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Note

Disordered hydrogen bonding in *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline

Valeri V. Mossine [a,*], Charles L. Barnes [b], Thomas P. Mawhinney [a]

[a] Department of Biochemistry, University of Missouri, Columbia, MO 65211, USA
[b] Department of Chemistry, University of Missouri, Columbia, MO 65211, USA

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ABSTRACT

We report on a ^{13}C NMR and a single-crystal X-ray diffraction study of *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline (D-fructose-*N*-allylaniline). In solution, an equilibrium of α-pyranose, β-pyranose, α-furanose, β-furanose, and acyclic keto tautomers of the carbohydrate was detected in the following respective proportions: 2.2%, 47.4%, 4.5%, 33.6%, and 12.3%. In the crystalline state, the compound exists exclusively as the β-pyranose form, in the normal $^2C_5$ chair conformation. Bond lengths and valence angles compare well with the average values from a number of β-fructopyranose derivatives. The structure displays two unusual features for this class of compounds. First, the molecule assumes an eclipsed conformation around the C1–C2 bond, apparently stabilized by an intramolecular O2–H···N hydrogen bond. Second, the O3, O4, and O5 hydroxyl groups are involved in an intermolecular hydrogen bonding, which forms 12-membered homodromic cycles. In the cycles, each determined hydrogen atom site is half occupied, possibly due to the ···H–O···H–O··· ⇌ ···O–H···O–H··· flip-flop type disorder.

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N-Derivatives of 1-amino-1-deoxy-D-fructose, also referred to as fructosamines or Amadori rearrangement products or compounds, belong to a family of key intermediates in the Maillard reaction.[1] As products of the nonenzymatic modification of amino acids, proteins, or other biologically relevant amines with D-glucose, these compounds are of a significant interest for the food and health sciences due to their impact on the nutritional and organoleptic quality of processed foods,[2,3] as well as their diagnostic use in clinics.[4,5]

A therapeutic potential has been recently demonstrated for some Amadori compounds which may inhibit tumorigenesis in vivo through blockage of tumor-associated lectins, interaction with other anti-tumor agents or antioxidant activity.[6,7] As a part of the structural identification of potential candidates for the biological studies, we have performed an X-ray diffraction study of *N*-(1-deoxy-D-fructos-1-yl)-*N*-allylaniline (D-fructose-*N*-allylaniline) and noticed an unusual hydrogen bonding pattern which exists in the crystal structure of this compound.

D-Fructose-*N*-allylaniline tautomerizes in aqueous solution, as expected, with β-pyranose as a predominant anomeric form (Table 1). It is followed by the β-furanose form, which amounts to one-third of the tautomeric population in the equilibrium. Both α-furanose and α-pyranose tautomers are present as minor forms. Notably, there is an unusually high (12%) proportion of the acyclic keto tautomer. Previously reported estimates for the population of the acyclic keto tautomer of *N*-(1-deoxy-D-fructos-1-yl)amines in aqueous solutions did not exceed 2% and generally were around or below 1%.[8,9] Apparently, the hydrophobic amino substituents, which are in close proximity to the carbonyl group, contribute to a significant increase in the acyclic keto tautomer proportion, while the hydrated keto form is not detectable. A similar phenomenon was previously observed in 1- and 3-deoxyhexoketose derivatives.[10] D-Fructose-*N*-allylaniline crystallized exclusively in the β-pyranose form, as evidenced by solid-state ^{13}C NMR data (Table 1) and the following X-ray diffraction study.

The ORTEP view of the molecule and numbering of atoms are shown in Figure 1. The molecule of D-fructose-*N*-allylaniline is a conjugate of 1-deoxy-D-fructose and *N*-allylaniline via its amino group. The β-D-pyranose ring of the crystalline Amadori compound exists in the $^2C_5$ chair conformation, with puckering parameters[11] of $Q = 0.5689$ Å, $\theta = 177.36°$, and $\varphi = 277.87°$. This conformation corresponds to the energy minimum for β-fructopyranose[12] and was experimentally established as the major or the only structure in both solution equilibria[8,13] and crystalline state of D-fructose,[14,15] a number of D-fructose-amino acids[16–19] and other 1-amino-1-deoxy-D-fructose derivatives.[20]

Bond distances and valence angles (Table 2) in the carbohydrate part of D-fructose-*N*-allylaniline compare well to the corresponding values for β-D-fructose,[14,15] other D-fructosamine derivatives and to the average values for a number of crystalline pyranose structures.[12,21] One noticeable difference is the elongated C1–C2 bond. The endocyclic torsions (Table 2) do not differ significantly from the 'standard' pyranoside torsions[21] with C–C–C–C(ring) at 53-

* Corresponding author. Tel.: +1 573 882 2608; fax: +1 573 884 4631.
E-mail address: MossineV@missouri.edu (V.V. Mossine).

