Acta Chemica Scandinavica B 32 (1978) 733—742

Molecular Structure and Conformational Studies of the Oxime Derivatives of D-Glucose and D-Arabinose in the Crystal Phase

ARVID MOSTAD

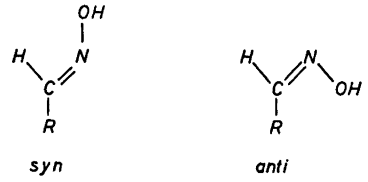
Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystal and molecular structures of D-glucose oxime as well as of both *syn* and *anti* isomers of D-arabinose oxime have been studied by X-ray crystallographic methods. The structures were refined to conventional *R*-factors of 0.049, 0.10 and 0.037, respectively. The e.s.d. for bond lengths and angles not involving hydrogen atoms are 0.01 Å and 0.5° for the glucose derivative, 0.01 Å and 0.8° for arabinose oxime in the *anti* form and 0.002 Å and 0.1° for arabinose oxime in the *syn* form.

The molecules of the glucose derivative appear in the crystals as *N*-β-D-glucopyranosylhydroxylamine. The conformation about the bond between the sp^3 and the sp^2 hybridized carbon atoms in the two isomers of arabinose oxime is discussed.

The oxime derivatives of D-arabinose and D-glucose are of interest as enzyme inhibitors.[1,2] Sugar oximes may be compared to the phenylhydrazones, in formation as well as in the several isomeric states in which they may exist. Phenylhydrazone derivatives of several sugars have been investigated by X-ray methods,[3–6] but no such studies have been carried out on sugar oximes.

The structure and conformation of the D-glucose and D-arabinose oximes have, however, been studied by various physical techniques and whereas the D-glucose oxime is reported to exist in the crystal as the β-pyranose isomer, the D-arabinose oxime is found in the acyclic *anti* form[1]. On the other hand, both arabinose- and glucose-phenylhydrazones were found to be in the pyranose form by X-ray studies of such crystals,[3,5] and therefore it was decided to investigate also the oxime derivatives by X-ray methods. The crystals of the glucose derivative were shown to contain the molecules in the *N*-pyranosylhydroxylamine form whereas two different types of crystals from the arabinose derivative contained the open chain structures of the *anti* and *syn* isomers. The compounds will be referred to accordingly in the following.



Scheme 1.

EXPERIMENTAL

Samples of D-glucose oxime and D-arabinose oxime were supplied by Dr. Paul Finch at Royal Holloway College, University of London. Both samples contained colorless crystals which might be used directly for the X-ray diffraction experiments. However, as the sample of arabinose oxime was large enough for recrystallization, suitable crystals were obtained from a solution of arabinose oxime in a water-ethanol mixture by slow addition of diethyl ether. These crystals proved to be different from those in the original sample and were subsequently used in a separate structure analysis. All intensity data were collected at room temperature on a SYNTEX $P\bar{1}$ four-circle diffractometer using graphite crystal monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). Cell parameters were determined by a least-squares fit to the diffractometer settings for 15 general reflections. Intensity data were recorded using $\theta/2\theta$ scanning mode with scan speed (2θ) of 2° min^{-1}. The scan range was from 1° below $2\theta(\alpha_1)$ to 1° above $2\theta(\alpha_2)$ and background counts were taken 0.35 times the scan time at each of the scan limits. All unique reflections with

$2° < 2\theta < 60°$ were measured and those with intensities larger than $2.5\sigma(I)$ were considered as observed and retained for the analysis of the respective structures. The standard deviations for the intensities were calculated by $\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$, where C_T is the total number of counts and C_N is the scan count minus background count. The intensity measurements were monitored by three test reflections at intervals of 57. The variation of the test reflections were found to be less than 2 % for all three sets of data. The usual corrections were made for Lorentz and polarization effects, but no corrections were made for absorption and extinction. Scattering factors used were those of Doyle and Turner for C, N and O,[7] and of Stewart, Davidson and Simpson for H.[8] Descriptions of the computer programs used are given in Refs. 9 and 10. The quantity minimized in the least-squares caulculations was $\sum w\Delta F^2$ where w is the inverse of the variance of the observed structure factors.

Glucopyranosylhydroxylamine. The crystal specimen used for data collection was a small prismatic needle with dimensions of about $0.05 \times 0.08 \times 0.20$ mm. The crystals are monoclinic, systematic absent reflections are k odd for $(0k0)$ and the space group is thus $P2_1$. Of the measured 1213 unique reflections only 570 showing intensities larger than $2.5(I)$ were considered as observed and used for the structure analysis.

*Arabinose oxime (*anti*).* The original sample of this compound consisted of small plate-formed crystals which readily split in thin flakes, and most of the crystals with suitable size for X-ray experiments gave diagrams indicating disorder. However, a suitable specimen of $0.1 \times 0.4 \times 0.5$ mm was eventually found and used for the structure analysis. The crystals are monoclinic and the systematic absent reflections are k odd for $(0k0)$, the space group thus being $P2_1$. 881 reflections had intensities larger than $2.5\sigma(I)$ and were used in the structure determination.

