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Note

X-ray crystallographic study of several 2′-deoxy-β-D-ribonucleosides with 1-deazapurine-derived aglycones

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Abstract—The 2′-deoxy-β-D-ribonucleosides of 1,3-deazapurine (benzimidazole (**1**)), 1-deazapurine (both 1*H*-imidazo[4,5-*b*]pyridine (**2**) and 3*H*-imidazo[4,5-*b*]pyridine (**3**)), and 6-benzoylamino-1-deazapurine (7-benzoylamino-3*H*-imidazo[4,5-*b*]pyridine (**4**)) have been prepared and structurally characterized by X-ray crystallography. Especially compounds **1**–**3** can serve as artificial nucleosides that may substitute 2′-deoxy adenosine because they lack the exocyclic amino group and one or two of the endocyclic nitrogen atoms and hence have a much smaller potential to engage in hydrogen bonds. In the latter respect, they are candidates for nucleosides in metal-ion mediated base pairs. The unit cell of compound **3** contains two crystallographically independent molecules. Compound **4** was crystallized from methanol and water, respectively, giving rise to two different solvates. Despite the closely related aglycones, the sugar conformations in **1**–**4** are found to be highly variable (**1**: $^2T_1$; **2**: $^3T_2$; **3**: ^3E and E_4; **4**: ^2E and $^2T_3$). The structures reported here confirm that there is no simple correlation between the sugar conformation and the character of the nucleoside, and they will hopefully contribute to a better understanding of the complex interplay of different effects that are in control of the conformational equilibrium.

Keywords: 2′-Deoxyribonucleosides, structure; 1-Deazapurine; 1,3-Deazapurine; Benzimidazole; 1-Deazaadenine, protected derivative

In the course of our studies[1–6] on the implementation of artificial nucleosides that are capable of forming metal-ion mediated base pairs[7–9] into oligonucleotides, we have been able to determine the solid state structures of several 2′-deoxy-β-D-ribonucleosides with aglycones that are derived from 1-deazapurine. These compounds lack the exocyclic amino group and one or two of the endocyclic nitrogen atoms that are present in the parent nucleoside adenosine. This results in a much smaller potential to engage in hydrogen bonds and makes them useful as synthetic deoxyribonucleosides, for example, in the formation of metal-ion mediated base pairs. We report here the molecular structures of the 2′-deoxy-β-D-ribonucleosides with the aglycones 1,3-deazapurine (benzimidazole) **1**, 1-deazapurine-*N*7 (1*H*-imidazo[4,5-*b*]pyridine) **2**, 1-deazapurine-*N*9 (3*H*-imidazo[4,5-*b*]pyridine) **3**, and 6-benzoylamino-1-deazapurine (7-benzoylamino-3*H*-imidazo[4,5-*b*]pyridine) **4** as determined by single crystal X-ray diffraction analysis. Chart 1 shows the different numbering schemes that are typically used for purine-based ring systems. In the following, the purine numbering will be adhered to. The chemical structural diagrams of **1**–**4** are depicted in Chart 2.

The molecular structures of the 2′-deoxy-β-D-ribonucleosides carrying as aglycones deazapurines without an exocyclic group, that is, compounds **1**–**3** are shown

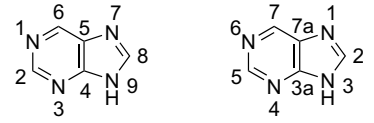

Chart 1. The purine ring system with its two different numbering schemes. The purine numbering is being used throughout this paper.

