showed a high correlation. These two atoms could form the hydrogen bonds with the binding site of an H_2 receptor as the electron acceptor and donor atoms, respectively. In particular, the D_{xy} and D_y components of N(3)···N(15), which are defined in Fig. 3, were most strongly correlated with the activities ($r = 0.8113$ and 0·8333, respectively). Thus the linear combination of ω_3, D_{xy} and D_y led to the following correlation:

$$\begin{aligned} \text{activity} &= \underset{(0.9160)}{1.9033} + \underset{(0.0040)}{0.0058\omega_3} - \underset{(0.0987)}{0.2678D_{xy}} - \underset{(0.1233)}{0.1613D_y}, \\ r &= \underset{(0.3012).}{0.9578} \end{aligned}$$

This equation clearly implies that the molecular conformation and spatial disposition of the N(15) atom with respect to the thiazole of imidazole ring are closely related to the emergence of antagonist activity.

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Structures of Two 2-Oxyimino-α-D-pyranosides

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Abstract

1-(3-Acetamido-2-acetoxyimino-4-*O*-acetyl-2,3-dideoxy-α-D-*threo*-pentopyranosyl)pyrazole (I), $C_{14}H_{18}N_4O_6$, $M_r = 338.32$, orthorhombic, $P2_12_12_1$, $a = 9.257$ (2), $b = 9.306$ (2), $c = 19.582$ (5) Å, $V = 1687$ (1) Å^3, $Z = 4$, $D_x = 1.324$ (1) Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0.907$ mm^{-1}, $F(000) = 712$, room temperature, $R = 0.042$ for 1566 reflections with $I > 2\sigma(I)$. 1-(3,4,6-Tri-*O*-acetyl-2-hydroxyimino-2-deoxy-α-D-*arabino*-hexopyranosyl)-pyrazole (II), $C_{15}H_{19}N_3O_8$, $M_r = 369.33$, monoclinic,

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$P2_1$, $a = 8{\cdot}994$ (2), $b = 15{\cdot}327$ (3), $c = 14{\cdot}030$ (3) Å, $\beta = 106{\cdot}66$ (2)°, $V = 1853$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}316$ (1) Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}940$ mm^{-1}, $F(000) = 776$, room temperature, $R = 0{\cdot}038$ for 3170 reflections with $I > 2\sigma(I)$. All valence bonds and angles of both compounds have normal values and the pyranoid rings adopt a distorted $^4C_1$ chair conformation. In both compounds, substituents at C(2) and C(3) are *syn*-equatorial. In the anomeric centers, bond shortening is observed and the axial pyrazole moieties have the energetically preferred orientations $-ac$ and $-sc$. In both crystals a network of N—H···O(Ac) (I), O—H···O(Ac) and O—H···N(oxime) (II) intermolecular hydrogen bonds exists.

Introduction

Oxime derivatives of pyranosides and ulosides are very useful in saccharide chemistry. These compounds are precursors in reduction reactions to important carbohydrates and their derivatives. For pyranosides with an endocyclic keto or oxyimine group one C atom is sp^2 rather than sp^3 hybridized. In these cases it was found that the reduction reactions tend to produce preferentially one of the two possible isomeric compounds. The direction of these reactions is attributed to the environment of the C_{sp^2} atom and the configuration of the pyranoid ring (Lemieux, James & Nagabhushan, 1973; Lemieux, James, Nagabhushan & Ito, 1973; Miljković, Grigorijević, Satoh & Miljković, 1974). Previous crystallographic studies of ulosides and oxime derivatives of pyranosides (Palmer & Palmer, 1976; Gnichtel, Gumprecht & Luger, 1984; Smiatacz, Myszka & Ciunik, 1988) showed that the pyranoid ring has a distorted chair conformation and that the O(carbonyl) or the N(oxime) atom is in a pseudo-equatorial position.

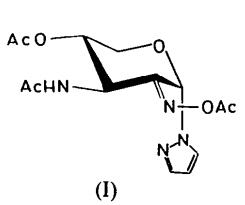
Experimental

The title compounds (I) and (II) were prepared and recrystallized by a previously reported method (Smiatacz, Szweda & Drewniak, 1985; Smiatacz & Myszka, 1989). The space groups were determined from oscillation and Weissenberg photographs (D_m were not measured). All measurements were made on a DEC micro-PDP 11-controlled Stoe diffractometer with Ni-filtered Cu $K\alpha$ radiation. In each case intensities were collected by the $\omega/2\theta$ scan procedure. The stability of each crystal was monitored by measurements of check reflections every 90 min; the data were corrected for decay by appropriate scaling. All data were corrected for Lorentz and polarization effects. No absorption correction. A summary of the data-collection and structure-refinement parameters for both structures is given in Table 1. The structures were solved by direct methods, the heavy atoms were refined (on F's) with isotropic and then with anisotropic temperature factors by full-matrix least squares. Some of the H-atom positions were calculated based on the geometry of the molecules (C—H and N—H = 0·95 Å), the remaining H atoms were found from ΔF syntheses. Only the H[N(acetamido)] atom of (I) was included in the refinement process. In the last stage of refinement of both structures, the default values of the isotropic extinction correction (Zachariasen, 1963, 1967), $g = 0{\cdot}03$, were included. Refinement converged with $R = 0{\cdot}042$ and 0·038, and $wR = 0{\cdot}041$ and 0·037 for (I) and (II), respectively. The final atomic parameters are given in Tables 2 and 3.* Bond distances, valency and selected dihedral angles are listed in Table 4.