*Arabinose oxime (*syn*).* The recrystallization described above yielded colorless prismatic needles suitable for X-ray work. A crystal of dimensions $0.15 \times 0.3 \times 0.5$ mm was used for data collection. These crystals are orthorhombic with systematic absent reflections where h odd for $(h00)$, k odd for $(0k0)$ and l odd for $(00l)$, the space group being $P2_12_12_1$. Of the 1530 measured reflections 1387 were observed having intensities larger than $2.5\sigma(I)$.

CRYSTAL DATA

Glucopyranosylhydroxylamine, $C_6NO_6H_{13}$, monoclinic, $a = 5.524(2)$ Å, $b = 13.877(3)$ Å, $c = 5.240(2)$ Å, $\beta = 96.59(2)°$, T = 281 K, $V = 399.0$ Å^3, $M = 195$, $Z = 2$, $F(000) = 208$, $D_x = 1.62$ g cm^{-1}, space group $P2_1$ (No. 4).

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations for non-hydrogen atoms in *N*-β-D-glucopyranosylhydroxylamine. The anisotropic temperature factor is given by $\exp -2\pi^2(U11a^{*2}h^2 + \ldots + 2U12a^*b^*hk + \ldots)$.

Atom	x	y	z	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
O1	0.3309(11)	0.2610(7)	−0.3091(11)	0.0327(36)	0.0242(34)	0.0366(31)	0.0117(32)	−0.0212(27)	0.0003(21)
O2	0.8756(10)	0.2653(7)	0.3267(10)	0.0440(35)	0.0176(26)	0.0279(27)	0.0032(29)	−0.0126(24)	−0.0056(29)
O3	1.1934(8)	0.1030(9)	0.3775(9)	0.0240(26)	0.0236(26)	0.0341(30)	−0.0013(36)	−0.0160(20)	−0.0084(36)
O4	0.9565(11)	−0.0753(6)	0.2181(11)	0.0251(29)	0.0144(30)	0.0396(32)	0.0004(27)	−0.0146(26)	0.0028(28)
O5	0.6160(7)	0.1015( )	−0.1863(7)	0.0315(27)	0.0133(20)	0.0194(25)	−0.0006(34)	−0.0070(19)	0.0010(32)
O6	0.3656(11)	−0.0615(8)	−0.3615(12)	0.0320(34)	0.0233(38)	0.0478(37)	−0.0022(33)	−0.0145(30)	0.0123(33)
N	0.5799(12)	0.2702(8)	−0.1781(12)	0.0214(37)	0.0221(39)	0.0272(33)	0.0025(31)	−0.0016(30)	−0.0049(37)
C1	0.6190(15)	0.1847(9)	−0.0242(15)	0.0170(45)	0.0214(52)	0.0236(45)	−0.0058(39)	−0.0105(35)	0.0001(35)
C2	0.8752(14)	0.1941(8)	0.1282(13)	0.0276(44)	0.0218(45)	0.0145(40)	0.0087(38)	0.0035(34)	0.0075(37)
C3	0.9447(12)	0.0995(9)	0.2685(13)	0.0152(36)	0.0227(33)	0.0203(38)	0.0036(46)	−0.0077(29)	0.0045(46)
C4	0.9175(14)	0.0149(9)	0.0855(16)	0.0105(34)	0.0214(49)	0.0234(39)	0.0083(35)	0.0020(34)	0.0123(39)
C5	0.6591(16)	0.0132(9)	−0.0468(16)	0.0372(55)	0.0036(39)	0.0204(44)	−0.0012(37)	−0.0009(42)	−0.0014(32)
C6	0.6099(15)	−0.0643(9)	−0.2479(16)	0.0328(48)	0.0132(43)	0.022(39)	0.0001(37)	−0.0097(35)	−0.0017(36)

Table 2. Fractional atomic coordinates and *B*-values for hydrogen atoms in glucopyranosylhydroxylamine. The standard deviations are 10^{-2}.

Atom	*x*	*y*	*z*	*B*
HC1	0.49	0.18	0.11	0.4
HC2	1.02	0.21	0.00	0.4
HC3	0.84	0.09	0.40	0.6
HC4	1.05	0.02	−0.04	0.4
HC5	0.57	0.01	0.11	4.0
H1C6	0.73	−0.06	−0.39	−0.4
H2C6	0.65	−0.13	−0.17	−0.3
HN	0.68	0.25	−0.33	3.1
HO1	0.24	0.31	−0.28	6.0
HO2	0.81	0.32	0.25	2.6
HO3	1.21	0.15	0.49	1.0
HO4	1.09	−0.07	0.29	2.5
HO6	0.34	−0.01	−0.43	0.5

Arabinose oxime (*anti*), $C_5NO_5H_{11}$, monoclinic, $a = 4.898(2)$ Å, $b = 5.160(3)$ Å, $c = 14.436(7)$ Å, $\beta = 90.98(4)°$, $T = 281$ K, $V = 364.8$ Å^3, $M = 165$, $Z = 2$, $F(000) = 166$, $D_y = 1.59$ g cm^{-1}, space group $P2_1$ (No. 4).

Arabinose oxime (*syn*), $C_5NO_5H_{11}$, orthorhombic, $a = 4.708(1)$ Å, $b = 8.955(4)$ Å, $c = 17.239(3)$ Å, $T = 281$ K, $V = 726.8$ Å^3, $M = 165$, $Z = 4$, $F(000) = 332$, $D_x = 1.61$ g cm^{-1}, space group $P2_12_12_1$ (No. 19).

