

Fig. 4. The unit-cell packing.

standard *MOPAC* program (QCPE No. 464). The energy was minimized with respect to all geometrical variables. The calculations showed that the conformation obtained from  $\varphi = -130^\circ$ ,  $\nu = 90^\circ$  has lowest energy, but the differences between the energies for all calculated conformers do not exceed  $1 \text{ kJ mol}^{-1}$ . Therefore, it is probable that this conformation is the one observed in solution.

The four molecules in the unit cell (Fig. 4) are packed in such a manner that two molecules with conformation (I) are almost seized by two molecules with conformation (II). As is clear from Fig. 4, different conformations of both pairs of the molecules result in a compact packing within the unit cell.

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## Structure of a Phenylhydrazone of Diacetone Protected 3-Keto-glucose

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**Abstract.** (*Z*)-3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3-phenylhydrazone- $\alpha$ -*D*-ribo-hexofuranose, C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub>,  $M_r = 348.40$ , monoclinic,  $P2_1$ ,  $a = 10.867$  (2),

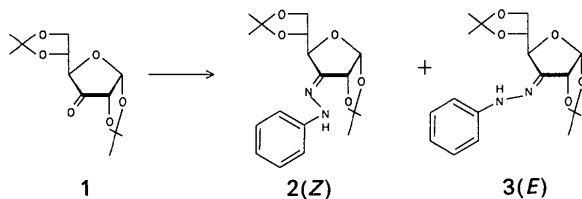
$b = 5.790$  (1),  $c = 14.740$  (2) Å,  $\beta = 94.75$  (1)°,  $V = 924.3$  (8) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.26 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 0.99 \text{ cm}^{-1}$ ,  $F(000) = 372$ ,  $T = 293 \text{ K}$ ,  $R = 0.068$  for 2597 observed reflections. The title compound possesses the *Z* configuration. The phenyl ring is nearly coplanar with the furanose ring. The *gauche* conformation around the C(14)—C(8) bond

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is in agreement with results obtained from NMR spectroscopy in solution. The dihedral angle O(4)—C(14)—C(8)—O(1) is 75.6 (6)°.

**Introduction.** The synthesis of chiral compounds starting from carbohydrates is one of the research objectives of our laboratory. The easily available 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-ribo-hexofuranos-3-ulose (1) (Baker, Horton & Tindall, 1976) is a versatile building block for this purpose and is obtained from natural D-glucose with known absolute configuration.



Compound (1) was converted by condensation with phenylhydrazine into a mixture of two compounds.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic analysis revealed these to be the isomeric (*Z*)- and (*E*)-3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-phenylhydrazono- $\alpha$ -D-ribo-hexofuranose, (2) and (3), but did not provide further basis for configurational assignments. Therefore, a single-crystal X-ray analysis was performed which gave unambiguous proof for the *Z* configuration of the major isomer (2).

**Experimental.** Full experimental details of the preparation of (2) have been published (de Wit, Cui Yi Qing, van Rantwijk, Maat & Kieboom, 1992). Compound (2) was isolated from the reaction mixture by crystallization from ethanol; m.p. 422–422.5 K;  $[\alpha]_D^{20} 291^\circ$  ( $c = 1$ , ethanol).

A crystal of dimensions 0.30 × 0.15 × 0.15 mm was mounted on an Enraf-Nonius CAD-4 diffractometer. Lattice parameters were determined from the setting angles of 25 reflections ( $10 < \theta < 13^\circ$ ). Intensity data were measured with  $\omega/2\theta$  scans to  $\theta_{\text{max}} = 30.0^\circ$ ; index range  $h - 15$  to 15,  $k 0$  to 8,  $l 0$  to 20. Three standard reflections measured every 2 h showed no significant variation over the period of data collection. 3031 reflections were scanned, of which 2599 were considered observed [ $I > 1.0\sigma(I)$ ]. No absorption correction was applied. The structure was solved using direct methods (*MULTAN*; Germain, Main & Woolfson, 1971). H-atom positions, except methyl H atoms, were obtained from a difference Fourier map. Coordinates of all atoms (except methyl H atoms) were refined using full-matrix least squares on  $F$  values; non-H atoms were assigned anisotropic thermal parameters and H atoms were given fixed isotropic parameters. The

