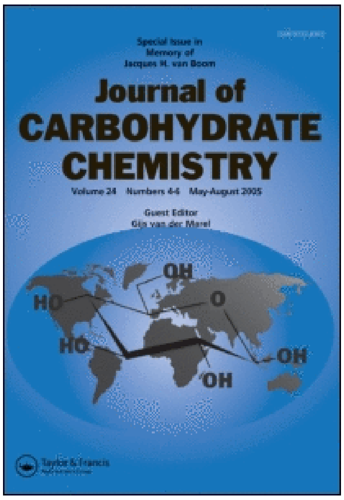

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CRYSTAL AND MOLECULAR STRUCTURE OF TWO 2-DEOXY-2-HYDROXYIMINO DERIVATIVES OF β-D-*ARABINO*-HEXOPYRANOSE

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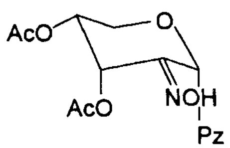
ABSTRACT

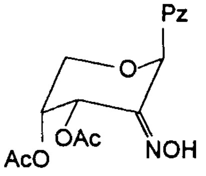
The crystal structure of *N*-acetyl-*N*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranosyl) amine (**1**) and 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranosyl azide (**2**) were determined by direct methods and refined by full-matrix least squares to a final value of $R = 0.034$ for 3114 (**1**) and 2924 (**2**) reflections. The pyranoid rings of both compounds have almost identical conformation between the $^{0}S_{2}$ twist-boat and the $^{3,0}B$ boat. It was found using semi-empirical quantum mechanical calculations that the conformation observed in the solid state for both compounds, similar to that in solution, is more stable than the other possible, $^{4}C_{1}$ conformation. Similarity of geometries of **1** and **2** suggests that the pyranoid ring is less flexible than those with a chair conformation in other 2-hydroxyimino derivatives of pyranosides. On the other hand the observed conformations of **1** and **2** as well as the postulated way for acetyl group migration during hydrogenation of 2-acetoxyimino analog of **2** (→**1**) confirm flexibility of the chair conformers. Results of conformation analysis of previous presented crystal structures of 2-oxyimino derivatives with a chair pyranoid ring and both title compounds suggest that the $^{4}C_{1}$ chair $\rightleftharpoons$ $^{0}S_{2}$ twist-boat/$^{3,0}B$ boat interconversion *via* the E_{5} half-boat is possible.

INTRODUCTION

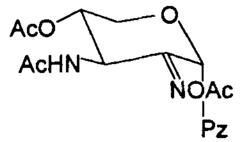
Recently we have solved several crystal structures of 2-deoxy-2-hydroxyiminopyranosides in the form of α- and β-D-*erythro*-pentopyranosides,[1] α-D-*threo*-pyranosides,[2] and α-D-*arabino*-pyranosides[2,3] with pyrazol-*N*-yl and ethoxy moiety as an aglycone. All these compounds have one *sp*^{2}-hybridised carbon atom vicinal to the anomeric centre.



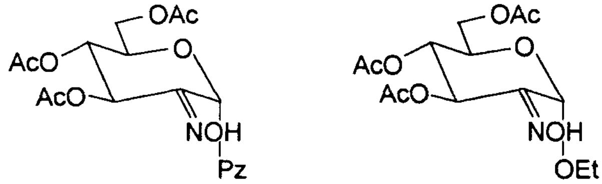
α-D-*erythro*-



β-D-*erythro*-



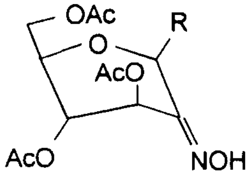
α-D-*threo*-pentopyranoside



α-D-*arabino*-hexopyranoside

The pyranoid rings have different distortions of the chair conformation, whereas the exocyclic substituents are similar and do not participate in any fused ring system. Moreover, the same chemical, but symmetry-independent molecules in the same crystal have quite different distorted pyranoid rings. For relatively large distortion of the $^4C_1$ chair conformation, deformation towards the E_5 half-boat was observed. Otherwise, the deformations are towards the $^4H_5$ or $^0H_5$ half-chair conformations. In the case of the $^1C_4$ chairs, the large and small deformations are towards the ^5E and $^5H_4$, respectively. These tendencies are comparable with those obtained from the studies on the interconversion pathway of the cyclohexane for which the half-chair (H) conformation lies lower on the energy surface than the half-boat (E) conformation.[4] The above observations, based only on the X-ray crystal structure analysis, suggest that pyranoid rings of the 2-deoxy-2-hydroxyiminopyranosides with a chair conformation are more flexible than the rings with all *sp*^{3}-hybridised carbon atoms.