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Table 1
Chemical shifts of the carbohydrate portion in ^{13}C NMR spectra (ppm relative TSPS or glycine standards) and tautomeric composition of *N*-(1-deoxy-D-fructos-1-yl)-*N*-allylaniline in D_2O–pyridine solution and in solid state at 25 °C

Carbon	Tautomers in solution					Cryst β-pyr
	α-pyr	β-pyr	α-fur	β-fur	keto	
C1	57.00	58.54	56.60	57.62	60.36	52.33
C2	101.52	102.11	108.95	105.76	214.91	97.12
C3	72.44	72.02	84.40	79.72	79.00	71.47
C4	73.99	72.91	80.37	77.42	75.15	71.6
C5	66.29	71.90	85.83	83.90	73.40	70.61
C6	62.04	65.80	64.34	65.02	65.8	64.25
Relative % of tautomer in equilibrium	2.2	47.4	4.5	33.6	12.3	100

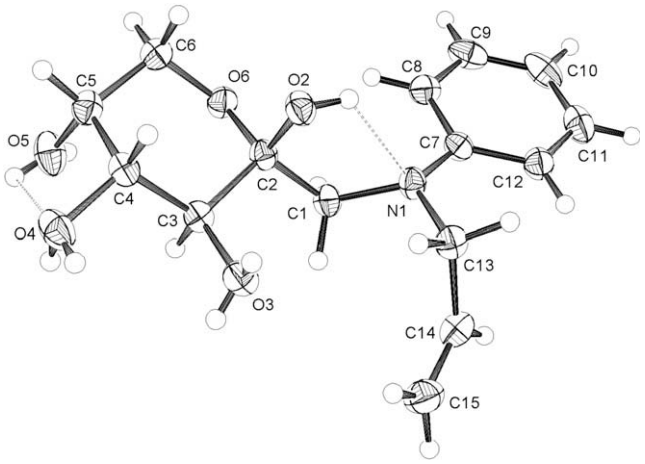

Figure 1. Atomic numbering and thermal ellipsoids (50% probability) for molecular conformations of *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline. Intramolecular hydrogen bonds are shown as dotted lines.

Table 2
Selected bond distances (Å) and angles (°) in crystalline *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline

Bond distances		*Valence angles*	
C1–C2	1.554(3)	C1–N1–C7	119.6(1)
C4–C5	1.523(2)	C1–N1–C13	113.5(1)
O6–C2	1.430(2)	C7–N1–C13	120.2(2)
C1–N1	1.461(2)	N1–C1–C2	113.6(2)
C2–O2	1.401(2)	O2–C2–C1	112.7(2)
N1–C7	1.403(2)	C1–C2–O6	106.0(1)
C14–C15	1.306(3)	C2–C3–O3	109.4(1)
		C4–C5–O5	109.8(2)
		C6–O6–C2	113.4(1)
Endocyclic torsion angles			
C2–C3–C4–C5	+56.2(2)		
C5–C6–O6–C2	−59.1(2)	*Exocyclic torsion angles*	
		N1–C1–C2–C3	−126.9(2)
Other torsions		N1–C1–C2–O2	−6.1(2)
C2–C1–N1–C7	−117.3(2)	N1–C1–C2–O6	+115.6(2)
C2–C1–N1–C13	+91.4(2)	C1–C2–C3–C4	−174.0(1)
C1–N1–C7–C8	+37.8(2)	O2–C2–C3–O3	−62.0(2)
C1–N1–C13–C14	+65.2(2)	O4–C4–C5–C6	−176.4(2)
N1–C13–C14–C15	−122.1(2)	O5–C5–C6–O6	−66.6(2)

54°, C-C–C–O(ring)—at 55–56°, and C–C–O–C at 59–60°. The exocyclic angles around the ring bonds are close to the 'ideal' 180° as well.