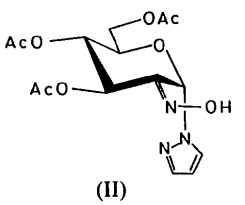
Table 1. *Summary of data-collection and structure-refinement parameters*

	(I)	(II)
Crystal size (mm)	0·84 × 0·60 × 0·50	0·50 × 0·60 × 0·65
No. of reflections used for cell constants	47	48
2θ range (°)	30–35	30–35
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan width (°)	1·18	1·10
Variable scan speed (° min^{-1})	1·33–8	1·33–8
Max. scan time per reflection (s)	106·2	99·0
Range for data collection		
Min./max. ($\sin\theta/\lambda$) (Å^{-1})	0·05/0·58	0·03/0·58
h	0/10	0/10
k	0/10	0/17
l	0/22	−16/15
No. of standards	3	2
Crystal decay (%)	2·1	12·5
Reflections measured		
Total	1632	3421
Unique	1612	3210
Observed [$I > 2\sigma(I)$]	1566	3170
Data/parameter ratio	7·1	6·7
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$
R, wR	0·042, 0·041	0·038, 0·037
Max. shift to e.s.d. (Δ/σ)	0·039	0·023
Min./max. electron density in final $\Delta\rho$ map (e Å^{-3})	−0·251/0·169	−0·162/0·205

All crystallographic computations were performed on a VAX/VMS V4.6 computer using *SHELXS*86 (Sheldrick, 1986), *XTAL*2.2 (Hall & Stewart, 1987) with the neutral-atom scattering factors and



(I)



(II)

* Lists of structure factors, anisotropic temperature factors, hydrogen-bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52028 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final positional* ($\times 10^4$) *and thermal non-H-atom parameters* ($\times 10^3$) *with e.s.d.'s in parentheses for* $C_{14}H_{18}N_4O_6$ (I)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
O(2)	1638 (3)	1061 (2)	4882 (1)	59·3 (9)
O(4)	1906 (3)	6358 (2)	3234 (1)	52·8 (8)
O(5)	−209 (3)	4755 (3)	4605 (1)	59·9 (9)
O(21)	2231 (4)	−1024 (3)	4370 (1)	98 (1)
O(31)	4932 (3)	3543 (3)	3216 (1)	81 (1)
O(41)	−144 (3)	7112 (3)	2761 (1)	88 (1)
N(1)	1579 (4)	4141 (3)	5422 (1)	57 (1)
N(2)	2099 (4)	1767 (3)	4272 (1)	53 (1)
N(3)	2551 (4)	3257 (3)	3108 (1)	48 (1)
N(11)	2989 (4)	4397 (4)	5356 (2)	81 (1)
C(1)	699 (4)	3660 (4)	4850 (2)	52 (1)
C(2)	1654 (4)	3065 (3)	4295 (2)	44 (1)
C(3)	2198 (4)	4049 (3)	−3730 (1)	42 (1)
C(4)	1106 (4)	5253 (4)	3593 (2)	46 (1)
C(5)	564 (4)	5865 (4)	4255 (2)	57 (1)
C(11)	3397 (6)	4800 (6)	5980 (2)	94 (2)
C(12)	2249 (7)	4808 (5)	6419 (2)	100 (2)
C(13)	1099 (6)	4402 (6)	6057 (2)	96 (2)
C(21)	1819 (5)	−402 (4)	4854 (2)	67 (2)
C(22)	1369 (6)	−1011 (4)	5534 (2)	86 (2)
C(31)	3904 (4)	3019 (4)	2923 (2)	54 (1)
C(32)	4054 (5)	2049 (5)	2310 (2)	78 (2)
C(41)	1119 (5)	7286 (4)	2864 (2)	60 (1)
C(42)	2014 (5)	8511 (5)	2618 (2)	91 (2)

anomalous-dispersion corrections (O, N and C atoms) as included in the program, the *XTAL* version of *ORTEP*II (Johnson, 1971), and *PUCK*2 (Luger & Bülow, 1983). The molecular-mechanics calculations were performed using *CHEM-X* (Chemical Design Ltd, 1988) programs. The latter calculations were performed using the full expression for potential energy, without optimization of the molecular geometry and additional parametrization.

Discussion

The numbering scheme, overall conformation and molecular packing diagrams of molecules in both crystals are shown in Figs. 1–3. The asymmetric unit of (II) consists of two symmetry-independent molecules *A* and *B*.