In this paper we present new crystal structures of two 2-deoxy-2-hydroxyimino derivatives of β-D-*arabino*-hexopyranose:



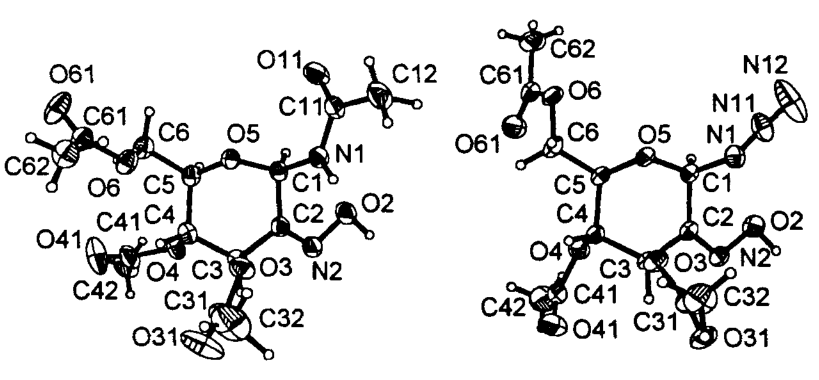
R: -NHAc (**1**), $-N_3$ (**2**)

Search of the β-D-*arabino*-hexopyranosides (Cambridge Crystallographic Data File,[5] updated January 1992) revealed only one crystal structure[6] with a fused ring system.

RESULTS AND DISCUSSION

The numbering scheme, overall conformation and molecular packing diagrams of molecules in both crystals are shown in Figs. 1-3. Bond distances, valency and selected dihedral angles are listed in Tables 1 and 2.

In both compounds, the pyranoid ring has the twist-boat conformation. The Cremer and Pople ring-puckering parameters[8] Q, θ and φ (calculated using program *PUCK2*[9]) for **1** [0.692(2) Å, 81.9(1) and 342.2(2)°, respectively] and for **2** [0.694(2) Å, 83.3(2) and 346.4(2)°, respectively] indicate the conformation between the $^{O}S_2$ twist-boat and the $^{3,O}B$ boat with a small distortion towards the $^4C_1$ chair.[10] This is the first example of two different 2-deoxy-2-hydroxyimino derivatives of carbohydrates with almost identical puckered pyranoid rings. A similar twist-boat conformation was found also in pyranosides with a fused ring systems, e.g. in the 1,2-*O*-alkylidene-α-D-allopyranose,[11,12] -α-D-glucopyranose,[13] -β-L-lyxopyranose[14] and other systems.[15-17] The presence of the fused rings in the sugars mentioned above and that of the *sp*^{2}-hybridised carbon atoms in both investigated compounds make it difficult to compare the geometry of these molecules. For this reason, to elucidate correlations between substituents and geometry parameters in the title compounds we have carried out semi-empirical quantum mechanical calculations for **1** and **2** as well as for several other systems using the AM1 Hamiltonian[18] in the MOPAC6 package.[19] After geometry optimization of **1** and **2** the conformations obtained for both compounds were almost identical with those observed in the crystal structures. The puckering parameters for molecules after the optimization were 0.659 Å, 83.4, and 339.8° for **1**, and 0.669 Å, 80.8, and 316.0° for **2**, respectively. These results agree well with the



1 **2**

FIG. 1. *ORTEP*[7] drawings of the molecular structures of **1** and **2**. The ellipsoids correspond to 30% probability contours of atomic displacements.

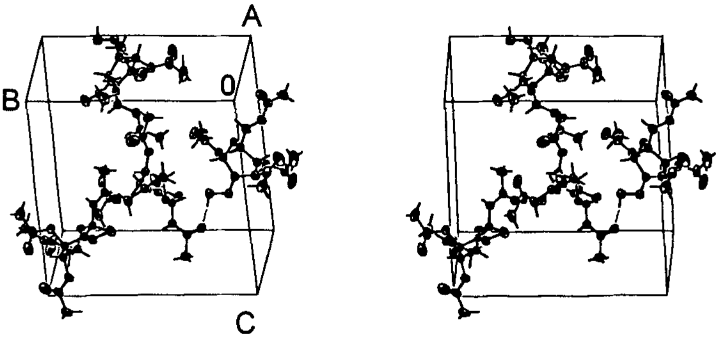


FIG. 2. Stereoview of the crystal packing in the unit cell for **1**. The hydrogen bond between molecules is represented by dotted line.