STRUCTURE DETERMINATION

All three structures were solved by direct methods using the program assembly MULTAN.[10] Tables of observed and calculated structure factors are available from the author.

Glucopyranosylhydroxylamine. Phases were determined for 150 reflections with $E > 1.3$ and an E map based on the set with highest AFOM (0.99) indicated the position of fragments of the molecule. Successive Fourier refinements revealed all the non-hydrogen atoms, whereas the hydrogen atoms were introduced from stereochemical considerations after a preliminary least-squares refinement. All positional parameters except y(O5), anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameter for hydrogen atoms were refined by least-squares methods to a conventional R-factor of 0.049, and a goodness of fit, $s = (\sum w\Delta^2/m-n)^{\frac{1}{2}}$, of 1.33. Final parameters are listed in Tables 1 and 2.

*Arabinose oxime (*anti*).* Phases were determined for 100 reflections with $E > 1.56$. An E-map based on a phase set with AFOM = 1.07 indicated a molecular fragment consisting of 11 non-hydrogen atoms. After preliminary Fourier and least-squares refinements the hydrogen atoms were introduced from stereochemical considerations and refinements continued until the least-squares refinements terminated at a conventional R-factor of 0.11 and $s = 6.7$.

All positional parameters except Y(O1) and the anisotropic thermal parameters for the non-hydrogen atoms were refined, whereas the isotropic thermal parameters were held constant at $B = 3.0$ for the hydrogen atoms. The final parameters used in the discussion below are given in Tables 3 and 4.

Table 3. Fractional atomic coordinates and thermal parameters with estimated standard deviations for non-hydrogen atoms in D-arabinose oxime, *anti*. The anisotropic temperature factor is given by exp $-2\pi^2(U11a^{*2}h^2 + ... + 2U12a^*b^*hk + ...)$.

Atom	*x*	*y*	*z*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
O1	0.3359(15)	0.7743	0.0785(5)	0.0628	0.0296	0.0455	0.0030	0.0235	0.0048
O2	−0.2048(14)	0.2796(21)	0.1987(5)	0.0320	0.0410	0.0459	0.0007	−0.0005	0.0055
O3	0.3190(13)	0.3210(20)	0.2907(5)	0.0350	0.0350	0.0522	0.0086	0.0093	0.0125
O4	−0.1476(15)	0.8550(19)	0.3107(4)	0.0429	0.0400	0.0420	0.0110	0.0096	0.0078
O5	0.3714(16)	0.9045(20)	0.4085(5)	0.0581	0.0269	0.0543	−0.0010	−0.0009	0.0040
N	0.2345(17)	0.5149(22)	0.0500(5)	0.0478	0.0416	0.0266	−0.0011	0.0060	0.0016
C1	0.1592(22)	0.3847(22)	0.0968(7)	0.0440	0.0365	0.0450	0.0048	−0.0076	−0.0083
C2	−0.0136(20)	0.4768(25)	0.1781(7)	0.0318	0.0300	0.0519	0.0017	0.0004	0.0104
C3	0.1669(20)	0.5470(27)	0.2584(6)	0.0427	0.0303	0.0262	0.0072	0.0038	0.0032
C4	0.0039(21)	0.6327(24)	0.3436(7)	0.0430	0.0186	0.0524	−0.0055	0.0209	0.0058
C5	0.1843(22)	0.6962(26)	0.4261(6)	0.0459	0.0454	0.0304	−0.0083	0.0107	−0.0011

Table 4. Fractional atomic coordinates and B-values for hydrogen atoms in D-arabinose oxime, anti. The standard deviations are $1-2\times10^{-2}$.

Atom	x	y	z	B
HC1	0.24	0.21	0.07	3.0
HC2	−0.19	0.58	0.14	3.0
HC3	0.30	0.70	0.24	3.0
HC4	−0.12	0.53	0.34	3.0
HlC5	0.05	0.73	0.41	3.0
H2C5	0.34	0.57	0.44	
HO1	0.53	0.14	0.97	3.0
HO2	1.12	0.79	0.77	3.0
HO3	0.50	0.69	0.74	3.0
HO4	1.25	0.13	0.66	3.0
HO5	0.65	−0.07	0.63	3.0

Arabinose oxime (syn). The phases for 100 reflections with $E > 1.4$ were determined and resulted in two sets with AFOM = 1.16. The first set which was tried indicated the positions of all the non-hydrogen atoms. After a preliminary least-squares refinement the hydrogen atoms were introduced in agreement with stereochemical requirements and the short oxygen–oxygen contacts indicating hydrogen bonds. All positional parameters, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms were refined by least-square methods to a conventional R-factor of 0.037 and a goodness of fit of $s = 2.1$. The final parameters are given in Tables 5 and 6.

DESCRIPTION OF THE STRUCTURES

1. Glucopyranose hydroxylamine. The packing of the molecules in the crystals and the hydrogen bonding is given in Fig. 1, where the numbering of the atoms is also indicated. Interatomic distances and bond angles are given in Table 7. Within the rather low accuracy the bond lengths and angles conform well with those found in similar structures.[5,11,12] It will be seen from Fig. 1 that the compound exists in the crystal in the pyranose form and thus as the hydroxylamine derivative. This is quite analogous to the p-bromophenylhydrazone derivative of D-glucose which in the solid state is found to exist as β-D-glucopyranosephenylhydrazine.[5] Moreover, similar conformations

Table 5. Fractional atomic coordinates and thermal parameters with estimated standard deviations for non-hydrogen atoms in D-arabinose oxime, *syn*. The anisotropic temperature factor is given by $\exp -2\pi^2(U11a^{*2}h^2+\ldots+2U12a^*b^*hk+\ldots)$.