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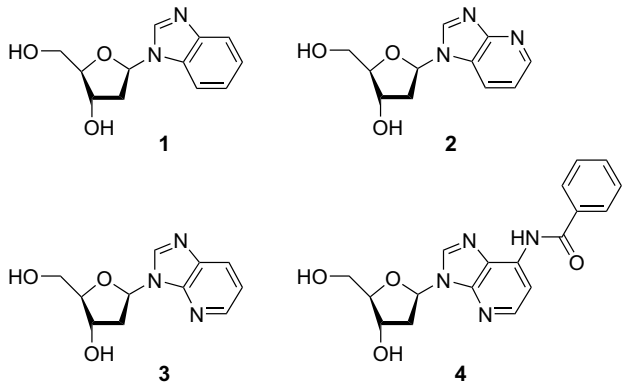

Chart 2. Molecular diagrams of the four 2′-deoxy-β-D-ribonucleosides discussed in this paper.

in Figure 1. Their structures will be discussed individually in the following. A list of structural parameters that define the conformations of the 2′-deoxy-β-D-ribonucleosides can be found in Table 1.

The sugar moiety of 1,3-deazapurine 2′-deoxy-β-D-ribonucleoside **1** adopts a $^{2}T_{1}$ conformation (S-type). The nucleobase is oriented *syn* with respect to the sugar ($\chi = -63.7(3)°$). This arrangement is identical to the one found for 4-fluoro-6-methyl-1*H*-benzimidazole as the aglycone[10] instead of the unsubstituted benzimidazole and might hence be a direct consequence of the presence of the apolar phenyl ring annealed to an imidazole. In the crystal lattice, the molecules of **1** are arranged in a zigzag-type chain structure (Fig. 2). The individual chains are held together by two short hydrogen bonds (O-3b–H···O5b and O-5b–H···N7a). One additional longer hydrogen bond further stabilizes this arrangement (C-2a–H···O-4b). Table S1 gives an overview over the geometries of these bonds. Despite the fact that no π stacking interactions are observed between nucleobases, the formation of discrete alternating hydrophobic and hydrophilic layers can be observed, occupied by the six-membered aromatic ring system and the deoxyriboses, respectively. In the hydrophobic layer, two neighboring aglycones are oriented almost at a 90° angle, with the hydrogen atoms attached to C-1a and C-2a directly pointing toward the adjacent phenyl ring system at a distance of ~3.0 Å. Such a perpendicular arrangement of aromatic residues is well-known and can be observed, for example, between a conserved tyrosine residue and the flavin cofactor in numerous flavoproteins.[11] Other occurrences include tyrosine–tyrosine interactions in some proteins.[12]

Unfortunately, the solid state structure of nucleoside **2** is of poor quality, especially with respect to the sugar part of the molecule. Hence, the assignment of the sugar pucker as $^{3}T_{2}$ (N-type) can only be given with reservations. However, due to interesting hydrogen bonding behavior, the structure of **2** is worthy of discussion anyway. Compound **2** forms a layer structure that is held