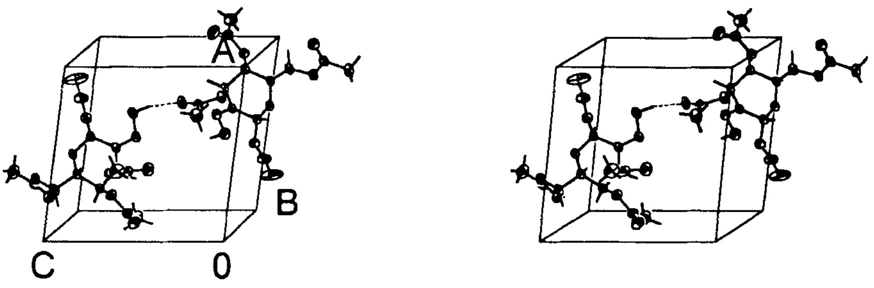


FIG. 3. Stereoview of the crystal packing in the unit cell for **2**. The hydrogen bond between molecules is represented by dotted line.

TABLE 1. Bond Lengths (Å) and Valency Angles (°) of **1** and **2** and their Standard Deviations.

	1	**2**		**1**	**2**
O(2)-N(2)	1.384(2)	1.397(2)	N(11)-N(1)-C(1)	-----	114.1(2)
O(3)-C(3)	1.453(2)	1.452(3)	N(1)-N(11)-N(12)	-----	172.7(3)
O(3)-C(31)	1.326(3)	1.344(2)	O(2)-N(2)-C(2)	110.8(2)	111.9(1)
O(4)-C(4)	1.434(2)	1.446(2)	O(5)-C(1)-N(1)	107.8(1)	105.4(1)
O(4)-C(41)	1.351(3)	1.340(3)	O(5)-C(1)-C(2)	109.5(1)	109.5(1)
O(5)-C(1)	1.416(2)	1.419(2)	N(1)-C(1)-C(2)	111.4(2)	110.4(1)
O(5)-C(5)	1.428(2)	1.427(2)	N(2)-C(2)-C(1)	125.7(2)	126.0(2)
O(6)-C(6)	1.444(2)	1.432(2)	N(2)-C(2)-C(3)	116.9(2)	116.9(1)
O(6)-C(61)	1.327(2)	1.355(3)	C(1)-C(2)-C(3)	117.3(2)	117.1(1)
O(11)-C(11)	1.220(3)	-----	O(3)-C(3)-C(2)	106.0(2)	109.1(1)
O(31)-C(31)	1.199(4)	1.198(3)	O(3)-C(3)-C(4)	108.7(2)	106.7(1)
O(41)-C(41)	1.199(4)	1.210(4)	C(2)-C(3)-C(4)	111.7(2)	111.2(1)
O(61)-C(61)	1.186(3)	1.203(3)	O(4)-C(4)-C(3)	107.0(2)	109.2(1)
N(1)-N(11)	----	1.215(3)	O(4)-C(4)-C(5)	107.7(2)	103.4(1)
N(1)-C(1)	1.436(2)	1.463(2)	C(3)-C(4)-C(5)	111.7(2)	111.5(1)
N(1)-C(11)	1.339(3)	-----	O(5)-C(5)-C(4)	109.7(1)	111.2(1)
N(11)-N(12)	----	1.121(3)	O(5)-C(5)-C(6)	107.6(2)	108.4(1)
N(2)-C(2)	1.273(3)	1.271(2)	C(4)-C(5)-C(6)	114.1(2)	111.1(1)
C(1)-C(2)	1.512(2)	1.517(2)	O(6)-C(6)-C(5)	107.0(2)	110.8(2)
C(2)-C(3)	1.493(2)	1.488(2)	O(11)-C(11)-N(1)	122.8(2)	----
C(3)-C(4)	1.531(3)	1.531(2)	O(11)-C(11)-C(12)	122.1(2)	-----
C(4)-C(5)	1.537(3)	1.535(2)	N(1)-C(11)-C(12)	115.2(2)	-----
C(5)-C(6)	1.503(3)	1.519(2)	O(3)-C(31)-O(31)	121.1(3)	122.1(2)
C(11)-C(12)	1.504(3)	-----	O(3)-C(31)-C(32)	111.5(3)	111.7(2)
C(31)-C(32)	1.502(5)	1.496(4)	O(31)-C(31)-C(32)	127.1(3)	126.2(2)
C(41)-C(42)	1.495(4)	1.486(5)	O(4)-C(41)-O(41)	122.4(3)	121.4(3)
C(61)-C(62)	1.485(3)	1.498(3)	O(4)-C(41)-C(42)	110.1(3)	111.1(3)
C(3)-O(3)-C(31)	117.2(2)	115.7(2)	O(41)-C(41)-C(42)	127.5(3)	127.4(3)
C(4)-O(4)-C(41)	116.8(2)	118.9(2)	O(6)-C(61)-O(61)	123.0(2)	123.2(2)
C(1)-O(5)-C(5)	111.1(1)	110.8(1)	O(6)-C(61)-C(62)	112.0(2)	111.3(2)
C(6)-O(6)-C(61)	116.4(2)	115.9(2)	O(61)-C(61)-C(62)	124.9(2)	125.4(2)
C(1)-N(1)-C(11)	121.5(2)	-----			