In both compounds, the pyranoid ring has the chair conformation. The Cremer & Pople (1975) ring-puckering parameters (Q, θ and φ) for (I) [0·534 (4) Å, 26·5 (4) and 304·4 (8)°, respectively] indicate a distortion of the $^4C_1$ conformation towards $B_{2,5}$ geometry (Jeffrey & Yates, 1979). For molecules *A* and *B* of (II), the respective parameters [0·537 (4) Å, 19·8 (4) and 291 (1)° for molecule *A*, and 0·523 (4) Å, 6·9 (5) and 281 (4)° for molecule *B*] indicate deformation of the $^4C_1$ conformation in a direction between $^1S_5$ and $B_{2,5}$. Similar deformations of the pyranoid rings were observed for the $^4C_1$ chair of 1-(3,4-di-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*erythro*-pentopyranosyl)pyrazole [$^4C_1$-α-EPPP, with an axial acetoxy group at C(3)] and for the $^1C_4$ chair

Table 3. *Final positional* ($\times 10^4$) *and thermal non-H-atom parameters* ($\times 10^3$) *with e.s.d.'s in parentheses for* $C_{15}H_{19}N_3O_8$ (II)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
Molecule *A*				
O(2)	−655 (3)	1538	5986 (2)	73 (1)
O(3)	3937 (2)	2078 (3)	6989 (2)	50·8 (8)
O(4)	5285 (3)	1999 (3)	9130 (2)	53·7 (8)
O(5)	1133 (3)	1924 (3)	8826 (2)	50·3 (8)
O(6)	3144 (3)	3131 (3)	10243 (2)	61·0 (9)
O(31)	5736 (4)	1047 (3)	7179 (3)	18 (2)
O(41)	5828 (4)	3378 (3)	8811 (3)	1 (2)
O(61)	5579 (4)	3172 (3)	11244 (3)	14 (2)
N(1)	379 (3)	542 (3)	8084 (2)	51 (1)
N(2)	963 (3)	1644 (3)	6284 (2)	55 (1)
N(11)	1633 (3)	11 (3)	8255 (3)	60 (1)
C(1)	547 (4)	1462 (3)	7922 (2)	49 (1)
C(2)	1521 (4)	1595 (3)	7221 (2)	45 (1)
C(3)	3251 (4)	1638 (3)	7672 (2)	46 (1)
C(4)	3664 (4)	2136 (3)	8642 (2)	47 (1)
C(5)	2752 (4)	1775 (3)	9324 (2)	48 (1)
C(6)	3144 (5)	2199 (4)	10329 (3)	62 (1)
C(11)	1114 (5)	−769 (3)	8413 (3)	67 (1)
C(12)	−468 (5)	−745 (4)	8350 (3)	72 (2)
C(13)	−898 (4)	98 (4)	8131 (3)	62 (1)
C(31)	5217 (4)	1725 (4)	6836 (3)	61 (1)
C(32)	5876 (5)	2321 (4)	6221 (3)	75 (2)
C(41)	6270 (5)	2681 (4)	9131 (3)	65 (2)
C(42)	7899 (5)	2392 (4)	9577 (3)	86 (2)
C(61)	4448 (5)	3548 (4)	10752 (4)	75 (2)
C(62)	4297 (6)	4509 (4)	10606 (5)	19 (2)
Molecule *B*				
O(2)	8007 (3)	5943 (3)	5307 (2)	85 (1)
O(3)	4865 (3)	7247 (3)	6322 (2)	55·7 (8)
O(4)	3069 (3)	6140 (3)	7244 (2)	54·9 (8)
O(5)	5475 (3)	4571 (3)	6420 (2)	59·8 (9)
O(6)	2296 (3)	4331 (3)	5690 (2)	75 (1)
O(31)	6853 (4)	7889 (3)	7409 (2)	99 (1)
O(41)	1351 (3)	6809 (3)	5976 (2)	82 (1)
O(61)	175 (4)	3756 (4)	5935 (3)	120 (2)
N(1)	7959 (4)	4922 (3)	7529 (2)	61 (1)
N(2)	7005 (4)	6443 (3)	5681 (2)	66 (1)
N(11)	7906 (4)	5418 (3)	8316 (2)	76 (1)
C(1)	6874 (4)	5044 (3)	6544 (3)	58 (1)
C(2)	6526 (4)	5989 (3)	6301 (2)	52 (1)
C(3)	5390 (4)	6419 (3)	6774 (2)	51 (1)
C(4)	3986 (4)	5836 (3)	6618 (2)	48 (1)
C(5)	4448 (4)	4910 (3)	6944 (3)	55 (1)
C(6)	3090 (5)	4298 (3)	6738 (3)	66 (1)
C(11)	9011 (6)	5085 (4)	9064 (3)	85 (2)
C(12)	9777 (5)	4404 (4)	8790 (4)	83 (2)
C(13)	9065 (5)	4303 (4)	7784 (4)	79 (2)
C(31)	5700 (6)	7945 (4)	6724 (3)	73 (2)
C(32)	5036 (7)	8763 (4)	6207 (4)	16 (2)
C(41)	1767 (4)	6594 (4)	6831 (3)	61 (1)
C(42)	941 (5)	6814 (4)	7572 (3)	87 (2)
C(61)	828 (6)	4035 (4)	5371 (4)	82 (2)
C(62)	204 (8)	4075 (5)	4303 (5)	132 (3)