One obviously outstanding feature of D-fructose-*N*-allylaniline structure is found in the nearly eclipsed (by 6°) conformation around the C1–C2 bond. The anomeric oxygen O2 and amino N1 are in the (−)*syn*-periplanar disposition, possibly due to a stabilizing effect of the intramolecular hydrogen bond between the two atoms (Fig. 1). Short intramolecular contacts between the anomeric hydroxy group and the amino group are the most common feature of the H-bonding network in crystalline Amadori compounds. As a rule, in ketosamine derivatives with an uncharged amino group, the anomeric hydroxyl acts a sole donor for the amine nitrogen acceptor.[20,22] When the amino group is protonated and charged, such as in D-fructose–amino acid zwitterions, the ammonium group donates its hydrogen(s) to multicentered heteroatom short contacts, which may involve the anomeric O2, the ring O6, and/or endocyclic O3 as acceptors.[16–19] However, in all 1-amino-1-deoxy-β-D-fructopyranose structures reported to date, the relevant configuration was closer to the staggered, regardless of the mutual disposition of the O2 and N1 atoms and the type of intramolecular hydrogen bonding. Hence, the crystal packing forces may have also contributed to such an unusual structure in *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline.

The intermolecular hydrogen bonding scheme in the crystalline D-fructose-*N*-allylaniline is relatively simple, as compared to that in other Amadori compounds. It is represented by only one cyclic pattern of short heteroatom contacts involving O3, O4, and O5 hydroxyl groups, all of which act as both donors and acceptors of the hydrogen bonding (Fig. 2). A unique feature of this H-bonding pattern is that each hydrogen atom position is only partially, one-half, occupied (Table 3). Such a situation would be possible in case of a superposition of two arrays of nonequivalent homodromic cycles, as shown in Figure 3, since O–H···H–O contacts in the cycles would be unlikely due to an overlapping of the hydrogen van-der-Waals radii. These alternative patterns must be of a similar energy, due to an equal occupancy for the alternative hydrogen sites, and probably in a fast equilibrium, as evidenced by an absence of any significant shift in the hydroxyl atom positions (Table 4). This phenomenon has previously been observed in crystalline cyclodextrin complexes,[23] and has been attributed to a type of temperature-

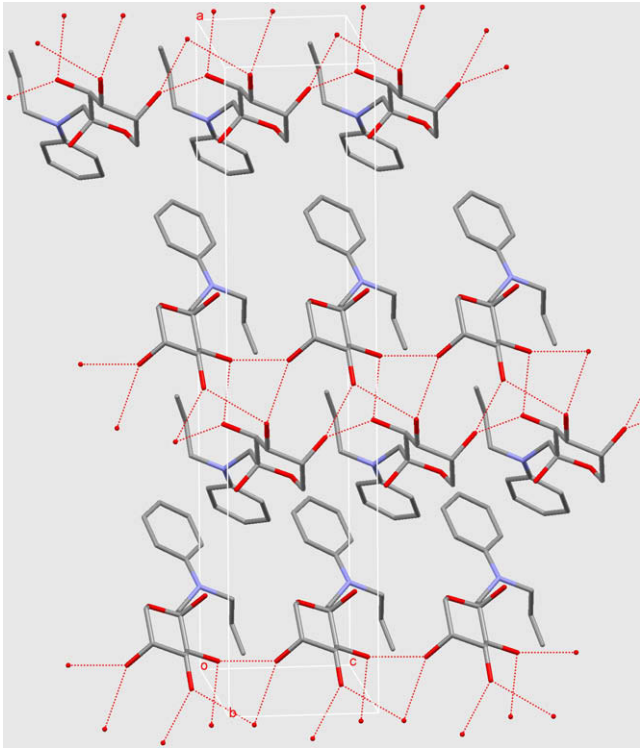

Figure 2. Crystal packing and intermolecular hydrogen bonding in *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline. Hydrogen atoms are not shown for clarity.

dependent, dynamic H-bonding disorder termed flip-flop hydrogen bonding.[24] It is assumed that the conformational change such as the one shown in Figure 3, is achieved by a concerted rotation of the hydroxyl groups from one H-bonded position into the other:

Besides cyclodextrins, such disorder has been observed in crystalline phenols,[25] calixarenes,[26] or ice. We are not aware of its confirmed presence in previously reported crystal structures of any fructosamine or other monosaccharide derivatives, although it would be reasonably expected to be found among the networks with homodromic hydrogen bonding patterns.

