Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

1-(2-Deoxy-β-D-*erythro*-pentofuranosyl)-4-nitro-1*H*-indazole

Frank Seela,[a]* Anup M. Jawalekar[a] and Henning Eickmeier[b]

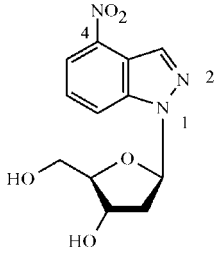
[a]Laboratorium für Organische und Bioorganische Chemie, Institut für Chemie, Universität Osnabrück, Barbarastraße 7, 49069 Osnabrück, Germany, and [b]Anorganische Chemie II, Institut für Chemie, Universität Osnabrück, Barbarastraße 7, 49069 Osnabrück, Germany
Correspondence e-mail: frank.seela@uni-osnabrueck.de

Received 17 February 2004
Accepted 1 April 2004
Online 11 May 2004

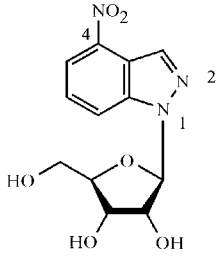
In the title compound, $C_{12}H_{13}N_3O_5$, the conformation of the glycosylic bond is *anti* [torsion angle = −105.3 (2)°]. The 2′-deoxyribofuranose moiety adopts an S-type sugar pucker and the orientation of the exocyclic C—C bond is −*sc* (*trans*).

Comment

Recently, it was shown that the regioisomeric 4-nitroindazole N^1- and N^2-(2-deoxy-β-D-ribofuranosides) can act as universal nucleosides, thereby stabilizing the DNA duplex structure by stacking interactions (Seela & Jawalekar, 2002). The 4-nitro analogue, (I), which was designed as a universal nucleoside, is expected to show enhanced stacking interactions as a result of the presence of the nitro group. Although the glycosylation positions of the regioisomeric 4-nitroindazole nucleosides are different, very little influence on the duplex stability was noticed. Seela *et al.* (2004) have investigated the X-ray structures of the regioisomeric 4-nitroindazole N^1- and N^2-β-D-ribofuranosides. We report here the single-crystal X-ray structure of the title compound, (I).



(I)



(II)

The structure of (I) is shown in Fig. 1; selected geometric parameters are summarized in Table 1 (systematic numbering is used throughout). The orientation of the nucleobase relative to the sugar moiety is *anti*, as defined by the χ (O4′—C1′—N9—C4) torsion angle for purine nucleosides (IUPAC–IUB Joint Commission on Biochemical Nomenclature, 1983). Normally, the preferred conformation at the *N*-glycosylic bond in purine nucleosides is in the range $-150 < \chi < -140°$. The corresponding torsion angle in (I), namely O4′—C1′—N1—C7*A*, is −105.3 (2)°. This value represents a conformation between *anti* and high-*anti*. Stereoelectronic effects and Coulombic repulsion between non-bonding electron pairs at atoms O4′ and N2 might induce this conformational change (Seela *et al.*, 2000). The conformation of the related 1-β-D-ribofuranosyl-4-nitro-1*H*-indazole, (II), is even more shifted towards high-*anti* (χ = −93.7°). The glycosylic bond length (N1—C1′) of (I) is 1.449 (2) Å, which is almost identical to that of (II) [1.450 (6) Å]. The 2′-deoxyribose ring of (I) shows an S-type pucker [C2′-*endo*, C3′-*exo* ($^{2'}T_{3'}$)], while that of (II) is N-type [C2′-*exo*, C3′-*endo* ($^{3'}T_{2'}$)]. The phase angle of pseudorotation of (I) (P = 192.6°) is in the south region, with τ_m = 37.5°; this value is in good agreement with the mean value [τ_m = 38.6 (3)°; Saenger, 1984]. The γ (O5′—C5′—C4′—C3′) torsion angle is −91.5 (2)°, which corresponds to −*sc*, a conformation often found in nucleosides with ($^{2'}T_{3'}$) sugar pucker.