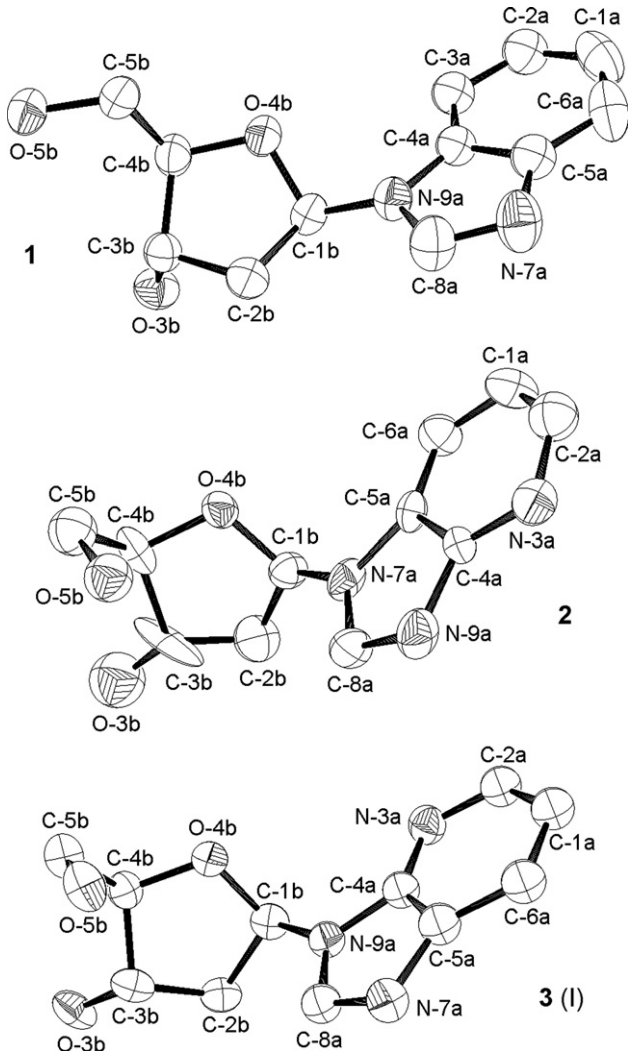

Figure 1. Molecular structures of **1**–**3** with atom numbering schemes. Hydrogen atoms have been omitted for clarity. Only one of the crystallographically independent molecules of **3** (i.e., molecule I) is shown. Displacement ellipsoids are drawn at the 50% probability level (compound **2**: 20%).

together by π stacking of the aglycone along continuous columns in the *x* direction (~3.3 Å) and by hydrogen bonds involving the sugar moieties in the other two directions. More precisely, neighboring deazapurine moieties stack to form hydrogen-bonded dimers via O-5b–H···N3-a (Fig. 3). The mutual orientation of the aromatic ring systems within a dimer is such that the aglycones are rotated about 75° around the crystallographic *x*-axis with respect to each other. Different dimers are interconnected by additional O3-b–H···N-9a hydrogen bonds (Table S2). The hydrogen bond angles found in compound **2** are unusually small, which is most likely due to the fact that the respective hydrogen atoms have been introduced at calculated position relative to the oxygen atoms of the poorly resolved sugar part of the molecule.

Table 1. Endocyclic torsion angles ν_i of the deoxyribose ring[13] that were used to calculate the phase angle of pseudorotation (P)[25] and the puckering amplitude ψ_m,[25] the backbone torsion angle γ (O5′-C5′-C4′-C3′), and the glycosidic bond angle χ[a]

	1	**2**	**3** (I)	**3** (II)	**4**·CH_3OH	**4**·H_2O
ν_0 (°)	−32.0(2)	13(1)	1.8(4)	−16.4(4)	−19.5(5)	−15.3(4)
ν_1 (°)	41.0(2)	−26(2)	−19.0(4)	−2.5(4)	34.2(5)	30.4(4)
ν_2 (°)	−34.0(2)	29(2)	27.6(4)	18.9(4)	−35.6(5)	−33.2(4)
ν_3 (°)	16.5(2)	−21(2)	−27.0(4)	−28.7(4)	25.4(5)	24.7(4)
ν_4 (°)	9.4(2)	5(1)	16.1(4)	28.4(4)	−4.1(5)	−6.1(4)
ψ_m (°)	40.2(3)	30(2)	28.5(4)	29.8(8)	36.5(5)	33.6(4)
P (°)	147.8(3)	−9(2)	14.7(6)	50.6(7)	167.5(6)	171.7(4)
	C2′-*endo* ($^2T_1$)	C2′-*exo* ($^3T_2$)	C3′-*endo* (^3E)	C4′-*exo* (E_4)	C2′-*endo* (^2E)	C2′-*endo* ($^2T_3$)
χ (°)	−63.7(3)	−74(1)	−82.8(4)	−90.1(4)	53.7(6)	57.3(5)
	syn (−*sc*)	*syn* (−*sc*)	*syn* (−*sc*)	*anti* (−*ac*)	*syn* (+*sc*)	*syn* (+*sc*)
γ (°)	−63.1(3)	44(2)	56.9(5)	50.8(5)	44.2(6)	44.8(5)
	−*sc*	+*sc*	+*sc*	+*sc*	+*sc*	+*sc*

[a] For compound **3**, I and II represent the two crystallographically independent molecules in the unit cell.

