

## Hydrogen-bonded sheets of $R_2^2(10)$ and $R_4^4(24)$ rings in 1-deoxy-1-morpholino-D-fructopyranose

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In the title compound,  $C_{10}H_{19}NO_6$ , both rings adopt almost perfect chair conformations and their mutual orientation is influenced by an intramolecular  $O-H \cdots N$  hydrogen bond. The molecules are linked by three independent  $O-H \cdots O$  hydrogen bonds into sheets containing equal numbers of  $R_2^2(10)$  and  $R_4^4(24)$  rings.

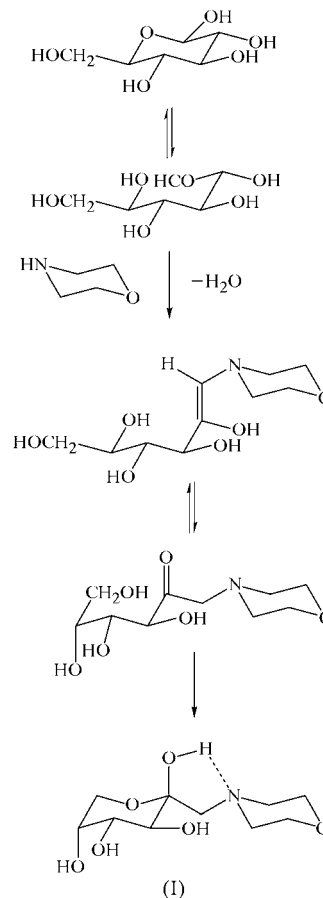
### Comment

As a possible intermediate for the synthesis of aza-sugars from glucose, we have prepared 1-deoxy-1-morpholino-D-fructopyranose, (I), by the reaction of D-glucose with morpholine, utilizing an Amadori rearrangement of the initially formed N-D-glucosylmorpholine (Hodge & Rist, 1953).

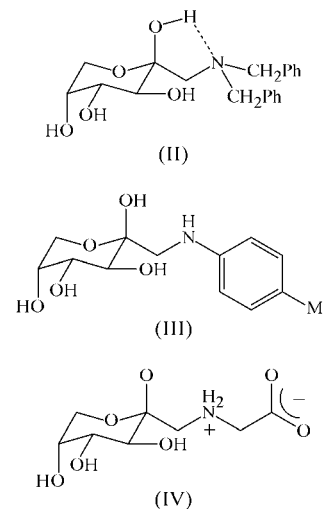
In (I), the sugar component has the pyranose form (Fig. 1) and the two independent rings both adopt almost perfect chair conformations. The ring puckering angle  $\theta$  (Cremer & Pople, 1975) is  $177.3(2)^\circ$  for the atom sequence O1–C2–C3–C4–C5–C6 and  $1.4(2)^\circ$  for the atom sequence O11–C12–C13–N14–C15–C16; the ideal values for a chair conformer are  $(180n)^\circ$ , where  $n$  represents zero or an integer. In the pyranose ring, the substituent atoms O2 and O5 both occupy axial sites but all other non-H substituents adopt equatorial sites. The mutual orientation of the two independent rings appears to be influenced, and possibly controlled, by the presence of an intramolecular  $O-H \cdots N$  hydrogen bond (Table 1). The coordination at the morpholine N atom is markedly pyramidal, with a sum of bond angles of  $333.6(2)^\circ$ ; the bond distances and the remaining bond angles show no unexpected features.

The overall conformation adopted by (I) is very similar to those found for three close analogues retrieved from the Cambridge Structural Database (Allen, 2002). In each of EDEVUU, (II), where the amine component in the synthesis

is dibenzylamine (Hou *et al.*, 2001), ZIVTON, (III), where the amine component is 4-toluidine (Gomez de Anderez *et al.*,



1996), and the zwitterionic YUXCUP, (IV), where the amine component is glycine (Mossine *et al.*, 1995), the hydroxy groups corresponding to O2 and O5 in (I) occupy axial sites. There is an intramolecular  $O-H \cdots N$  hydrogen bond in (II) exactly analogous to that in (I), while in (IV) the two intramolecular hydrogen bonds are both of  $N-H \cdots O$  type; the H atoms bonded to N and O atoms in (III) could not be located.



Each of the other three hydroxyl groups in (I) acts as a donor in intermolecular hydrogen bonds, all with O atoms as

acceptors (Table 1), leading to the formation of a hydrogen-bonded supramolecular structure which is two-dimensional. Since the only symmetry operations available are translations, the formation of the supramolecular structure is very readily analyzed in terms of two simple one-dimensional substructures. In the first of these substructures, atoms O3 and O4 in the molecule at  $(x, y, z)$  act as hydrogen-bond donors, respectively, to atoms O1 and O5, both in the molecule at  $(x, 1 + y, z)$ , so generating a  $C(5)C(5)[R_2^2(10)]$  chain of rings (Bernstein *et al.*, 1995) running parallel to the  $[010]$  direction (Fig. 2). In the second substructure, atom O5 in the molecule at  $(x, y, z)$  acts as a hydrogen-bond donor to morpholine atom O11 in the molecule at  $(1 + x, 1 + y, 1 + z)$ , so generating a simple  $C(11)$  chain running parallel to the  $[111]$  direction (Fig. 2). The combination of the  $[010]$  and  $[111]$  chains generates a sheet lying parallel to  $(10\bar{1})$  and containing alternating ribbons of antidromic (Steiner, 2002)  $R_2^2(10)$  and antidromic  $R_4^4(24)$  rings, both running parallel to the  $[010]$  direction (Fig. 2). There are no significant direction-specific interactions between adjacent sheets.