1. Experimental

1.1. *N*-(1-Deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline (D-fructose-*N*-allylaniline)

A suspension of 3.6 g of D-glucose in a solution of 3.8 mL *N*-allylaniline, 0.5 mL of HOAc and 8 mL of 2-propanol was stirred in a

Table 3
Hydrogen-bonding in *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline

D–H···A	Occupancy	D···A (Å)	D–H (Å)	H···A (Å)	∠ (D–H···A) (°)
O2–H···N1	1	2.683	0.81(3)	2.16	123
O3–HA···O3[a]	½	2.688	0.73(4)	1.96	171
O3–HB···O5[b]	½	2.723	0.76(5)	2.02	154
O4–HA···O5[c]	½	2.790	0.74(6)	2.09	157
O4–HB···O4[a]	½	3.030	0.78(6)	2.27	164
O5–HA···O3[d]	½	2.723	0.74(6)	2.06	149
O5–HB···O4[c]	½	2.790	0.73(5)	2.19	141
O5–HB···O4	½	2.795	0.73(5)	2.53	104
Suspected H-bonding contacts					
C1–H1···O3	1	2.932	0.99	2.55	103
C15–H1···O4[e]	1	3.379	0.95	2.53	149
Intramolecular syndiaxial contacts					
C3–H···O5	1	2.953	1.00	2.62	99
C4–H···O2	1	2.883	1.00	2.56	99
C6–H1···O2	1	2.820	0.99	2.52	97

Symmetry codes: [a] $-x+1, y, -z+2$; [b] $x, y, z+1$; [c] $-x+1, y, -z+1$; [d] $x, y, z-1$; [e] $-x+1, y-1, -z+2$.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline

	x	*y*	*z*	*U*(eq)
N1	6414(1)	6850(2)	9635(2)	25(1)
C1	6091(1)	7598(2)	8032(3)	26(1)
O2	6503(1)	9964(2)	9406(2)	29(1)
C2	6170(1)	9388(2)	7844(3)	23(1)
O3	5493(1)	9963(2)	10,231(2)	30(1)
C3	5683(1)	10,266(2)	8119(3)	23(1)
O4	5292(1)	12,824(2)	7908(3)	36(1)
C4	5747(1)	12,001(2)	7702(3)	25(1)
O5	5606(1)	11,805(2)	3820(3)	38(1)
C5	5961(1)	12,243(2)	5440(3)	28(1)
O6	6345(1)	9656(2)	5684(2)	28(1)
C6	6425(1)	11,280(3)	5203(3)	31(1)
C7	6755(1)	5725(2)	8951(3)	25(1)
C8	7000(1)	5918(2)	6960(3)	29(1)
C9	7358(1)	4863(3)	6314(3)	37(1)
C10	7484(1)	3602(3)	7621(4)	41(1)
C11	7244(1)	3399(3)	9580(4)	39(1)
C12	6882(1)	4432(2)	10,236(3)	30(1)
C13	6201(1)	6755(2)	11,819(3)	27(1)
C14	5752(1)	5730(3)	11,957(3)	32(1)
C15	5325(1)	6229(3)	12,631(4)	40(1)
H(1A)	5744	7397	8436	31
H(1B)	6146	7115	6589	31
H(3)	5442	9850	7019	28
H(4)	5986	12,425	8803	30
H(5)	6044	13,372	5251	34
H(6A)	6547	11,381	3693	37
H(6B)	6682	11,696	6199	37
H(8)	6920	6779	6047	35
H(9)	7518	5006	4959	44
H(10)	7731	2888	7178	49
H(11)	7328	2539	10,487	47
H(12)	6718	4262	11,577	36
H(13A)	6111	7821	12,298	33
H(13B)	6454	6355	12,845	33
H(14)	5781	4667	11,534	38
H(15A)	5287	7287	13,063	47
H(15B)	5053	5535	12,689	47
H(2O)	6677(11)	9230(40)	9700(50)	57(9)
H(3OA)	5224(14)	10,040(50)	10,190(60)	9(9)
H(3OB)	5615(15)	10,430(60)	11,140(80)	19(11)
H(4OA)	5100(20)	12,380(80)	7300(90)	47(17)
H(4OB)	5193(19)	12,760(80)	9100(100)	51(17)
H(5OA)	5649(16)	11,130(60)	3090(80)	24(12)
H(5OB)	5391(16)	12,310(60)	3880(70)	17(11)

U(eq) is defined as 1/3 of the trace of the orthogonalized *U*ij tensor.