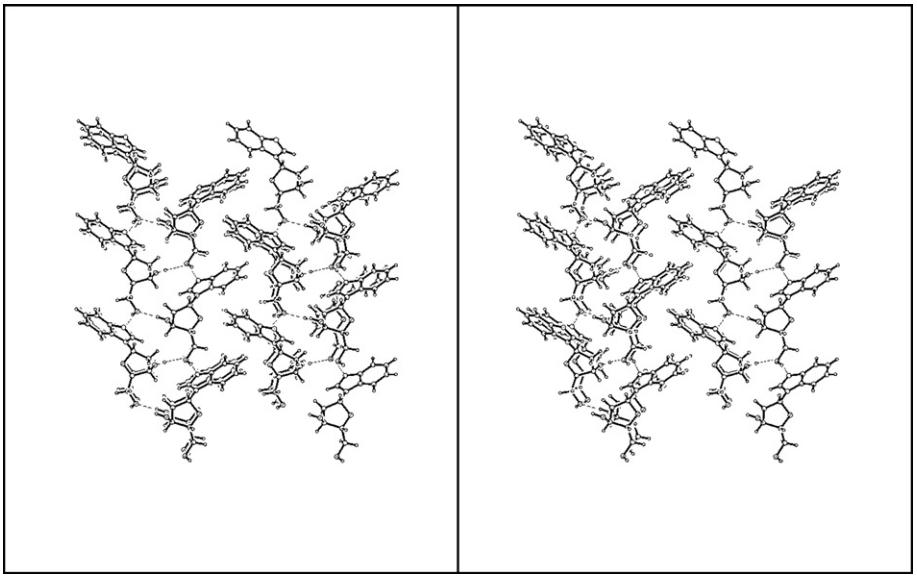

Figure 2. Stereo view along the crystallographic x-axis in the crystal structure of **1** showing the zigzag arrangement of the individual molecules. Dotted lines indicate hydrogen bonds.

The unit cell of compound **3** contains two crystallographically independent molecules I and II. Their sugar conformations are ^3E and E_4, respectively (both N-type). The latter conformation is rather unusual for 2′-deoxyribofuranose rings of β-D-nucleosides,[13] and it has not been reported previously for any purine-based β-D-deoxyribonucleoside.[14] Compound **3** also shows continuous π stacking of the aglycones along the crystallographic x-axis (~3.3 Å), with the formation of hydrogen-bonded dimers of molecules I and II via their O-5b and N-7a positions (Fig. 4). However, the dimer geometry in compound **3** is different from that in compound **2**. In the former, the deazapurine moieties are rotated about 25° around the crystallographic x-axis with respect to each other, compared to 75° in the latter. The aglycones are now arranged in a *head–tail* fashion, meaning that the endocyclic N-3 atoms of neighboring molecules are facing opposite directions. The dimers aggregate three-dimensionally via additional hydrogen bonds originating from their respective O-3b positions: Molecule I is involved in an O-3b–H···N-3a hydrogen bond to molecule II of a neighboring dimer, while molecule II is connected via O3b–H···O-5b to molecule I of another neighboring dimer. The geometrical details of these hydrogen bonds are summarized in Table S3.

Compound **4** was crystallized from two different solvents, giving rise to two different solvates, that is, **4**·CH_3OH and **4**·H_2O. The nucleosides display almost identical conformations in both solvates (Fig. 5), with the phase angle of pseudorotation P of the deoxyribose amounting to 167.5(6)° and 171.7(4)°, respectively (both S-type). In both cases, the aglycone is oriented *syn* with respect to the sugar, and the 5′-OH group is in a +*sc* conformation, pointing toward the purine ring (Table