Atom	x	y	z	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
O1	1.4495(3)	0.1042(2)	0.4859(1)	0.0461(7)	0.0343(7)	0.0232(5)	−0.0025(7)	−0.0141(6)	0.0038(5)
O2	0.8767(2)	0.2693(1)	0.3239(1)	0.0219(5)	0.0274(6)	0.0276(6)	0.0016(5)	0.0001(5)	−0.0035(5)
O3	1.3849(3)	0.3030(1)	0.2376(1)	0.0237(5)	0.0261(6)	0.0290(6)	−0.0054(5)	−0.0057(5)	0.0002(5)
O4	0.8817(3)	0.0473(1)	0.1532(1)	0.0270(6)	0.0272(6)	0.0271(6)	−0.0048(5)	−0.0090(5)	0.0010(5)
O5	1.4035(3)	0.0964(2)	0.0700(1)	0.0264(6)	0.0494(8)	0.0263(5)	−0.0031(6)	0.0002(5)	−0.0087(6)
N	1.2607(3)	0.1750(2)	0.4332(1)	0.0318(7)	0.0298(7)	0.0172(5)	−0.0002(7)	−0.0025(5)	0.0028(5)
C1	1.2403(4)	0.0996(2)	0.3715(1)	0.0311(8)	0.0230(7)	0.0201(7)	−0.0001(8)	−0.0017(7)	0.0015(6)
C2	1.0484(3)	0.1442(2)	0.3060(1)	0.0245(8)	0.0206(7)	0.0196(6)	−0.0012(7)	−0.0013(6)	−0.0008(6)
C3	1.2260(3)	0.1688(2)	0.2319(1)	0.0199(7)	0.0195(7)	0.0185(6)	0.0014(7)	−0.0010(6)	−0.0007(6)
C4	1.0387(3)	0.1836(2)	0.1601(1)	0.0231(7)	0.0200(7)	0.0199(6)	0.0005(6)	−0.0037(6)	−0.000(6)
C5	1.2078(4)	0.2132(2)	0.0868(1)	0.0349(9)	0.0343(10)	0.0200(7)	−0.0024(8)	−0.0026(7)	0.0054(7)

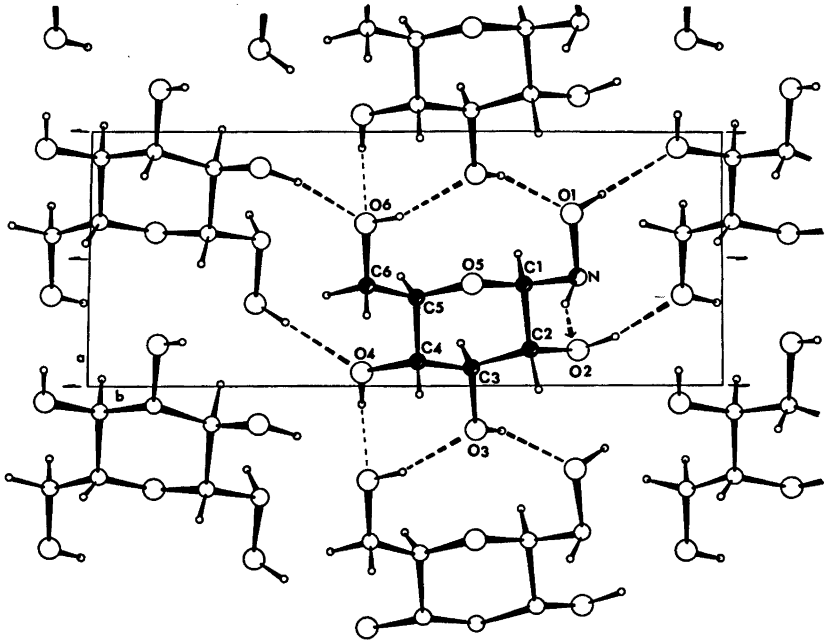


Fig. 1. Packing of glucosehydroxylamine molecules as viewed along the *c*-axis.