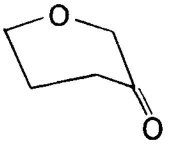
^{1}H NMR spectrum obtained for **1** and related compounds.[20] Great similarity between the observed and calculated conformations of the pyranoid rings of both compounds suggests that intermolecular interactions in the solid state have a minor impact upon the ring geometries; on the other hand, they influence orientation of the ring substituents.

The β-N substituents [-NHAc (**1**) and -N_3 (**2**)] at C(1) are in the *equatorial* positions which are more characteristic for the $^{3,0}B$ than for the $^0S_2$ conformation (for the twist-boat this orientation is *isoclinal*). The C(5)-O(5)-C(1)-N(1) dihedral angles are

TABLE 2. Selected Torsion Angles (°) of **1** and **2** and their Standard Deviations.

Atoms	**1**	**2**
C(31)-O(3)-C(3)-C(2)	-149.4(2)	-88.8(2)
C(41)-O(4)-C(4)-C(3)	140.6(2)	80.5(2)
C(5)-O(5)-C(1)-N(1)	-174.4(1)	-172.7(1)
C(5)-O(5)-C(1)-C(2)	-53.0(2)	-54.0(2)
C(1)-O(5)-C(5)-C(4)	73.2(2)	70.6(2)
C(61)-O(6)-C(6)-C(5)	178.0(2)	89.0(2)
N(11)-N(1)-C(1)-O(5)	----	-118.9(2)
C(11)-N(1)-C(1)-O(5)	-78.5(2)	----
O(2)-N(2)-C(2)-C(1)	0.8(3)	1.2(3)
O(5)-C(1)-C(2)-N(2)	168.7(2)	173.7(2)
O(5)-C(1)-C(2)-C(3)	-7.1(2)	-5.3(2)
C(1)-C(2)-C(3)-O(3)	-71.8(2)	-69.9(2)
C(1)-C(2)-C(3)-C(4)	46.4(2)	47.5(2)
C(2)-C(3)-C(4)-O(4)	91.2(2)	82.4(2)
C(2)-C(3)-C(4)-C(5)	-26.4(2)	-31.3(2)
C(3)-C(4)-C(5)-O(5)	-28.4(2)	-23.3(2)
C(3)-C(4)-C(5)-C(6)	-149.1(2)	-144.0(2)
O(5)-C(5)-C(6)-O(6)	-62.7(2)	73.0(2)

-174.4(1)° for **1** and -172.7(1)° for **2**. The respective angles calculated for the tetrahydro-2H-pyran-3-one



in the pure $^{1,4}B$ and $^{1}S_{3}$ conformation (both geometries were calculated using MOPAC6) are [C-O-C-H(*equatorial*)] -175.7° for the boat and [C-O-C-H(*isoclinal*)] -161.9° for the twist-boat. The O(5)-C(1)-C(2)-N(2) dihedral angles are 168.7(2)° for **1** and 173.7(2)° for **2**. These values are exactly between the calculated O-C-C-O dihedral angles for both conformers of the tetrahydro-2H-pyran-3-one (-175.0° for the boat and 159.8° for the twist-boat). Positions of other exocyclic substituents in the title compounds are: the O(3) between the *quasi-axial* (the boat) and the *axial* (the twist-boat) in **1** and **2**; the O(4) near the *isoclinal* (the twist-boat) in **1**, and the *axial* (the boat) in **2**; the C(6) in **1** and **2**, near the *equatorial* (the twist-boat) of the pyran derivative. In both compounds the acetoxy substituents have different orientations with regard to the ring. The dihedral angles C(2)-C(3)-O(3)-C(31) [-149.4(2) and -88.8(2)° for **1** and **2**, respectively] and the C(3)-C(4)-O(4)-C(41) [140.6(2) and 80.5(2)° for **1** and **2**, respectively] differ about 60°.

In the case of the third group, at C(6), the O(5)-C(5)-C(6)-O(6) dihedral angles are -62.7(2) and 73.0(2)° for **1** and **2**, and the C(5)-C(6)-O(6)-C(61) are 178.0(2) and 89.0(2)° for **1** and **2**, respectively.

