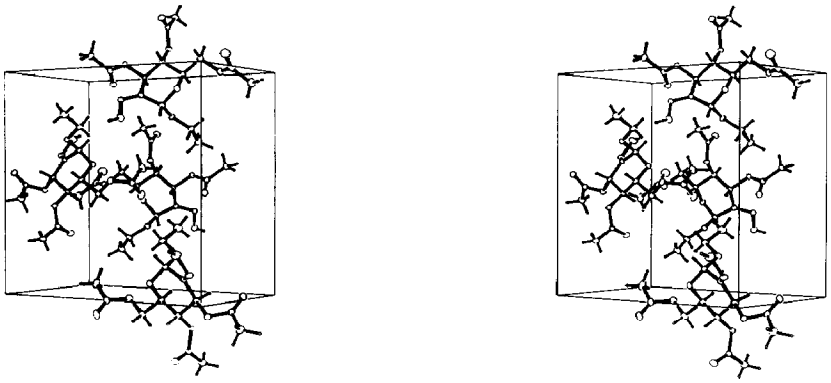

Fig. 2. Molecular packing.

TABLE I

Bond lengths (Å) and valency angles (degrees)[a]

O-1–C-1	1.400(4)	C-6–O-6–C-61	117.3(3)
O-1–C-11	1.440(4)	O-2–N–C-2	110.4(3)
O-2–N	1.395(4)	O-1–C-1–O-5	112.4(3)
O-3–C-3	1.452(4)	O-1–C-1–C-2	108.2(3)
O-3–C-31	1.355(4)	O-5–C-1–C-2	110.4(3)
O-4–C-4	1.421(4)	N–C-2–C-1	127.9(3)
O-4–C-41	1.352(4)	N–C-2–C-3	117.3(3)
O-5–C-1	1.418(4)	C-1–C-2–C-3	114.7(3)
O-5–C-5	1.426(4)	O-3–C-3–C-2	111.9(3)
O-6–C-6	1.450(5)	O-3–C-3–C-4	104.1(2)
O-6–C-61	1.339(5)	C-2–C-3–C-4	111.3(3)
O-31–C-31	1.170(5)	O-4–C-4–C-3	107.3(3)
O-41–C-41	1.188(5)	O-4–C-4–C-5	107.9(3)
O-61–C-61	1.206(6)	C-3–C-4–C-5	109.9(3)
N–C-2	1.273(5)	O-5–C-5–C-4	109.4(3)
C-1–C-2	1.481(5)	O-5–C-5–C-6	106.6(3)
C-2–C-3	1.516(5)	C-4–C-5–C-6	110.5(3)
C-3–C-4	1.530(5)	O-6–C-6–C-5	105.9(3)
C-4–C-5	1.537(5)	O-1–C-11–C-12	108.6(3)
C-5–C-6	1.522(5)	O-3–C-31–O-31	124.8(3)
C-11–C-12	1.486(7)	O-3–C-31–C-32	108.9(3)
C-31–C-32	1.501(6)	O-31–C-31–C-32	126.3(3)
C-41–C-42	1.483(6)	O-4–C-41–O-41	122.3(3)
C-61–C-62	1.479(6)	O-4–C-41–C-42	111.0(3)
C-1–O-1–C-11	113.7(3)	O-41–C-41–C-42	126.7(3)
C-3–O-3–C-31	116.7(3)	O-6–C-61–O-61	121.7(4)
C-4–O-4–C-41	118.3(3)	O-6–C-61–C-62	111.6(4)
C-1–O-5–C-5	112.5(3)	O-61–C-61–C-62	126.7(4)

[a] Estimated standard deviations in parentheses.

TABLE II

Selected torsion angles (degrees)[a]

O-5–C-1–C-2–C-3	50.6(4)
C-1–C-2–C-3–C-4	−45.0(4)
C-2–C-3–C-4–C-5	46.8(4)
C-3–C-4–C-5–O-5	−56.7(3)
C-4–C-5–O-5–C-1	65.2(3)
C-5–O-5–C-1–C-2	−61.3(4)
C-5–O-5–C-1–O-1	59.6(3)
O-5–C-1–O-1–C-11	63.2(3)
C-1–O-1–C-11–C-12	175.8(3)
C-1–O-5–C-5–C-6	−175.3(3)
O-5–C-5–C-6–O-6	65.3(3)
C-5–C-6–O-6–C-61	−137.5(3)
C-6–O-6–C-61–O-61	−1.0(6)
O-5–C-1–C-2–N	−126.1(4)
N–C-2–C-3–O-3	16.1(4)

[a] Estimated standard deviations in parentheses.

The pyranoid ring has the chair conformation. The Cremer and Pople ring-puckering parameters[9], $Q = 0.543(4)$ Å, $\theta = 11.4(3)°$, and $\varphi = 328(2)°$, indicated a small distortion of the $^4C_1$ conformation towards the $^{\circ}H_5$ half-chair. This distortion is similar to that observed in other 2-deoxy-2-oxyiminopyranosides[1,2] with the $^4C_1$ conformation. Including the current data, the Q, θ, and φ parameters for these compounds are in the ranges 0.522(5)–0.543(4) Å, 6.9(5)–26.5(4)°, and 281(4)–328(2)°, respectively. For molecules with relatively large distortion of the $^4C_1$ chair conformation [$\theta \geq 19.8(4)°$], the φ parameters indicate deformations towards the E_5 half-boat conformation ($B_{2,5}$ on the equator of the puckering stereogram[10]). Otherwise, for $\theta \leq 11.4(4)°$, the deformations are towards the $^4H_5$ and $^0H_5$ half-chair conformations (S_5 and $^0S_2$ on the equator, respectively). For compounds with the $^1C_4$ conformation, a similar tendency was observed. A ring with large distortion was deformed more towards ^5E than towards $^5H_4$, and a ring with a small deformation more towards $^5H_4$ than E_4.

These tendencies of the pyranoid ring in the 2-oxyimino derivatives of carbohydrates are consistent with studies of the interconversion pathway of the cyclohexane for which the half-chair (H) conformation is lower on the energy surface than the half-boat (E) conformation[11].

The geometry of the anomeric centre of the molecule (bond lengths, valency angles, and the *gauche/trans* orientation of the EtO-1 group) is typical for acetals with conformations determined by the anomeric and *exo*-anomeric effects[12].

Bond lengths and valency angles of other external groups and their conformations (in particular the *gauche/gauche* conformation of the acetoxymethyl group at C-5 and the planar Z conformation of the oxyimino group at C-2) are as expected[13] and observed[14,15] in other compounds of this type.

The hydrogen atom of the hydroxyimino group is involved in a weak, intermolecular O-2–H-2···O-41 ($\frac{3}{2}-x$, $1-y$, $-\frac{1}{2}+z$) hydrogen bond with the H···O length ~1.98 Å, the O-H···O angle ~134°, and the C-2–N–O-2–H-2 torsion angle ~147°.

ACKNOWLEDGMENT

This work was supported by the Ministry of Science and Higher Education (project RP II 10).

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