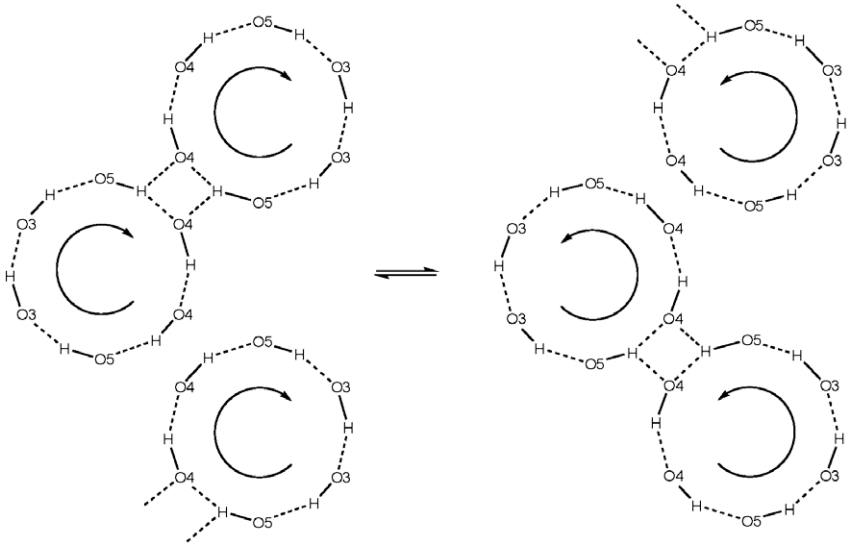

Figure 3. Proposed hydrogen bonding scheme in the crystal structure of *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline. The homodromic cycles are formed by intermolecular hydrogen bonds and linked in pairs by the intramolecular H-bonds. There is a fast equilibrium between the hydroxyl groups orientations, resulting in a statistical one-half occupancy of the hydrogen atom positions on the electron density maps.

Table 5
Crystal data, structure determination and refinement data for *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*N*-allylaniline

Empirical formula	$C_{12}H_{19}NO_6$
Formula weight	273.28
Crystal system, space group	Monoclinic, C_2
Unit cell dimensions	
a(Å)	27.142(4)
b(Å)	8.567(1)
c(Å)	6.1331(9)
β(°)	90.523(2)
U(Å^3)	1426.0(4)
Z	4
Crystal size (mm)	0.50 × 0.25 × 0.25
D_{calc} (cm^{-3})	1.273
μ (cm^{-1})	1.02
F(0 0 0)	584
Radiation Mo Kα, graphite monochromator (Å)	λ = 0.71073
Diffractometer	Enraf–Nonius CAD4
Temperature (K)	173 ± 2
Data collection range (°)	1.50 < θ < 27.12
Limiting indices	$-34 \leqslant h \leqslant 34$, $-10 \leqslant k \leqslant 10$, $-7 \leqslant l \leqslant 7$
No. of observed/unique data	5130/1670 [R_{int} = 0.0240]
Completeness to θ = 27.12°	99.5%
Absorption correction	Semi-empirical from equivalents
Max/min transmission	0.97/0.78
Refinement method	Full-matrix least-squares on F^2
No. of restraints/parameters	1/218
R indices (all data)	R_1 = 0.0309, wR_2 = 0.0751
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0277, wR_2 = 0.0725
Goodness of fit on F^2	1.036
Absolute structure parameter 0	(10)
Largest difference in peak and hole (e Å^{-3})	0.206 and −0.128

cap-closed vial at 87 °C for 14 h. Completion of the reaction was confirmed by TLC. The dark amber solution was diluted with 50 mL of Et_2O and left at 4 °C. Within a week, the crystalline title compound was separated as light-amber prisms, mp 120–121 °C. See Table 1 for NMR data. Anal. Calcd for $C_{15}H_{21}NO_5$: C, 61.0; H, 7.17; N, 4.74. Found: C, 60.7; H, 7.08; N, 4.77.

1.2. Single-crystal X-ray diffraction study

Crystal data and experimental details of the crystallographic studies are given in Table 5. The crystal structure was solved with the direct methods program SHELXS-97[27] and was refined by full-matrix least squares techniques with the SHELXL-97[28] suite of programs, with the help of X-Seed.[29] Data were corrected for Lorentz and polarization effects, but not for absorption. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydroxyl hydrogen atoms were located in difference Fourier maps and were refined with fixed isotropic thermal parameters. The remaining H-atoms were placed at calculated positions. Positional and thermal parameters are listed in Table 4.

2. Supplementary data

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 717417. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).

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