The *antiperiplanar* 2-hydroxyimino groups have the *Z* configuration. They are a key factor for the conformation of both compounds under investigation. In all previously presented crystal structures of 2-hydroxyiminopyranosides these residues have the *Z* configuration as well but substituents at the anomeric centers have an *axial* orientation. The latter is imposible for the β-D-*arabino*-hexopyranosides[21] (without a fused ring) which can adopt only the $^4C_1$(D) conformation (as the β-D-glucopyranose[22,23]) and/or for this presented here, both with *equatorial* oriented substituent at C(1). In the first case, the $^4C_1$, all substituents are equatorial. In a hypothetical 2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranoside with this conformation, the =NOH group is in the *pseudo-equatorial* position. The dihedral angles between vicinal substituents [at C(1) and C(2), and at C(2) and C(3)] for this structure are about 0°. Steric interactions between these groups, in particular between the 2-hydroxyimino and the 1-acetamido group in **1** and the 1-azido group in **2**, are the factor controlling the conformation of the ring. We have optimized the geometry of such conformers. The calculated heat of formation for molecules with the chair conformation is about 9 and 14.6 kJ·mol^{-1} higher, respectively, than for those with a hybrid boat / twist-boat conformation (as observed in the title crystal structures). These small differences confirm the possibility of a migration process of the oxime acetyl residue during hydrogenation of the 2-acetoxyimino derivative of **2**, which in effect gives **1**.[20]

Deformations of chair pyranoid rings observed in previously solved crystal structures of 2-oxyimino derivatives suggest that these rings are flexible and the direct chair $\rightleftharpoons$ boat / twist-boat interconversion for **1** and **2** is possible. Apart from that it is interesting to note that values of the heat of formation for the chair conformers of both title compounds with opposite orientations of the 2-hydroxyimino groups (*Z* and *E*) are very similar.

Both presented compounds have very similar respective bond lengths and valency angles. Some differencies between them arise from different substituents at C(1) and various orientations of remainder. The pyranoid rings have all bond lengths and five endocyclic valency angles the same (in the range of 3σ). Only the O(5)-C(5)-C(4) angles [109.7(1) for **1**, and 111.2(1)° for **2**] differ more than 3σ. The difference between the C(1)-N(1) bond lengths [1.436(2) for **1**, and 1.463(2) Å for **2**] correlate with charges calculated from population analysis (MOPAC6) for both molecules. Surprisingly, the N(1) atom from the acetylamino group appears here as more electronegative than from the azido group. On the other hand, it is well known that the azido group, as a moiety with a more axial preference than the acetamido residue, is more electronegative.[24] Explanation of this phenomenon (as was pointed out earlier[25]) may be based on the two canonical forms of the azido group:

$$\mathrm{R{-}\overline{N}{=}N^{\oplus}{=}\overline{N}|^{\ominus}} \leftrightarrow \mathrm{R{-}\overline{N}|^{\ominus}{-}N^{\oplus}{\equiv}\overline{N}}$$

which contribute with various weights to the real structure. The lengthening of the C(1)-N(1) and some shortening of the N(1)-N(11) and N(11)-N(12) bonds in comparison to other crystal structures[25-27] suggest that the first form is dominant but the second one is not negligible. Our theoretical calculations for **2** and for CH_3N_3 confirm this point of view. The hydroxyimino groups in both crystals have different N(2)-O(2) bond lengths [1.384(2) for **1**, and 1.397(2) Å for **2**]. These groups, similar as in previously reported crystal structures of 2-hydroxyiminopyranosides, participate in different hydrogen-bond systems and the variation range of the observed N-O bonds is about 0.05 Å [1.358(5) - 1.404(4) Å].

There exists a network of intermolecular hydrogen bonds O-H···O and N-H···O in the investigated crystals. The hydrogen atoms from the 2-hydroxyimino groups participate in the linear hydrogen bonds with the O(11) atom [H(2)···O(11) = 1.68(5), O(2)···O(11) = 2.685(3) Å, and ∠O(2)-H(2)···O(11) = 165(4)°] from position 1/2+*x*, 3/2-*y*, 2-*z* of **1**, and with the O(31) atom [H(2)···O(31) = 1.81(3), O(2)···O(31) = 2.773(2) Å, and ∠O(2)-H(2)···O(31) = 166(3)°] from position 1-*x*, 1/2+*y*, 1-*z* of **2**. The hydrogen atom from the -NHAc group in **1** interacts with the O(61) atom [H(N1)···O(61) = 2.06(3), N(1)···O(61) = 2.869(3) Å, and ∠N(1)-H(N1)···O(61) = 163(3)°] from position 1+*x*, *y*, *z*. There were no significant intermolecular contacts occur.