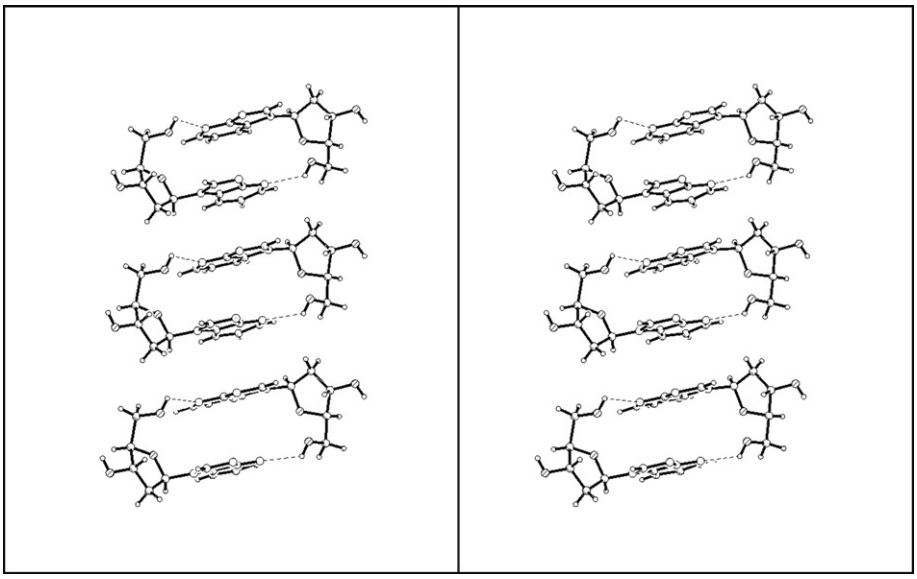

Figure 3. Stereo view of stacking dimers in the solid state structure of compound **2**. The dotted lines indicate hydrogen bonds.

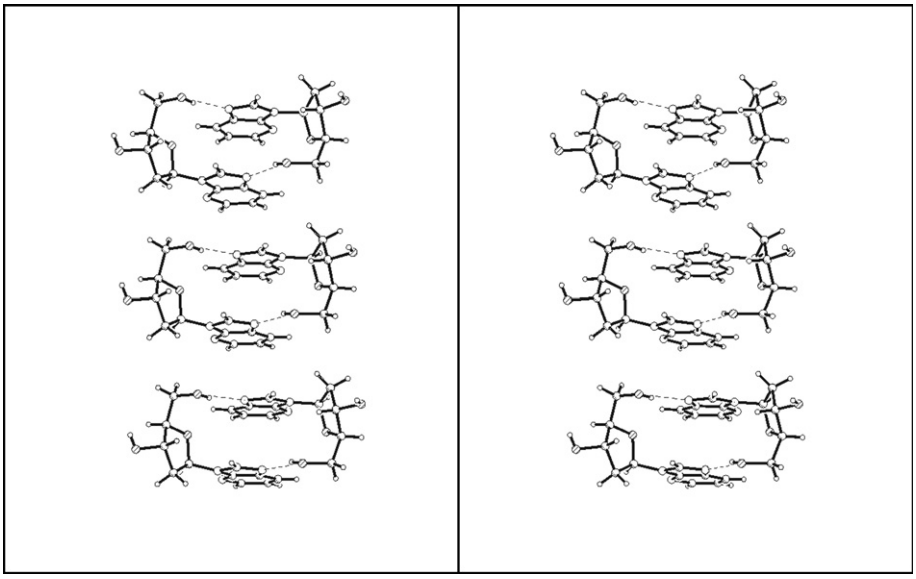

Figure 4. Stereo view of stacking dimers of the two crystallographically independent molecules I and II in the crystal structure of **3**. The dotted lines indicate hydrogen bonds.