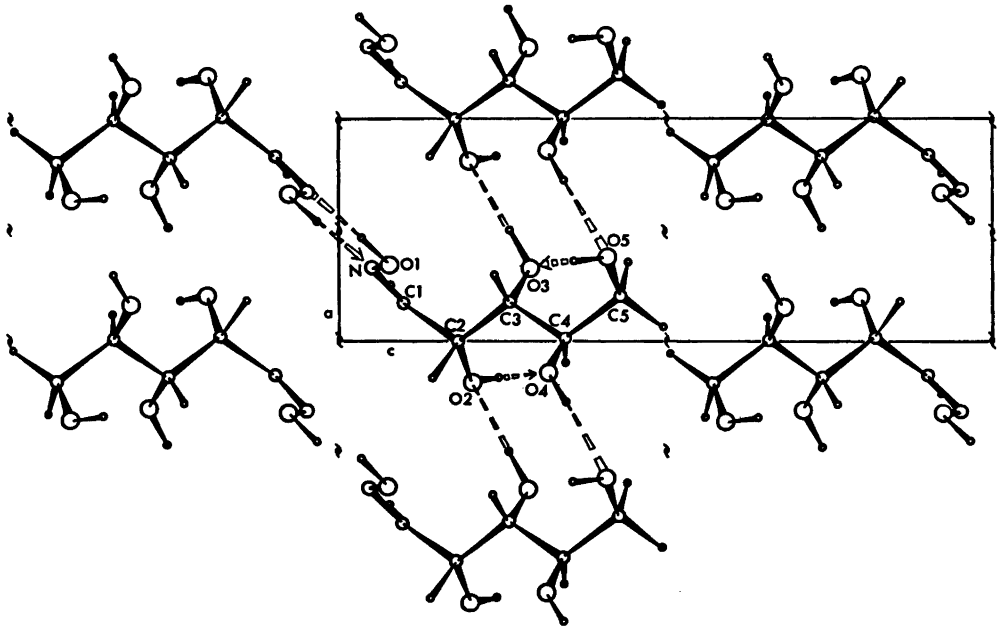


Fig. 2. Packing of D-arabinose oxime, *anti* molecules as viewed along the *b*-axis.

Table 6. Fractional atomic coordinates and *B*-values for hydrogen atoms in D-arabinose oxime, *syn*.

Atom	*x*	*y*	*z*	*B*
H1C1	1.354(3)	0.009(2)	0.367(0)	3.1(4)
HC3	1.354(3)	0.084(1)	0.224(0)	1.2(3)
H1C5	1.075(4)	0.225(2)	0.045(1)	2.8(4)
HO1	1.517(5)	0.170(2)	0.512(1)	4.7(6)
HO3	1.525(5)	0.291(2)	0.265(1)	3.1(4)
HO5	1.309(5)	0.023(2)	0.051(1)	4.8(6)
HC2	0.180(4)	0.061(2)	0.297(0)	1.8(3)
HC4	0.902(4)	0.268(2)	0.168(1)	1.9(3)
H2C5	1.324(4)	0.307(2)	0.092(1)	3.8(4)
HO2	0.982(5)	0.338(3)	0.327(1)	3.6(6)
HO4	0.740(4)	0.071(2)	0.127(1)	2.2(4)

Table 7. Structural data for *N*-β-D-glucopyranosylhydroxylamine. Estimated standard deviations in bond lengths and angles are 10^{-2} Å and 0.5°, respectively, when hydrogen atoms are not involved.

Bond lengths (Å)		Bond angles (°)	
C1 – C2	1.55	O5 – C1 – C2	108.8
C2 – C3	1.53	C1 – C2 – C3	109.8
C3 – C4	1.51	C2 – C3 – C4	111.1
C4 – C5	1.51	C3 – C4 – C5	108.8
C5 – C6	1.51	C4 – C5 – O5	108.3
C1 – N	1.44	C5 – O5 – C1	113.4
N – O1	1.47	C4 – C5 – C6	114.6
C2 – O2	1.43	O5 – C5 – C6	104.5
C3 – O3	1.43	C5 – C6 – O6	111.2
C4 – O4	1.44	O5 – C1 – N	110.1
C5 – O5	1.43	C2 – C1 – N	106.8
C1 – O5	1.43	C1 – N – O1	105.2
C6 – O6	1.41	C1 – C2 – O2	110.9
		C3 – C2 – O2	105.2
Average values		C2 – C3 – O3	109.7
C – H	1.01	C4 – C3 – O3	107.5
N – H	1.06	C3 – C4 – O4	111.6
O – H	0.84	C5 – C4 – O4	106.9

about the C1 – N and C5 – C6 bonds are found in the two structures, the value of the torsional angles C2 – C1 – N – O1 and C4 – C5 – C6 – O6 in the present structure being – 177.1 and 179.7°, respectively, as compared to – 165 and 162° found in the phenylhydrazine derivative.

In the suggested hydrogen bond system, all oxygen atoms except the ring oxygen (O5) are involved in hydrogen bonding, both as donors and acceptors. The oxygen atom O6 is involved in three such bonds, whereas the N – HO2 contact may be dubious. The distances and angles describing the geometry of the hydrogen