CONCLUSION

Results presented here confirm our previous suggestions about flexibility of the chair 2-oxyiminopyranosides, particularly in the case of *N*-glycosides, with preference for the equatorial configuration of the anomeric center. This preference of *N*-aglycone moieties and flattening of the ring around the sp^2-hybridised carbon atom gives rise to destabilization of pure chair conformers. These effects are the most evident in both presented structures. For the chair conformers, deformations of pyranoid ring in a wide range of the Cremer and Pople θ parameter (from 6.9 to 26.5° for the $^4C_1$-chair conformation) were observed. In two cases of the presence of two independent molecules in one unit cell, differences between the θ parameters of this same chemical molecules were 12 and 13°. The respective differences for pyranosides with all sp^3-hybridised carbon atom have the

TABLE 3. Crystal and Experimental Data.

	1	2
Molecular formula	$C_{14}H_{20}N_2O_9$	$C_{12}H_{16}N_4O_8$
Molecular weight	360.32	344.28
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
Lattice parameters:		
a (Å)	8.216(3)	10.004(2)
b	14.702(2)	8.256(1)
c	15.642(2)	10.119(2)
β (°)		100.29(2)
V ($Å^3$)	1889.4(8)	822.3(3)
F(000)	760	360
Z	4	2
D_c ($Mg\ m^{-3}$)	1.267	1.390
Radiation	CuKα	CuKα
λ (Å)	1.5418	1.5418
μ(CuKα) (mm^{-1})	0.88	0.98
Crystal size (mm)	0.30 × 0.35 × 0.40	0.30 × 0.30 × 0.40
No. of setting reflections	25	25
θ range (°)	11 - 17	12 - 17
Intensity data collection		
Scan type	ω /2θ	ω /2θ
Scan width, Δω (°)	1.3 + 0.35tanθ	1.2 + 0.35tanθ
Scan range, 2θ (°)	4 - 160	4 - 160
Scan speed ($°min^{-1}$)	0.9 - 9.0	0.9 - 9.0
Check reflections	2,3,1; 1,4,-3; 2,2,3	0,0,-3; -2,1,1; 1,2,-1
Crystal decay (%)	<3%	<3%
Ranges of h,k,l	0 → 9, 0 → 18, -20 → 20	0 → 12, -9 → 9, -12 → 12
No. of reflections:		
Total	4275	3533
Unique	3674	3249
Observed, $F \geq 6\sigma(F)$	3114	2924
R_{int} for equivalent reflections	0.017	0.023
Structure refinement (on F's)	Full matrix	Full matrix
No. of parameters	307	281
Weighting scheme (w)	$[\sigma^2(F) + 0.000454F^2]^{-1}$	$[\sigma^2(F) + 0.000668F^2]^{-1}$
Extinction parameter	0.006(1)	0.023(5)
R	0.034	0.034
wR	0.042	0.040
S	0.40	1.62
Max./av. shift to e.s.d. (Δ/σ)	0.084/0.010	0.103/0.036
Min./max. final Δρ ($e.Å^{-3}$)	-0.26/0.33	-0.23/0.25

TABLE 4. Final Atomic Parameters and their Standard Deviations of **1**.

Atom	x	y	z	U_{eq}(Å^2)
O(2)	0.2179(2)	0.7965(1)	1.0733(1)	0.0678(5)
O(3)	1.0236(2)	1.0594(1)	0.9966(1)	0.0617(5)
O(4)	0.7334(2)	0.9685(1)	1.1462(1)	0.0595(5)
O(5)	0.8466(2)	0.8984(1)	0.9361(1)	0.0435(4)
O(6)	0.5843(2)	1.0119(1)	0.9103(1)	0.0566(4)
O(11)	0.9935(2)	0.7297(1)	0.8378(1)	0.0737(6)
O(31)	0.9958(5)	1.1737(1)	1.0862(2)	0.1407(11)
O(41)	0.5232(3)	1.0637(2)	1.1312(2)	0.1187(11)
O(61)	0.3298(2)	0.9971(1)	0.8667(2)	0.0885(8)
N(1)	1.1058(2)	0.8518(1)	0.9008(1)	0.0468(5)
N(2)	1.1609(2)	0.8817(1)	1.0961(1)	0.0565(5)
C(1)	0.9879(2)	0.8554(1)	0.9685(1)	0.0421(5)
C(2)	1.0513(2)	0.9084(1)	1.0443(1)	0.0457(5)
C(3)	0.9716(3)	0.9973(1)	1.0635(1)	0.0496(6)
C(4)	0.7858(3)	0.9899(1)	1.0611(1)	0.0498(6)
C(5)	0.7292(2)	0.9125(1)	1.0021(1)	0.0458(5)
C(6)	0.5678(3)	0.9295(1)	0.9598(1)	0.0539(6)
C(11)	1.0964(3)	0.7895(1)	0.8386(1)	0.0532(6)
C(12)	1.2240(4)	0.7973(2)	0.7701(2)	0.0780(10)
C(31)	1.0360(4)	1.1466(2)	1.0170(2)	0.0834(11)
C(32)	1.0889(7)	1.2030(2)	0.9418(3)	0.1237(19)
C(41)	0.5962(4)	1.0096(2)	1.1739(2)	0.0719(9)
C(42)	0.5506(4)	0.9743(2)	1.2602(2)	0.0869(12)
C(61)	0.4550(3)	1.0373(1)	0.8655(1)	0.0511(6)
C(62)	0.4865(4)	1.1209(2)	0.8149(2)	0.0667(8)