of 1-(3,4-di-*O*-acetyl-2-deoxy-2-hydroxyimino-β-D-*erythro*-pentopyranosyl)pyrazole [$^1C_4$-β-EPPP, with an equatorial acetoxy group at C(3)]. In the latter case the deformation of the pyranoid ring has the opposite direction (Smiatacz, Myszka & Ciunik, 1988). The above observations suggest that the main reason for the deformation of these pyranoid rings is the sp^2 hybridization of the C(2) ring atom, but in spite of the presence of this hybridization these rings are still flexible. This is supported by the differences

Table 4. *Interatomic distances* (Å), *valency and selected dihedral angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II) Mol. *A*	(II) Mol. *B*
O(2)—N(2)	1·428 (3)	1·404 (4)	1·396 (5)
O(2)—C(21)	1·373 (4)		
O(3)—C(3)		1·447 (5)	1·437 (6)
O(3)—C(31)		1·344 (5)	1·335 (6)
O(4)—C(4)	1·448 (4)	1·438 (4)	1·444 (5)
O(4)—C(41)	1·343 (5)	1·370 (6)	1·343 (5)
O(5)—C(1)	1·405 (4)	1·416 (5)	1·420 (5)
O(5)—C(5)	1·432 (4)	1·441 (4)	1·432 (5)
O(6)—C(6)		1·435 (7)	1·440 (5)
O(6)—C(61)		1·346 (5)	1·346 (6)
O(21)—C(21)	1·176 (5)		
O(31)—C(31)	1·213 (5)	1·183 (7)	1·198 (5)
O(41)—C(41)	1·198 (5)	1·182 (7)	1·196 (5)
O(61)—C(61)		1·200 (6)	1·192 (8)
N(1)—N(11)	1·333 (5)	1·356 (5)	1·352 (6)
N(1)—C(1)	1·456 (5)	1·443 (6)	1·457 (4)
N(1)—C(13)	1·341 (5)	1·353 (6)	1·346 (6)
N(2)—C(2)	1·277 (4)	1·267 (4)	1·281 (6)
N(3)—C(3)	1·460 (4)		
N(3)—C(31)	1·323 (5)		
N(11)—C(11)	1·332 (6)	1·326 (7)	1·323 (6)
C(1)—C(2)	1·508 (5)	1·507 (5)	1·500 (7)
C(2)—C(3)	1·522 (4)	1·504 (4)	1·520 (6)
C(3)—C(4)	1·533 (5)	1·511 (5)	1·510 (6)
C(4)—C(5)	1·502 (5)	1·532 (5)	1·512 (7)
C(5)—C(6)		1·499 (5)	1·502 (6)
C(11)—C(12)	1·368 (8)	1·400 (6)	1·366 (9)
C(12)—C(13)	1·334 (8)	1·357 (8)	1·382 (6)
C(31)—C(32)	1·508 (6)	1·492 (7)	1·484 (8)
C(41)—C(42)	1·489 (6)	1·487 (6)	1·479 (7)
C(61)—C(62)		1·487 (9)	1·443 (8)
N(2)—O(2)—C(21)	112·7 (3)		
C(3)—O(3)—C(31)		117·7 (4)	116·6 (3)
C(4)—O(4)—C(41)	116·1 (3)	117·1 (4)	119·0 (3)
C(1)—O(5)—C(5)	112·8 (3)	114·9 (3)	115·6 (4)
C(6)—O(6)—C(61)		116·7 (3)	118·6 (4)
N(11)—N(1)—C(1)	121·9 (3)	119·7 (3)	122·1 (4)
N(11)—N(1)—C(13)	112·5 (4)	111·4 (4)	112·1 (3)
C(1)—N(1)—C(13)	125·6 (4)	128·9 (4)	125·8 (4)
O(2)—N(2)—C(2)	108·0 (3)	111·7 (3)	109·6 (4)
C(3)—N(3)—C(31)	121·7 (3)		
N(1)—N(11)—C(11)	103·8 (4)	104·8 (3)	103·6 (4)
O(5)—C(1)—N(1)	112·0 (3)	112·1 (3)	112·3 (4)
O(5)—C(1)—C(2)	111·7 (3)	112·3 (3)	110·2 (3)
N(1)—C(1)—C(2)	109·9 (3)	110·0 (4)	112·3 (4)
N(2)—C(2)—C(1)	124·2 (3)	123·6 (3)	126·2 (4)
N(2)—C(2)—C(3)	116·0 (3)	119·2 (3)	117·3 (4)
C(1)—C(2)—C(3)	119·8 (3)	117·2 (3)	116·3 (4)
O(3)—C(3)—C(2)		109·1 (3)	111·5 (3)
O(3)—C(3)—C(4)		108·7 (3)	107·7 (3)
N(3)—C(3)—C(2)	112·1 (3)		
N(3)—C(3)—C(4)	111·8 (3)		