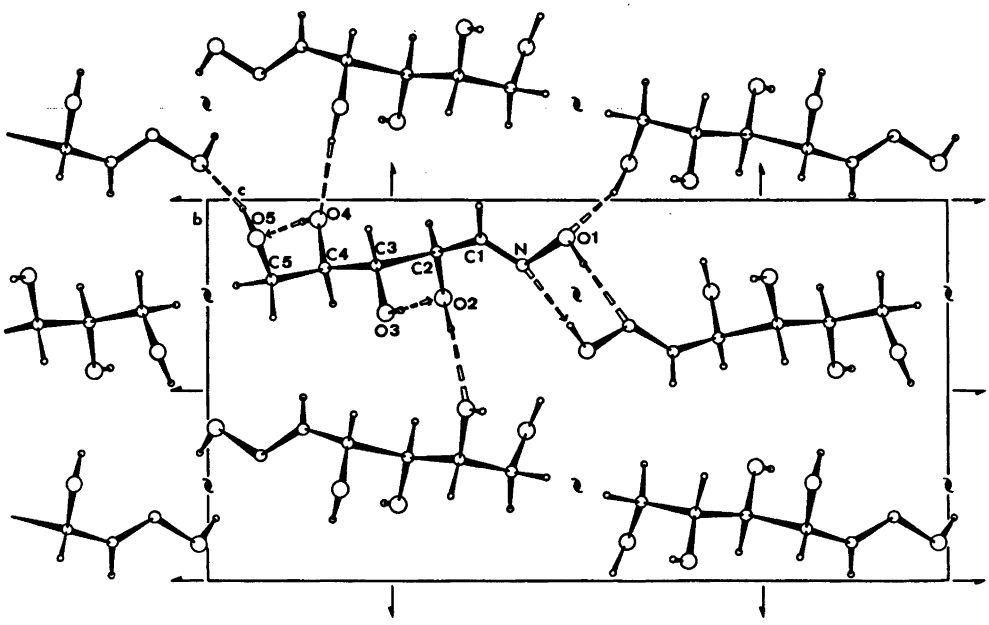


Fig. 3. Packing of D-arabinose oxime, *syn* molecules as seen along the *a*-axis.

Table 8. Hydrogen bonds in the crystal structure of glucopyranosylhydroxylamine between donor atoms (D) in the molecule given in Table 1 and acceptor atoms (A) in surrounding molecules.

D	A	Ekv. pos.	D–A	D–H	H–A	∠DHA
O2	O6	$1-x,\frac{1}{2}+y,-z$	2.77	0.93	2.01	136.8
N	O2	$x,y,z-1$	3.22	1.06	2.21	158.7
O3	O1	$1+x,y,1+z$	2.79	0.81	2.02	160.5
O6	O3	$x-1,y,z-1$	2.77	0.81	1.98	164.4
O4	O6	$1+x,y,1+z$	2.98	0.79	2.25	153.7
O1	O4	$1-x,\frac{1}{2}+y,-z$	2.84	0.83	2.01	178.5

Table 9. Structural data for D-arabinose oxime, *anti*. The e.s.d. in bond lengths and angles not involving hydrogen atoms are 10^{-2} Å and 0.8°, respectively.

Bond lengths (Å)		Bond angles (°)	
O1–N	1.40	O1–N–C1	112.2
N–C1	1.26	N–C1–C2	127.7
C1–C2	1.53	C1–C2–O2	108.0
C2–C3	1.49	C1–C2–C3	110.2
C3–C4	1.54	O2–C2–C3	113.4
C4–C5	1.50	C2–C3–O3	110.2
C2–O2	1.42	C2–C3–C4	112.5
C3–O3	1.46	O3–C3–C4	104.1
C4–O4	1.42	C3–C4–O4	106.5
C5–O5	1.44	C3–C4–C5	113.0
		O4–C4–C5	109.8
		C4–C5–O5	112.8
Average values			
C–H	1.04		
O–H	0.86		

Selected tortional angles (°)			
O1–N–C1–C2	−1.6	C2–C3–C4–C5	178.2
N–C1–C2–O2	169.6	C2–C3–C4–O4	−61.2
N–C1–C2–C3	−66.0	O3–C3–C4–C5	56.9
O2–C2–C3–C4	−56.8	O3–C3–C4–O4	179.6
O2–C2–C3–O3	58.8	C3–C4–C5–O5	60.7
C1–C2–C3–C4	−178.1	O4–C4–C5–O5	−58.0
C1–C2–C3–O3	−62.5		

Table 10. Hydrogen bonds in the crystal structure of D-arabinose oxime, *anti* between donor atoms (D) in the molecule given in Table 3 and acceptor atoms (A) in surrounding molecules.

D	A	Ekv. pos.	D–A	D–H	H–A	∠DHA
O1	N	$1-x,y-\frac{1}{2},2-z$	2.80	1.07	1.72	177.6
O2	O4	$x,1+y,z$	2.78	0.66	2.27	135.2
O3	O2	$x-1,y,z$	2.70	0.98	1.73	174.4
O5	O3	$x,y-1,z$	2.75	0.99	1.76	169.7
O4	O5	$1+x,y,z$	2.73	0.60	2.13	173.0

Table 11. Structural data for D-arabinose oxime, *syn*. The e.s.d. are 2×10^{-3} Å for bond lengths not involving hydrogen atoms and 2×10^{-2} Å for those where hydrogen atoms are involved. The e.s.d. in angles are 0.1 – 0.2° and 1 – 2°, respectively.