greatest values of 5.6 and 5.8° [in crystals of 1,6-anhydro-β-allopyranose (allosan)[28] where three independent molecules with fused ring system exist].

Similar values of the phase angle φ (in the range of 291 - 304°) for different $^4C_1$ chair conformers of the 2-oxyimino *N*-pyranosides with a large values of the θ parameter (in the range of 19.8 - 26.5°) show the E_5 as a transition state conformation in the chair $\rightleftharpoons$ boat/twist-boat interconversion pathway. The calculated heat of formation for **2** with this pure half-boat ring is about 33 kJ·mol^{-1} greater than those for a molecule with the conformation as in the crystals and about 18 kJ·mol^{-1} greater than for the $^4C_1$ structure. Location of **1** and **2** on the pseudorotation sphere suggests that the boat / twist-boat $\rightleftharpoons$ chair interconversion *via* the ^0E half-boat is possible also. In this way the transition state is about 44 kJ·mol^{-1} above the boat / twist-boat and about 30 kJ·mol^{-1} above the $^4C_1$ structure. Optimization of **2** with the $^0H_5$ geometry [the C(1)-C(2)-C(3)-C(4) = 0° were fixed] gave the E_5 structure.

TABLE 5. Final Atomic Parameters and their Standard Deviations of **2**.

Atom	x	y	z	U_{eq}(Å^2)
O(2)	0.3951(2)	1.2766(3)	0.2757(1)	0.0616(5)
O(3)	0.6774(2)	0.8720(2)	0.2584(1)	0.0533(4)
O(4)	0.8632(1)	1.2428(2)	0.2204(1)	0.0564(5)
O(5)	0.5927(1)	1.0505(-)	0.0095(1)	0.0410(3)
O(6)	0.7524(1)	1.1386(3)	-0.1982(1)	0.0555(4)
O(31)	0.6482(2)	0.8669(3)	0.4713(2)	0.0770(7)
O(41)	1.0034(2)	1.1215(4)	0.3864(2)	0.0986(9)
O(61)	0.8925(2)	1.3510(3)	-0.1436(2)	0.0728(6)
N(1)	0.3808(2)	1.0251(2)	0.0637(2)	0.0501(5)
N(11)	0.2783(2)	1.0945(3)	0.0097(2)	0.0681(7)
N(12)	0.1766(3)	1.1440(5)	-0.0374(6)	0.1467(22)
N(2)	0.5193(2)	1.2017(3)	0.3243(1)	0.0492(5)
C(1)	0.5027(2)	1.1264(3)	0.0840(1)	0.0386(4)
C(2)	0.5671(2)	1.1305(3)	0.2315(1)	0.0400(5)
C(3)	0.6995(2)	1.0456(3)	0.2711(1)	0.0427(5)
C(4)	0.7982(2)	1.0904(3)	0.1775(2)	0.0433(5)
C(5)	0.7228(1)	1.1268(3)	0.0347(1)	0.0390(5)
C(6)	0.8033(2)	1.0680(3)	-0.0698(2)	0.0516(6)
C(31)	0.6481(2)	0.7969(3)	0.3675(2)	0.0567(6)
C(32)	0.6158(4)	0.6216(4)	0.3410(3)	0.0877(11)
C(41)	0.9682(2)	1.2433(4)	0.3233(2)	0.0681(9)
C(42)	1.0261(4)	1.4086(6)	0.3478(4)	0.1047(14)
C(61)	0.8081(2)	1.2824(3)	-0.2237(2)	0.0559(6)
C(62)	0.7463(3)	1.3456(5)	-0.3597(2)	0.0846(11)