The base moiety of (I) is essentially planar. The nitro group is slightly out of the plane, with C3*A*—C4—N4—O42 and C5—C4—N4—O41 torsion angles of −9.5 (3) and −5.6 (3)°, respectively. The mean deviation of the ring atoms (N1/N2/C3/C3*A*/C4–C7/C7*A*) from their calculated least-squares plane is 0.0143 Å, with maximum deviations of 0.024 (1) (for N1) and 0.019 (2) Å (for C5). The ring substituents N4 and C1′ show significant deviations [0.095 (3) and −0.051 (3) Å, respectively] but lie on the same side of the nucleobase.

In solution, the S-conformer population of (I) is shifted more towards N and shows nearly equal population of N and S conformers (N: 46%; S: 54%), a situation that is very similar to that for (II) (N: 53%; S: 47%). The puckering was determined from the vicinal ^3J(H,H) coupling constants of the ^{1}H NMR spectra measured in D_2O, applying the *PSEUROT* program (Van Wijk & Altona, 1993). The increase in the N-conformer population can be attributed to the crystal packing. In solution, interactions with water molecules have to be considered.

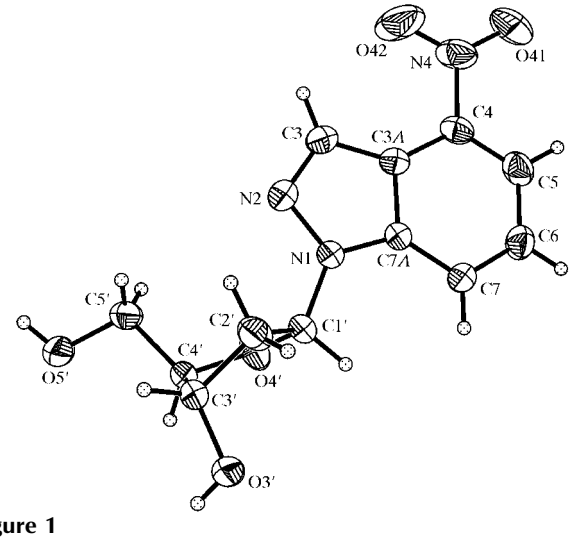


Figure 1
A perspective view of (I). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

 DOI: 10.1107/S0108270104008005

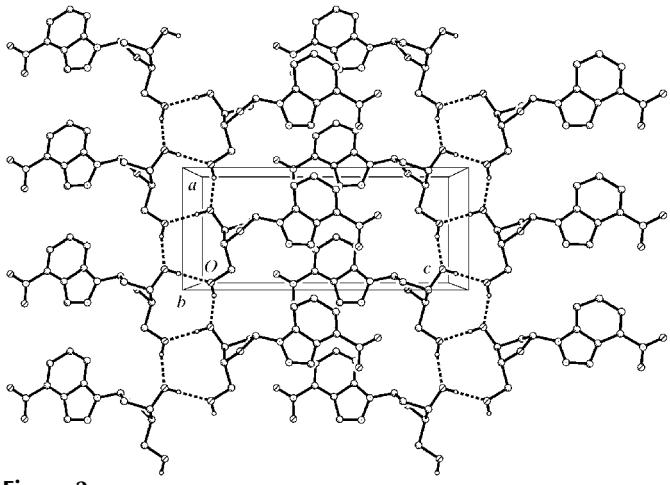


Figure 2
The ribbon structure of (I), viewed parallel to the *b* axis.

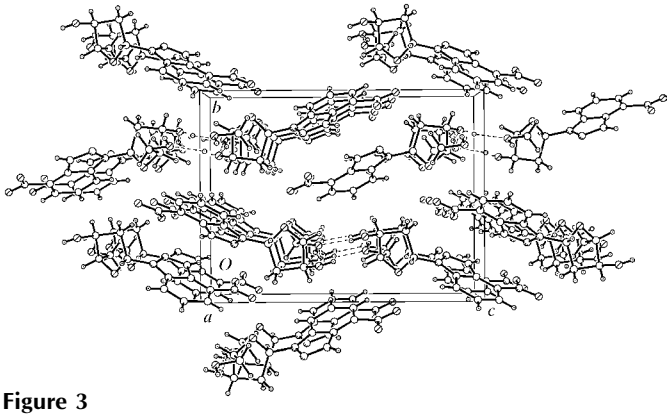


Figure 3
A perspective view, demonstrating the stacking between the layers.