C(2)—C(3)—C(4)	110·4 (3)	111·0 (3)	108·6 (4)
O(4)—C(4)—C(3)	105·4 (3)	108·0 (3)	108·6 (3)
O(4)—C(4)—C(5)	108·7 (3)	107·5 (3)	105·9 (3)
C(3)—C(4)—C(5)	110·3 (3)	110·1 (3)	111·4 (3)
O(5)—C(5)—C(4)	107·8 (3)	106·7 (3)	110·3 (4)
O(5)—C(5)—C(6)		108·7 (3)	106·5 (4)
C(4)—C(5)—C(6)		114·1 (3)	113·0 (3)
O(6)—C(6)—C(5)		111·0 (3)	108·1 (4)
N(11)—C(11)—C(12)	111·0 (5)	111·5 (4)	113·4 (4)
C(11)—C(12)—C(13)	106·5 (4)	105·0 (4)	104·4 (4)
N(1)—C(13)—C(12)	106·2 (5)	107·4 (4)	106·5 (5)
O(2)—C(21)—O(21)	124·1 (3)		
O(2)—C(21)—C(22)	107·7 (3)		
O(21)—C(21)—C(22)	128·2 (4)		
O(31)—C(31)—O(3)		123·1 (4)	122·3 (5)
O(31)—C(31)—N(3)	120·0 (3)		
O(31)—C(31)—C(32)	123·0 (4)	126·7 (4)	125·9 (5)
O(3)—C(31)—C(32)		110·2 (4)	111·8 (4)
N(3)—C(31)—C(32)	114·0 (3)		
O(4)—C(41)—O(41)	122·3 (4)	122·8 (4)	123·9 (4)
O(4)—C(41)—C(42)	111·4 (3)	109·4 (5)	111·5 (3)
O(41)—C(41)—C(42)	126·3 (4)	127·8 (5)	124·5 (4)
O(6)—C(61)—O(32)		122·9 (5)	121·6 (5)
O(6)—C(61)—C(62)		111·4 (4)	112·6 (5)
O(61)—C(61)—C(62)		125·7 (5)	125·9 (5)
C(1)—C(2)—C(3)—C(4)	−30·2 (4)	−39·1 (5)	−48·1 (4)
C(2)—C(3)—C(4)—C(5)	44·2 (4)	51·1 (4)	51·2 (4)
C(3)—C(4)—C(5)—O(5)	−64·2 (4)	−63·0 (4)	−57·3 (4)
C(4)—C(5)—O(5)—C(1)	70·1 (3)	64·7 (5)	59·1 (4)
C(5)—O(5)—C(1)—C(2)	−52·8 (4)	−52·0 (5)	−53·3 (4)
O(5)—C(1)—C(2)—C(3)	33·6 (4)	38·1 (5)	48·1 (4)
C(5)—O(5)—C(1)—N(1)	71·0 (4)	72·5 (4)	72·6 (5)
O(5)—C(1)—N(1)—N(11)	−106·6 (4)	−81·3 (4)	−86·2 (5)
O(5)—C(1)—C(2)—N(2)	−149·0 (3)	−144·1 (4)	−126·4 (4)
C(1)—C(2)—N(2)—O(2)	−4·8 (5)	−1·5 (6)	−4·3 (5)
C(2)—N(2)—O(2)—C(21)	168·4 (3)		
N(2)—O(2)—C(21)—O(21)	−4·0 (6)		
O(5)—C(5)—C(6)—O(6)		−70·9 (4)	−64·2 (4)
C(5)—C(6)—O(6)—C(61)		−124·9 (4)	−161·8 (4)
N(2)—C(2)—C(3)—O(3)		23·3 (6)	8·4 (4)
N(2)—C(2)—C(3)—N(3)	26·9 (4)		

between the θ parameters for molecules *A* and *B* of (II) and similar values for $^1C_4$-β-EPPP.

Both compounds have normal bond lengths. The C(5)—O(5) bond lengths are slightly longer than the C(1)—O(5) ones. These differences agree with the theoretical predictions for α-D-pyranosides (Jeffrey, Pople, Binkley & Vishveshwara, 1978). Bond angles at O(5) are similar to those for other pyranosides. The majority of the endocyclic C—C—C and C—C—O angles differ from the tetrahedral angle. The C(1)—C(2)—C(3) angles are in the range 116·3 (4)–119·8 (3)°. The geometry of external C—O bonds [including the C(6)—O(6) bonds] and of planar acetoxy groups is normal and similar to other acetylated carbohydrates. According to the terminology proposed by Sundaralingam (1968), the acetoxymethyl group in molecule *A* of (II) has the energetically prefered *gauche/gauche* conformation (Pérez, St-Pierre & Marchessault, 1978) and is *gauche/trans* in molecule *B*.