Bond lengths (Å)		Bond angles (°)	
O1 – N	1.420	O1 – N – C1	110.4
N – C1	1.263	N – C1 – C2	122.5
C1 – C2	1.501	C1 – C2 – O2	113.0
C2 – C3	1.543	C1 – C2 – C3	109.5
C3 – C4	1.527	O2 – C2 – C3	112.2
C4 – C5	1.517	C2 – C3 – O3	110.4
C2 – O2	1.416	C2 – C3 – C4	111.6
C3 – O3	1.420	O3 – C3 – C4	106.6
C4 – O4	1.425	C3 – C4 – O4	106.7
C5 – O5	1.424	C3 – C4 – C5	112.7
C1 – HC1	0.97	O4 – C4 – C5	110.3
C2 – HC2	0.98	C4 – C5 – O5	112.4
C3 – HC3	0.98	N – O1 – HO1	105.9
C4 – HC4	1.00	C2 – O2 – HO2	105.7
C5 – H1C5	0.96	C3 – O3 – HO3	110.2
C5 – H2C5	1.01	C4 – O4 – HO4	109.8
O1 – HO1	0.81	C5 – O5 – HO5	107.5
O2 – HO2	0.79	N – C1 – HC1	118.0
O3 – HO3	0.82	C2 – C1 – HC1	119.5
O4 – HO4	0.83	C1 – C2 – HC2	106.7
O5 – HO5	0.85	O2 – C2 – HC2	106.2
		C3 – C2 – HC2	109.1
		C2 – C3 – HC3	109.3
		O3 – C3 – HC3	110.4
		C4 – C3 – HC3	108.4
		C3 – C4 – HC4	108.7
		O4 – C4 – HC4	109.4
		C5 – C4 – HC4	108.9
		C4 – C5 – H1C5	107.9
		O5 – C5 – H1C5	110.5
		C4 – C5 – H2C5	111.1
		O5 – C5 – H2C5	106.2
		H1C5 – C5 – H2C5	108.8

Selected tortional angles (°)			
O1 – N – C1 – C2	178.0	C3 – C4 – C5 – O5	60.4
N – C1 – C2 – O2	– 5.6	O4 – C4 – C5 – O5	– 58.8
N – C1 – C2 – C3	120.2	C1 – C2 – O2 – HO2	68.1
O2 – C2 – C3 – C4	– 65.1	C2 – C3 – O3 – HO3	78.4
O2 – C2 – C3 – O3	53.3	C3 – C4 – O4 – HO4	158.2
C1 – C2 – C3 – C4	168.7	C4 – C5 – O5 – HO5	76.2
C1 – C2 – C3 – O3	– 73.0	O2 – C2 – C1 – HC1	174.0
C2 – C3 – C4 – C5	178.0		
C2 – C3 – C4 – O4	– 60.7		
O3 – C3 – C4 – C5	57.4		
O3 – C3 – C4 – O4	178.6		

Table 12. Hydrogen bonds in the crystal structure of D-arabinose, *syn* between donor atoms (D) in the molecule given in Table 5 and acceptor atoms (A) in surrounding molecules.

D	A	Ekv. pos.	D – A	D – H	H – A	∠DHA
O1	N	$x-\frac{1}{2},\frac{3}{2}-y,1-z$	2.829	0.81	2.03	168.4
O2	O4	$-x,y-\frac{1}{2},\frac{3}{2}-z$	2.759	0.79	2.00	158.9
O3	O2	$x-1,y,z$	2.769	0.82	1.95	175.5
O4	O5	$1+x,y,z$	2.717	0.83	1.88	177.8
O5	O1	$\frac{1}{2}+x,2-y,\frac{1}{2}+z$	2.844	0.85	2.01	163.7

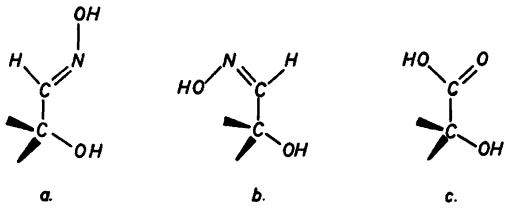


Fig 4. Comparison of the conformations about the C(sp^3)–C(sp^2) bond in arabinose oxime, *syn* (a), arabinose oxime, *anti* (b) and α-hydroxycarboxylic acids (c).

bonds are given in Table 8. Each molecule appears to be connected to six neighbour molecules through 12 hydrogen bonds forming a "network" throughout the crystal.

2. Arabinose oxime, anti. The structure of the molecule is illustrated in Fig. 2 where the numbering of the atoms is also given. The interatomic distances and angles are given in Table 9 together with some selected torsional angles. The low accuracy is mostly due to the difficulty in obtaining a suitable crystal without disorder, as described above. Nevertheless, the geometrical data conform with those found for similar compounds.[13–15] The molecules are seen to exist as open chains and in the *anti*-form, the compound being a true oxime with a normal C–N double bond of 1.26 Å. The sugar part of the molecule is found to be in an extended nearly planar zigzag chain as usually observed in such substances [13–15] and as discussed by Durette and Horton.[16]

The O1–N–C1–C2 group is planar and makes an angle of about 10° with the C1–C2–O2 plane and of about 66° with the C1–C2–C3 plane. Thus the C1–H bond is almost eclipsed with the C2–O2 bond. A similar conformation is found in Mannose *p*-bromophenylhydrazone,[15] where the planar RN–N=C_1–C_2 group makes an angle of about 124° with the carbon chain, although in that structure it is the C1=N1 bond that is eclipsed to the C2–H bond. The packing of the molecules and the suggested hydrogen bond system is illustrated in Fig. 2 and hydrogen bond distances and angles are given in Table 10. The nitrogen atom and all the oxygen atoms are involved in the hydrogen bonding system, N as an acceptor, O1 as a donor and the rest of the oxygen atoms as both donors and acceptors. Through these 10 hydrogen bonds each molecule is connected to four neighbouring units translated in the directions of the *a* and *b* axes and to two molecules related by one of the screw axes. In this way the crystal is constructed of well interconnected molecules forming bimolecular layers parallel to (001) and between which there appears to be only weak van der Waals' forces. These features explain the described tendency of the crystals to split in thin flakes.