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
N(1)	6235 (5)	10563 (12)	2593 (4)	50 (2)
N(2)	7441 (4)	10957 (10)	2881 (3)	56 (2)
C(1)	5620 (5)	12057 (12)	1983 (3)	58 (2)
C(2)	6191 (6)	13979 (13)	1649 (4)	68 (2)
C(3)	5514 (8)	15428 (16)	1048 (5)	84 (3)
C(4)	4294 (8)	14975 (18)	773 (5)	90 (3)
C(5)	3743 (7)	13038 (20)	1105 (5)	89 (3)
C(6)	4394 (5)	11570 (15)	1702 (4)	68 (2)
C(7)	7975 (5)	9475 (12)	3415 (3)	50 (2)
C(8)	9306 (5)	9658 (12)	3751 (3)	52 (2)
C(9)	8472 (6)	6440 (12)	4462 (4)	59 (2)
C(10)	7434 (5)	7323 (11)	3794 (4)	56 (2)
C(11)	6938 (5)	8018 (12)	5268 (4)	57 (2)
C(12)	6031 (6)	6997 (16)	5880 (4)	84 (3)
C(13)	7265 (7)	10518 (14)	5491 (5)	85 (3)
C(14)	10204 (5)	9486 (12)	3025 (4)	54 (2)
C(15)	10044 (6)	8403 (13)	1502 (4)	67 (2)
C(16)	10247 (7)	11612 (13)	2423 (5)	71 (2)
C(17)	11271 (7)	7314 (20)	1270 (6)	115 (4)
C(18)	8951 (7)	7758 (26)	877 (5)	127 (5)
O(1)	9522 (3)	7782 (10)	4374 (2)	66 (1)
O(2)	8024 (4)	6617 (9)	5311 (3)	68 (1)
O(3)	6436 (3)	7747*	4343 (2)	61 (1)
O(4)	9816 (4)	7697 (8)	2404 (2)	58 (1)
O(5)	10193 (7)	10806 (11)	1549 (4)	129 (3)

\* Parameter kept fixed during refinement.

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

N(1)—N(2)	1.364 (7)	C(9)—O(1)	1.396 (8)
N(1)—C(1)	1.380 (9)	C(9)—O(2)	1.383 (7)
C(1)—C(2)	1.384 (10)	C(10)—O(3)	1.427 (7)
C(2)—C(3)	1.386 (11)	C(11)—C(12)	1.510 (9)
C(3)—C(4)	1.379 (12)	C(11)—C(13)	1.520 (11)
C(4)—C(5)	1.380 (14)	C(11)—O(2)	1.429 (8)
C(5)—C(6)	1.376 (11)	C(11)—O(3)	1.435 (6)
C(6)—C(1)	1.391 (8)	C(14)—C(16)	1.520 (10)
C(7)—N(2)	1.271 (8)	C(14)—O(4)	1.423 (7)
C(7)—C(8)	1.493 (7)	C(15)—C(17)	1.539 (11)
C(7)—C(10)	1.505 (9)	C(15)—C(18)	1.490 (10)
C(8)—C(14)	1.510 (8)	C(15)—O(4)	1.432 (7)
C(8)—O(1)	1.429 (8)	C(15)—O(5)	1.402 (10)
C(9)—C(10)	1.523 (8)	C(16)—O(5)	1.367 (9)
C(1)—N(1)—N(2)	120.0 (6)	O(2)—C(11)—O(3)	103.2 (4)
N(1)—N(2)—C(7)	117.2 (5)	O(2)—C(11)—C(12)	109.2 (5)
N(1)—C(1)—C(2)	121.9 (5)	O(2)—C(11)—C(13)	110.7 (5)
N(1)—C(1)—C(6)	117.8 (6)	O(3)—C(11)—C(12)	108.0 (5)
C(2)—C(1)—C(6)	120.2 (6)	O(3)—C(11)—C(13)	111.9 (5)
C(1)—C(2)—C(3)	119.0 (6)	C(12)—C(11)—C(13)	113.3 (6)
C(2)—C(3)—C(4)	121.3 (8)	C(8)—C(14)—C(16)	114.4 (6)
C(3)—C(4)—C(5)	119.0 (8)	C(8)—C(14)—O(4)	109.2 (5)
C(4)—C(5)—C(6)	120.9 (7)	O(4)—C(14)—C(16)	103.7 (5)
C(5)—C(6)—C(1)	119.6 (7)	O(4)—C(15)—O(5)	105.4 (5)
N(2)—C(7)—C(8)	122.5 (5)	O(4)—C(15)—C(17)	108.0 (6)
N(2)—C(7)—C(10)	128.0 (5)	O(4)—C(15)—C(18)	108.2 (6)
C(8)—C(7)—C(10)	109.5 (5)	O(5)—C(15)—C(17)	108.6 (8)
C(7)—C(8)—O(1)	105.2 (5)	O(5)—C(15)—C(18)	111.2 (8)
C(7)—C(8)—C(14)	115.2 (4)	C(17)—C(15)—C(18)	114.9 (7)
O(1)—C(8)—C(14)	108.9 (5)	C(14)—C(16)—O(5)	105.8 (6)
O(1)—C(9)—C(10)	108.7 (5)	C(8)—O(1)—C(9)	113.0 (4)
O(1)—C(9)—O(2)	113.3 (5)	C(9)—O(2)—C(11)	110.7 (4)
O(2)—C(9)—C(10)	105.2 (5)	C(10)—O(3)—C(11)	108.1 (4)
C(7)—C(10)—C(9)	103.1 (4)	C(14)—O(4)—C(15)	108.9 (5)
C(7)—C(10)—O(3)	114.0 (5)	C(15)—O(5)—C(16)	112.4 (5)
O(3)—C(10)—C(9)	104.4 (4)		