The acetamido group in (I) has almost planar geometry [torsion angle C(3)—N(3)—C(31)—O(3) = −6·8 (5)°] with orientation characteristic for acetoxy groups in acetylated carbohydrates.

The acetoxyimino group in (I) and the hydroxyimino groups in (II) have expected geometries and orientations. The values of the torsion angles C(1)—C(2)—N(2)—O(2) [−4·8 (5), −1·5 (6) and −4·3 (5)° for (I) and for molecules *A* and *B* in (II), respectively] indicate a *Z* conformation for this group as predicted by Lemieux, Earl, James & Nagabhushan (1973). As in other structures (Toure, Lapasset, Boyer & Lamaty, 1979; Edwards, Kirby, Raithby & Jones, 1987; Heeg, 1987; Smiatacz, Myszka & Ciunik, 1988) the *syn* C—C—N angle is larger than the *anti* one. In both structures the

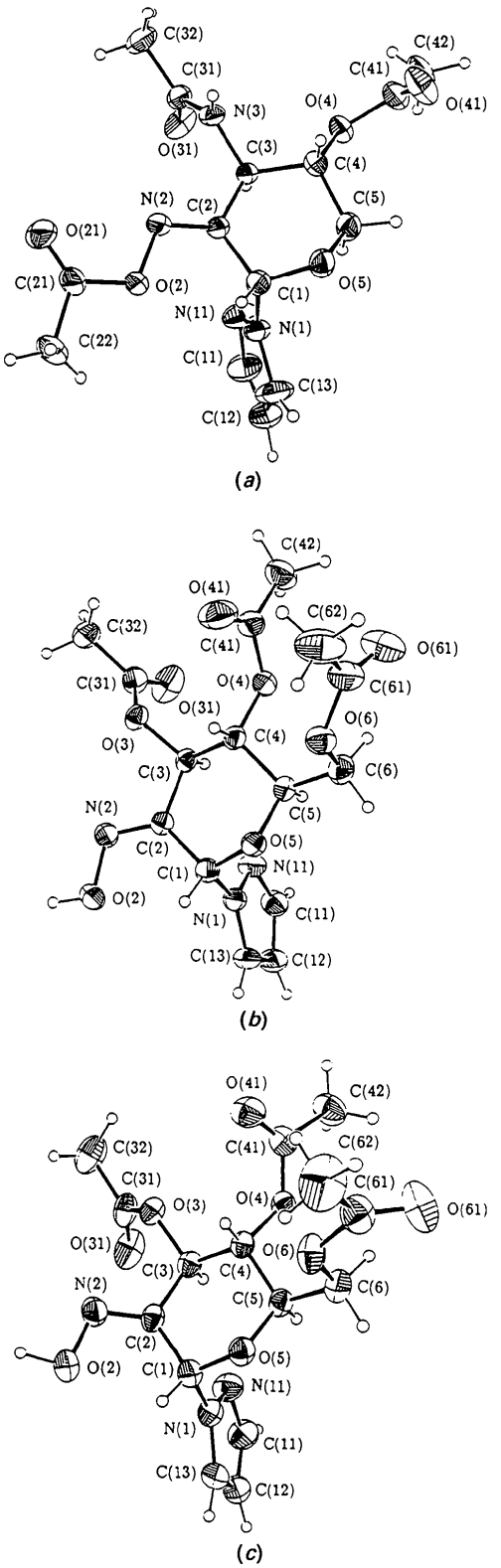


Fig. 1. *ORTEP* drawings of the molecular structures of (*a*) (I), (*b*) molecule *A* and (*c*) molecule *B* in (II) with crystallographic numbering schemes. The ellipsoids correspond to 30% probability contours of atomic displacement.

oxyimine groups have equatorial orientation and are *syn*-equatorial to the vicinal group at C(3). In all structures of carbohydrates with the sp^2 C atom in position 2 of the pyranoid ring and with an equatorial substituent at C(3), the torsion angle, substituent(2)—C(2)—C(3)—substituent(3), is proportional to the deformation of the chair conformation. For a description of this ring deformation from the chair conformation we used a $\Delta\theta$ parameter ($\Delta\theta = \theta$ for $^4C_1$ conformation and $\Delta\theta = 180° - \theta$ for $^1C_4$, where θ is one of the ring-puckering parameters) which is more useful in this case. This dependence, plotted in Fig. 4, is linear and is likely to be helpful, *e.g.*, in the case of NMR investigation of these compounds.

The pyrazole rings at C(1) have an axial orientation. This is probably a consequence of the *Z* conformation of the oxyimine groups, and can be explained as a combination of steric effects and dipole–dipole interactions.