3. Arabinose, oxime, syn. The interatomic distances and bond angles are given in Table 11, whereas the molecular conformation is depicted in Fig. 3 where the numbering of the atoms are also indicated. It will be seen from Fig. 3 that the process of recrystallization has led to a transformation from the *anti* to the *syn* isomer.

There is furthermore a difference in the conformation angle at the C1–C2 bond by about 180°. Thus in the present case it is the C1–N double bond which is eclipsed to the C2–O2 bond retaining an approximate planarity of the –C(OH)–CH=N– group. There is only a small difference in the torsion angle about the C2–C3 bond, the value being –178 and 169°, respectively, in the *anti* and *syn* isomers. The rest of the conformation angles appears to be in excellent agreement in the two structures.

The hydrogen bond system and the arrangement of the molecules in the crystal are illustrated in Fig. 3, and the hydrogen bond lengths as well as the angles involved are given in Table 12. Each molecule is connected to eight neighbouring molecules through 10 hydrogen bonds as was found in the *anti* isomer, but in the present case the hydrogen bonds form a three-dimensional network producing a well-ordered crystal structure.

DISCUSSION

As mentioned above there is only a small deviation from planarity in the HO–C–C=N groups in the two isomers of D-arabinoseoxime. This conformation about the C1–C2 bond, which is a bond between an sp^3 and an sp^2 hybridized carbon atom, is of the same type as that usually found about such bonds in

carboxylic acids. Thus in α-hydroxy-carboxylic acids the hydroxy group is in general found to be close to the plane of the carboxylic group, the OH−C−C=O torsional angle usually being less than 15°.[20] This particular conformation in different types of α-substituted carboxylic acids has been discussed by several authors.[18–20] In Fig. 4 the conformations found in the present compounds are compared with those in α-hydroxy-carboxylic acids. The conformation found in the *anti* isomer of arabinose oxime is explained by the steric repulsion between the OH-group on the N-atom and the substituents on C2 preventing eclipsing of the C=N bond with any of the bonds to the C2 substituents whereas the eclipsing of the C1−H bond with one of these bonds (C2−OH) is stabilized through the O1−C3 and O1−HC2 distances of 2.97 and 2.89 Å, respectively. The similarity between the conformations found in the *syn* isomer of arabinose oxime and that reported for the carboxylic acids is, however, obvious. It is interesting to note that in *p*-bromomannose phenylhydrazone[15] and *p*-bromoribosephenylhydrazone[4] both representing *syn* forms, the C−N bond is found to be eclipsed with the C2−H bond and not with the C2−OH bond.

Whether or not these results indicate a significant conformational difference between phenylhydrazones and oximes, the conformations found in the different types of compounds seem to indicate as a general trend, that the conformation about a $C(sp^2)-C(sp^2)$ bond is such as to bring one of the bonds to the $C(sp^2)$ atom in an almost synclinal position with respect to one of the bonds to the $C(sp^2)$ atom.

Acknowledgement. The author wishes to express his thanks for a grant given by "Norges almenvitenskapelige forskningsråd".

REFERENCES

1. Finch, P. and Merchant, Z. *J. Chem. Soc. Perkin Trans. 1* (1975) 1682.
2. Finch, P. and Merchant, Z. *9th Int. Symp. Carbohydr. Chem.*, London 1978.
3. Furberg, S. and Petersen, C. S. *Acta Chem. Scand. 16* (1962) 1539.
4. Bjåmer, K., Furberg, S. and Petersen, C. S. *Acta Chem. Scand. 18* (1964) 587.
5. Dukefos, T. and Mostad, A. *Acta Chem. Scand. 19* (1965) 685.
6. Furberg, S. and Solbakk, J. *Acta Chem. Scand. 23* (1969) 3248.
7. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A 24* (1968) 390.
8. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
9. Groth, P. *Acta Chem. Scand. 27* (1973) 1837.
10. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A 27* (1971) 368.
11. Mo, F. and Jensen, L. H. *Acta Crystallogr. B 31* (1975) 2867.
12. Jeffrey, G. A., McMullan, R. K. and Takagi, S. *Acta Crystallogr. B 33* (1977) 728.
13. Littleton, C. D. *Acta Crystallogr. 6* (1953) 775.
14. Furberg, S. and Helland, S. *Acta Chem. Scand. 16* (1962) 2373.
15. Furberg, S. and Solbakk, J. *Acta Chem. Scand. 23* (1969) 3248.
16. Durette, P. L. and Horton, D. *Adv. Carbohydr. Chem. 26* (1971) 69.
17. Leiserowitz, L. and Schmidt, G. M. J. *Acta Crystallogr. 18* (1965) 1058.
18. Dunitz, J. D. and Strickler, P. *Structural Chemistry and Molecular Biology*, Freeman 1968, p. 595.
19. Kanters, J. A., Kroon, J., Peerdeman, A. F. and Schoone, J. C. *Tetrahedron 23* (1967) 4027.
20. van Eijck, B. P. *Rec. Trav. Chim. Pays-Bas 85* (1966) 1129.

Received June 19, 1978.