chirality was assigned from that of the starting material. Refinement of 262 variables converged to  $R = 0.068$ ,  $wR = 0.066$  ( $w = 1$ ) and  $S = 1.13$  for 2597 observed reflections (2599 minus two low-order reflections). The maximum shift/e.s.d. of the final cycle was 0.7. The final  $\Delta F$  syntheses had  $|\rho| <$

0.32 e Å<sup>-3</sup>. All calculations were performed on the Delft University Amdahl 470/V7B computer using XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic scattering factors are from XRAY72.

**Discussion.** Atomic coordinates are listed in Table 1\* and bond lengths and bond angles in Table 2. Fig. 1 shows the atomic numbering used in this report. The hydrazono group can adopt two configurations: the *Z* and *E* configuration. From the NMR spectra it remains questionable which part represents the *Z* or the *E* configuration. Fig. 1 shows the crystalline compound to be the *Z* isomer. NMR spectroscopy of this crystalline compound gives, now, unequivocally the data for the *Z* isomer.

The angle O(4)—C(14)—C(8)—O(1) is 75.6°. Thus, the position of the protons connected to C(14) and C(8), respectively, is *gauche*. In solution, a coupling constant for these two protons of 2 Hz was found. This value also points to a *gauche* conformation. Apparently, the average conformation in solution resembles the conformation in the crystalline state. The phenyl ring is nearly coplanar with the furanose ring of the sugar: the maximum deviations from the least-squares plane defined by 13 atoms

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55323 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0535]

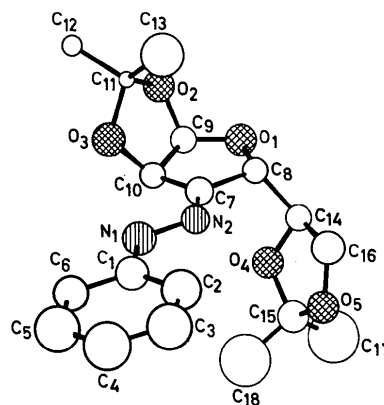


Fig. 1. View of the molecule showing the atomic numbering scheme. H atoms have been omitted for clarity.

[C(1), C(2),...C(10), N(1), N(2) and O(1)] is 0.07 Å [C(9)]. The two isopropylidene groups are at either side of the least-squares plane.

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## Structures of 4β-(Nitromethyl)-2α,6α-diphenyl-4α-piperidinol and 4β-(Nitromethyl)-2β,6β-diphenyl-4α-piperidinol

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**Abstract.** 4β-(Nitromethyl)-2α,6α-diphenyl-4α-piperidinol, isomer (2a), C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>, *M<sub>r</sub>* = 312.37, orthorhombic, *Ccm*2<sub>1</sub>, *a* = 10.548 (6), *b* = 19.590 (11), *c* = 7.729 (3) Å, *V* = 1597 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.30 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, μ = 0.8 cm<sup>-1</sup>, *F*(000) = 664, *T* = 298 K, *R* = 0.066 for 796 reflections with intensities ≥ 3σ(*I*). 4β-(Nitromethyl)-2β,6β-diphenyl-4α-piperidinol,

isomer (2b), C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>, *M<sub>r</sub>* = 312.37, triclinic, *P*1̄, *a* = 5.573 (2), *b* = 11.852 (6), *c* = 13.440 (7) Å, α = 68.42 (4), β = 89.46 (4), γ = 79.82 (3)°, *V* = 810.9 (6) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.28 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, μ = 0.8 cm<sup>-1</sup>, *F*(000) = 332, *T* = 298 K, *R* = 0.0604 for 2874 reflections with intensities ≥ 3σ(*I*). Both isomers were isolated from the same reaction mixture. They differ only in the orientation