The view along the *b* axis shows a ribbon structure parallel to the short *a* axis (Fig. 2); the molecules of (I) are linked by two hydrogen bonds, *viz*. O3′—H3′*A*···O5′^{i} and O3′—H3′*A*···O5′^{ii} (see Table 2 for symmetry codes and geometry). The NO_2 group does not take part in hydrogen bonding.

In the closely packed structure (Fig. 3), the bases and the sugar moieties are stacked. In addition to the above-mentioned classical hydrogen bonding, there is also an interaction between atoms C5(H) and O4′, with an H···O distance of 2.47 Å, which is still within the range of hydrogen bonding. The electron-withdrawing nitro group might be responsible for the acidity of the C5—H group.

Experimental

Pale-yellow crystals (m.p. 413 K) were grown from methanol.

Crystal data

$C_{12}H_{13}N_3O_5$
M_r = 279.25
Orthorhombic, $P2_12_12_1$
a = 6.7444 (12) Å
b = 11.718 (3) Å
c = 15.734 (2) Å
V = 1243.4 (5) Å^3
Z = 4
D_x = 1.492 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
θ = 5.2–15.0°
μ = 0.12 mm^{-1}
T = 293 (2) K
Block, yellow
0.52 × 0.43 × 0.30 mm

Table 1
Selected geometric parameters (Å, °).

N1—C1′	1.449 (2)		
N2—N1—C7*A*	111.84 (14)	C7*A*—N1—C1′	128.23 (15)
N2—N1—C1′	119.66 (14)		
C7*A*—N1—N2—C3	−1.0 (2)	C1′—C2′—C3′—O3′	81.89 (18)
C1′—N1—N2—C3	−175.43 (16)	C1′—C2′—C3′—C4′	−35.74 (17)
N1—N2—C3—C3*A*	0.2 (2)	N1—C1′—O4′—C4′	−127.01 (15)
C4—C3*A*—C7*A*—C7	−1.6 (2)	C1′—O4′—C4′—C5′	103.93 (18)
C3—C3*A*—C7*A*—C7	179.92 (16)	C1′—O4′—C4′—C3′	−19.54 (17)
N2—N1—C1′—O4′	68.2 (2)	C2′—C3′—C4′—O4′	34.58 (17)
C7*A*—N1—C1′—O4′	−105.3 (2)	O3′—C3′—C4′—C5′	158.45 (13)
C7*A*—N1—C1′—C2′	135.96 (19)	O4′—C4′—C5′—O5′	150.32 (17)
O4′—C1′—C2′—C3′	25.36 (18)	C3′—C4′—C5′—O5′	−91.51 (19)
N1—C1′—C2′—C3′	145.47 (15)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3′—H3′*A*···O5′^{i}	0.821 (17)	1.914 (16)	2.734 (2)	177 (3)
O5′—H5′*A*···O3′^{ii}	0.819 (19)	1.971 (12)	2.761 (2)	162 (4)

Symmetry codes: (i) $x-\frac{1}{2},\frac{1}{2}-y,1-z$; (ii) $1+x,y,z$.

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
2725 measured reflections
2072 independent reflections
1896 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 30.0°
$h = -9 \rightarrow 1$
$k = -1 \rightarrow 16$
$l = -1 \rightarrow 22$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.105
S = 1.06
2072 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.1969P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

In the absence of significant anomalous scattering, Friedel opposites could not be used to determine the absolute structure. Refinement of the Flack (1983) parameter led to an inconclusive value (Flack & Bernadinelli, 2000) for this parameter [1.7 (12)]. Therefore, Friedel pairs were merged before the final refinements. The known configuration of the parent molecule was used to define the enantiomer employed in the refined model. All H atoms were initially found in a difference Fourier synthesis. In order to maximize the data/parameter ratio, H atoms bonded to C atoms were placed in idealized positions (C—H = 0.93–0.98 Å) and constrained to ride on their parent atoms, with U_{iso}(H) values of $1.2U_{eq}$(C). The hydroxy H atoms were initially placed in the positions found from the difference map, and were then positioned geometrically and constrained to ride on their parent O atoms, although the chemically equivalent O—H bond lengths were allowed to refine while being constrained to be equal [O—H = 0.819 (19) and 0.821 (17) Å].

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON for Windows* (Spek, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1612). Services for accessing these data are described at the back of the journal.

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