The bond lengths, valency angles and the planar conformation (within the experimental precision) of all these five-membered rings show the delocalization of the double bonds. The geometry of these aglycone moieties is similar to the geometry of the pyrazole

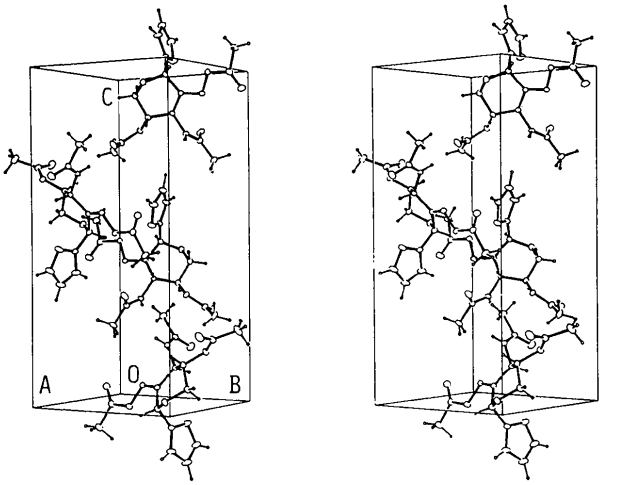


Fig. 2. Stereoview of the crystal packing in the unit cell for (I).

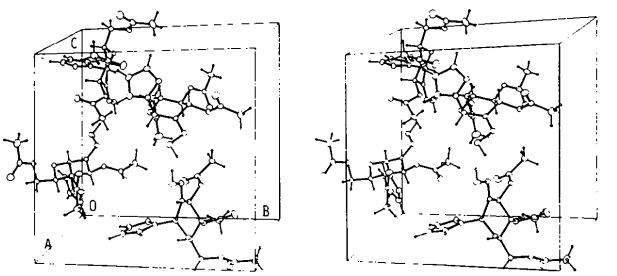


Fig. 3. Stereoview of the crystal packing in the unit cell for (II).

groups in 1,1′-carbonyldipyrazole (Belluce, Einstein, Peterson & Vogel, 1977), in 1-(1-adamantyl)-pyrazoles (Cabildo, Claramunt, Sanz, Foces-Foces, Cano, Catalan & Elguero, 1985) and in $^1C_4$-β- and $^4C_1$-α-EPPP.

The values of the C(1)—N(1) bond lengths in pyranosides with the pyrazole group as the aglycone moiety (except $^4C_1$-α-EPPP) are in the range 1·443 (6)–1·457 (4) Å (the average value is 1·451 Å) while in 1,1′-carbonyldipyrazole the external average C—N bond length is 1·393 Å and in 1-(1-adamantyl)pyrazoles it is 1·488 Å. These differences suggest the bond-shortening effect observed for compounds with two or more electronegative substituents bound to the same C atom. This effect is associated with the differentiation of the valency angles in the anomeric center in carbohydrates (Jeffrey, Pople, Binkley & Vishveshwara, 1978). In fact, in (I) and in molecule *A* of (II) as well as in the remaining pyranosides connected with the pyrazole moiety, the O(5)—C(1)—N(1) valency angle is larger than the C(2)—C(1)—N(1) one.

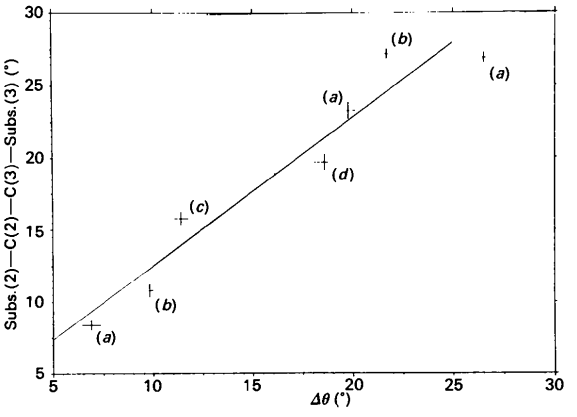


Fig. 4. Dependence of the dihedral angle, substituent(2)—C(2)—C(3)—substituent(3), on the deformation of the pyranoid ring for pyranosides with the C_{sp^2} atom in position 2 of the ring and equatorial substituent at C(3). The deformation parameter $\Delta\theta$ is defined in the text. References: (*a*) this paper; (*b*) Smiatacz, Myszka & Ciunik (1988); (*c*) unpublished results for ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroximino-α-D-*arabino*-hexopyranoside (Ciunik, Szweda & Smiatacz, 1987); (*d*) Palmer & Palmer (1976).

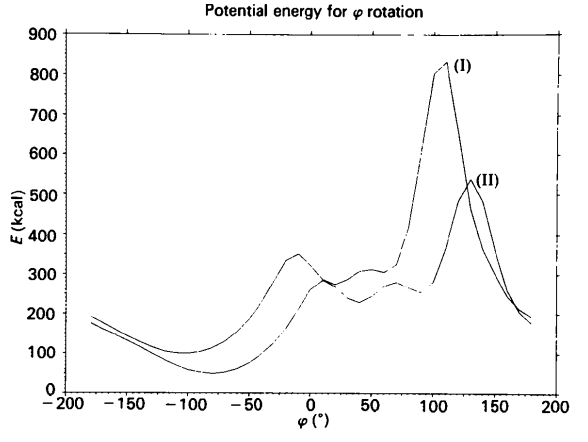


Fig. 5. Potential-energy profile for the pyrazole ring rotation around the C(1)—N(1) bond in (I) and (II). 1 kcal = 4·1868 kJ.