The two-dimensional hydrogen-bonded supramolecular structure found here for (I) may be contrasted with the one-

and three-dimensional structures found in (II) and (IV), respectively. In (II), the combination of three intermolecular  $O-H \cdots O$  hydrogen bonds generates a complex chain of rings (Hou *et al.*, 2001), while in (IV), a combination of four intermolecular  $O-H \cdots O$  hydrogen bonds and two intermolecular  $N-H \cdots O$  hydrogen bonds links the molecules into a single three-dimensional framework structure (Mossine *et al.*, 1995). Although the H atoms bonded to the N and O atoms in (III) were not located (Gomez de Anderez *et al.*, 1996), the close intermolecular contacts involving N and O atoms suggest that the hydrogen-bonded supramolecular structure is probably two-dimensional. Hence, modest changes in the nature of the amino component can readily alter the dimensionality of the hydrogen-bonded structure.

### Experimental

A sample of compound (I) was prepared according to a published procedure (Hodge & Rist, 1953). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in methanol [m.p. 419–421 K; literature m.p. 418–419 K (Hodge & Rist, 1953)].

#### Crystal data

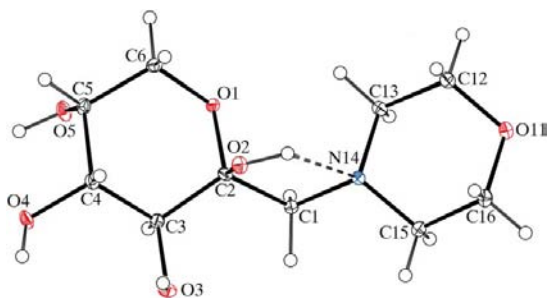
$C_{10}H_{19}NO_6$   
 $M_r = 249.26$   
 Triclinic,  $P1$   
 $a = 5.2767$  (8) Å  
 $b = 5.5375$  (5) Å  
 $c = 10.2809$  (13) Å  
 $\alpha = 104.598$  (10)°  
 $\beta = 90.393$  (12)°  
 $\gamma = 104.834$  (10)°  
 $V = 280.19$  (6) Å<sup>3</sup>  
 $Z = 1$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.12$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 $0.52 \times 0.27 \times 0.06$  mm

#### Data collection

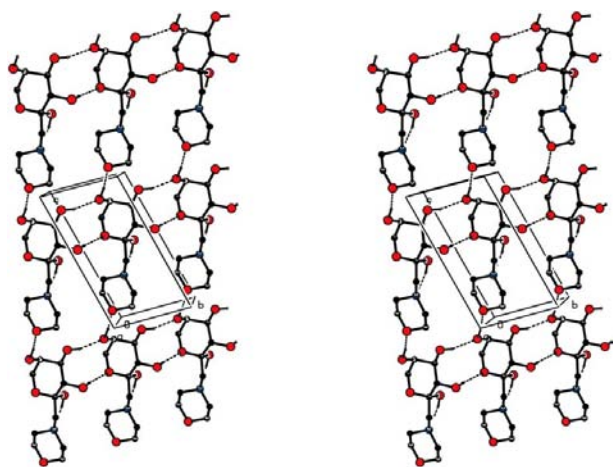
Bruker–Nonius KappaCCD diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{min} = 0.979$ ,  $T_{max} = 0.993$   
 7471 measured reflections  
 1279 independent reflections  
 1163 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.024$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.075$   
 $S = 1.13$   
 1279 reflections  
 154 parameters  
 3 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{max} = 0.29$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.23$  e Å<sup>-3</sup>



**Figure 1**  
 A molecule of (I), showing the atom-labelling scheme and the intramolecular hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**  
 A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet of  $R_2^2(10)$  and  $R_4^4(24)$  rings. For the sake of clarity, H atoms bonded to C atoms have been omitted.

**Table 1**  
 Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H2 \cdots N14$	0.91	2.06	2.652 (3)	122
$O3-H3 \cdots O1^i$	0.93	1.99	2.874 (2)	158
$O4-H4 \cdots O5^i$	0.86	1.98	2.785 (2)	158
$O5-H5 \cdots O11^{ii}$	0.91	2.01	2.897 (2)	164

Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $x + 1, y + 1, z + 1$ .

Crystals of compound (I) are triclinic; space group  $P1$  was selected and confirmed by the structure analysis. The labelling of the C atoms in the sugar component follows the conventional labelling for the glucose starting material. All H atoms were located in difference maps and then treated as riding atoms. H atoms bonded to C atoms

were placed in geometrically idealized positions, with C–H distances of 0.99 (CH<sub>2</sub>) or 1.00 Å (CH), and with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$ ; H atoms bonded to O atoms were permitted to ride at the positions deduced from the difference maps, with  $U_{\text{iso}}(\text{H})$  values of  $1.5U_{\text{eq}}(\text{O})$ , giving O–H distances in the range 0.86–0.93 Å. The only restraints were those required by the space group to fix the origin. In the absence of significant resonant scattering, the Friedel-equivalent reflections were merged and the absolute configuration was set by reference to the known absolute configuration of the starting D-glucose material.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3112). Services for accessing these data are described at the back of the journal.

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