EXPERIMENTAL

The compounds **1** and **2** were prepared and crystallized by separately reported methods.[20] The space groups were determined from Weissenberg photographs. All measurements were made on a KUMA KM4 (Kuma Diffraction, Poland) four-circle κ-axis diffractometer with graphite monochromated Cu*K*α radiation. The stability of each crystal was monitored by measurements of three standards every 100 reflections. All data were corrected for Lorentz and polarization effects but not for absorption. A summary of the crystal data, data-collection and structure-refinement parameters for both structures is given in Table 3. The structures were solved by direct methods.[29] The H-atom positions were found from ΔF syntheses. In the last stages of full-matrix least squares refinement[30] of both structures the heavy atoms co-ordinates with anisotropic and the H atoms with isotropic thermal parameters were refined. The final atomic parameters are given in Tables 4 and 5. During the structure calculations the neutral-atom scattering factors and anomalous-dispersion corrections (for O, N, and C atoms) as included in the program were used. Lists of structure factors are available from the first author. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre (University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.).

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REFERENCES

1. Z. Smiatacz, H. Myszka and Z. Ciunik, *Carbohydr. Res.*, **172**, 171 (1988).
2. Z. Ciunik, H. Paulsen, P. Luger, Z. Smiatacz and H. Myszka, *Acta Crystallogr.*, **B45**, 512 (1989).
3. Z. Ciunik, R. Szweda and Z. Smiatacz, *Carbohydr. Res.*, **219**, 9 (1991).
4. U. Burkert and N.L. Allinger, *Molecular Mechanics*; American Chemical Society, Washington, DC, 1982, p.92.
5. F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, **16**, 146 (1983).
6. P. Koll and J. Kopf, *Carbohydr. Res.*, **45**, 189 (1979).
7. C. K. Johnson, *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA, 1971.
8. D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 1354 (1975).
9. P. Luger and R. Bülow, *J. Appl. Crystallogr.*, **16**, 431 (1983).
10. G. A. Jeffrey and J. H. Yates, *Carbohydr. Res.*, **74**, 319 (1979).
11. C. Foces-Foces, A. Alemany, M. Bernabe and M. Martin-Lomas, *J. Org. Chem.*, **45**, 3502 (1980).
12. F. H. Cano, C. Foces-Foces, J. Jimenez-Barbero, M. Bernabe and M. Martin-Lomas, *Carbohydr. Res.*, **145**, 319 (1986).
13. J. A. Heitmann, G. F. Richards and L. R. Schroeder, *Acta Crystallogr.*, **B30**, 2322 (1974).

14. F.H. Cano, C. Foces-Foces, J. Jimenez-Barbero, A. Alemany, M. Barnabe and M. Martin-Lomas, *Carbohydr. Res.*, **175**, 119 (1988).

15. S.J. Danishefsky, C.J. Maring, M.R. Barbachyn and B.E. Segmuller, *J. Org. Chem.*, **49**, 4564 (1984).

16. C. Foces-Foces, F.H. Cano, M. Bernabe, S. Penades and M. Martin-Lomas, *Carbohydr. Res.*, **135**, 1 (1984).

17. J.W. Krajewski, P. Gluziński, Z. Urbańczyk-Lipkowska, A. Zamojski, G. D. Andretti and G. Bocelli, *Carbohydr. Res.*, **148**, 1 (1986).

18. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).

19. *Quantum Chemistry Program Exchange,* No. 455, Chemistry Department, Indiana University, Bloomington, IN.

20. (a) R. Walczyna, Z. Smiatacz and Z. Ciunik, *J. Carbohydr. Chem.* (1993), *in press.* (b) *ibid.* (1993) manuscript in preparation.

21. J. F. Stoddart, *Stereochemistry of Carbohydrates*; Wiley-Interscience: New York, 1971, p 59.

22. W.G. Ferrier, *Acta Crystallogr.*, **16**, 1023 (1963).

23. S.S.C. Chu and G.A. Jeffrey, *Acta Crystallogr.*, **B24**, 830 (1968).

24. A.J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer Verlag: Berlin, 1983, p 14.

25. H.-J. Schmidt, P. Luger and H. Paulsen, *Acta Crystallogr.*, **B36**, 2646 (1980), and references therein.

26. P. Luger and H. Paulsen, *Chem. Ber.*, **107**, 1579 (1974).

27. P. Luger and H. Paulsen, *Acta Crystallogr.*, **B32**, 2774 (1976).

28. R. Norrestam, K. Bock and C. Pedersen, *Acta Crystallogr.*, **B37**, 1265 (1981).

29. G.M. Sheldrick, *Acta Crystallogr.*, **A46**, 467 (1990).

30. G.M. Sheldrick, *SHELX76*; Program for Crystal Structure Determination, University of Cambridge, England, 1976.