The orientation of the axial pyrazole group with regard to the O(5)—C(1) bond is −anticlinal (−*ac*) in (I) [dihedral angle O(5)—C(1)—N(1)—N(11) is −106·6 (4)°] and −synclinal (−*sc*) in (II) [the respective dihedral angles are −81·3 (4) and −86·2 (5)° for molecules *A* and *B*]. A similar *sc* conformation in the anomeric center in $^1C_4$-β-EPPP suggests that these orientations of the pyrazole moiety are energetically preferable. This point of view is supported by the results of molecular-mechanics calculations which are presented in Fig. 5. Although the potential energies obtained may be approximations only, the energy profiles for the rotation of the pyrazole moiety around the C(1)—N(1) bond show a tendency to the −*ac* [in (I)] and −*sc* orientations [in (II)]. In the case of two *syn*-axial substituents in $^4C_1$-α-EPPP the pyrazole group has the *sc* orientation but simultaneously the C(1)—N(1) bond length [1·473 (6) Å] is longer than in (I), (II) and $^1C_4$-β-EPPP.

There exists a network of intermolecular, linear hydrogen bonds in the crystals investigated. The acetamido group in (I) participates in a weak hydrogen bond with O(41) [N—H···O = 2·16 Å], the hydroxyimino groups in (II) participate in strong hydrogen bonds: O(2)—H of molecule *A* is connected with O(41) of molecule *B* (O—H···O = 1·78 Å) and O(2)—H of molecule *B* with N(2) of molecule *A* (O—H···N = 1·90 Å).

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Commission on Biological Macromolecules

Policy on Publication and the Deposition of Data from Crystallographic Studies of Biological Macromolecules

I. *Preamble*

1. Crystallographic analyses of protein, nucleic-acid and virus structures produce an extraordinary amount of information, and these results are widely recognized as having unique value. Available information transcends that which can be recorded in usual scientific publications, and the Protein Data Bank is often used as a supplementary repository for such results. As in all science, it is imperative that sufficient information be made available so that the structural results can be reproduced and verified.

2. The importance of preserving the fundamental data and results from diffraction studies is recognized alike by producers and users of this information. There are, however, concerns that results from the early stages of analysis will be inaccurate in detail and that investigators should have the opportunity to complete the analysis and interpretation of their data. On the other hand, an open-ended protection of authors' interests conflicts with the general scientific good and it creates the risk that valuable data will be lost forever. Accordingly, the deposition policy promulgated below stipulates immediate deposition of atomic coordinates and diffraction data supporting publications on structure, but it provides for the possibility of a specified delay in the release of this information for public use.

II. *Policy*

1. The Commission on Biological Macromolecules of the International Union of Crystallography endorses a deposition policy for crystallographic studies to permit independent verification of the results and to preserve the primary data for future use. Scientific publications reporting results from crystallographic determinations of macromolecular structure should be accompanied by a deposition of atomic coordinates and structure-factor information at a level appropriate to the description given in the paper.

Specific provisions of the policy are elaborated below:

(*a*) *Provisions for atomic coordinates.* Two different levels of description arise with respect to the coordinates of macromolecular structures. In the case of chain-tracing descriptions, the α-carbon coordinates for proteins or phosphorus positions for nucleic acids are appropriate for deposition. If the interpretation presented depends on atomic details as shown in figures of side chains or numbers derived from atomic coordinates, then the full coordinate list should be deposited. Atomic displacement parameters (*B* values) and occupancy factors that are part of a model should also be deposited. Investigators might choose to flag regions of a structure that are judged to be particularly unreliable or subject to revision.

(*b*) *Provisions for diffraction data.* Native structure-factor magnitudes should be deposited to the limit of Bragg spacings stated in the paper. The deposition of additional data used in phase determination (heavy-atom isomorph data, Bijvoet mates, multiple wavelength measurements, *etc.*) is also encouraged. In the case of structure reports that do not involve atomic models (*e.g.* low-resolution studies) both structure amplitudes and phases used in Fourier syntheses that are reported should be deposited.

(*c*) *Provision for publications in methodology.* The policy applies to reports on structural results. Those papers that describe purely advances in methodology are exempt from this policy even if diffraction data or structural results were required for their development.

(*d*) *Provision for manner of deposition.* The Protein Data Bank at Brookhaven National Laboratory is recognized by the Commission on Biological Macromolecules of the International Union of Crystallography as the appropriate repository for results from macromolecular crystallography. Accordingly, data should be deposited in machine form as instructed by the Protein Data Bank.