1). This orientation is stabilized by an intramolecular hydrogen bond (O-5b–H···N-3a). Interestingly, this hydrogen bond is also observed for 1-deaza-2′-deoxy-β-D-adenosine (i.e., compound **4** without the protecting group) in solution but not in the solid state.[15] Each solvent molecule in **4** is bonded to one nucleoside via two hydrogen bonds, originating from N-6a (N-6a–H···O-1x with $x = $ m for **4**·CH_3OH and $x = $ w for **4**·H_2O) and from the oxygen atom of the solvent (O-1x–H···N-7a with $x = $ m for **4**·CH_3OH and $x = $ w for **4**·H_2O), respectively. Two neighboring nucleosides are connected by one additional hydrogen bond between the sugar entities (O-3b–H···O-5b, not shown in Fig. 5). Hence, the local geometries of the two solvates of compound **4** are very much alike (see Tables S4 and S5 for a summary of the hydrogen bond geometries). However, when compared with the methanol entity in **4**·CH_3OH, the water moiety in **4**·H_2O is able to engage in yet another hydrogen bond that comprises its second proton (O-1w–H···O-4b). This interaction appears to be responsible for the completely different packing patterns of **4**·CH_3OH and **4**·H_2O (Fig. 6). In both cases, continuous stacking creates an alteration of benzoylamino and deazapurine rings along the crystallographic x-axis. For **4**·CH_3OH, the imidazole part of a 1-deazapurine entity stacks with the phenyl ring of a neighbor-

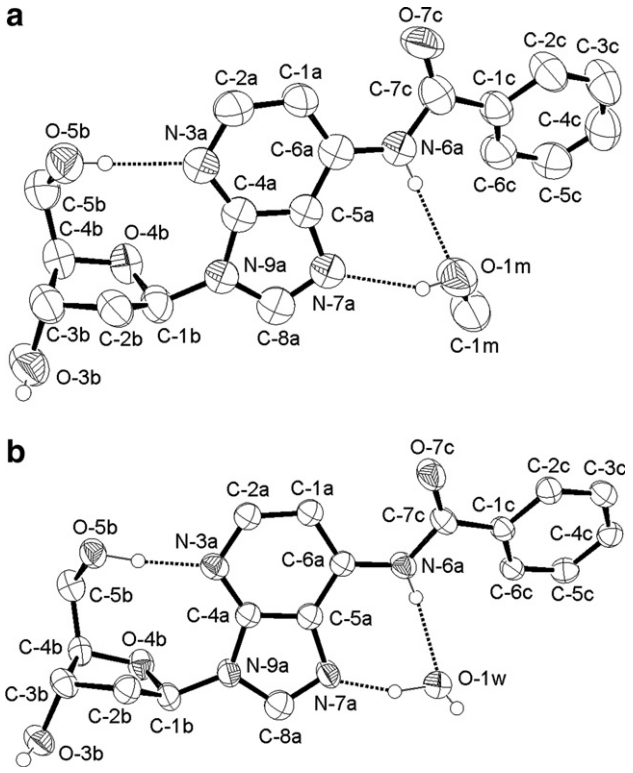

Figure 5. Molecular structures of (a) **4**·CH_3OH and (b) **4**·H_2O with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dotted lines represent hydrogen bonds. Only those hydrogen atoms that are involved in hydrogen bonding are shown.

ing molecule, leading to a complex interwoven three-dimensional structure (Fig. 6a). For **4**·H_2O, the continuously stacked columns comprise dimers formed of two formula units, with the pyridine part of one 1-deazapurine entity and the phenyl ring of the other nucleoside stacking on top of each other (Fig. 6b). This gives rise to a packing with alternating layers of nucleosides and water along the crystallographic *z*-axis that are interconnected by the above-mentioned hydrogen bonds O-3b–H···O-5b and O-1w–H···O-4b.

A total of five structures of 2′-deoxy-β-D-ribonucleosides of the deazapurines 1-deazapurine, 1,3-deazapurine, and 6-benzoylamino-1-deazapurine have been characterized by X-ray crystallography. All nucleosides have puckering amplitudes ψ_m in the range that is typically found for 2′-deoxy-β-D-ribonucleosides.[16] The glycosidic torsion angles χ show that the artificial nucleobases are in a *syn* orientation with respect to the sugar moiety, maybe except of structure **3** II, where a classification as *syn* or *anti* is difficult due to the value of $\chi = -90.1(4)°$. In the 1-deazapurine nucleosides **2** and **3**, the sugar adopts an N-type conformation, whereas in benzimidazole nucleoside **1** and the two solvates of 1-deaza-6-benzoylamino-2′-deoxynebularine **4**, an S-type conformation is found. A common feature in all structures except of **1** is the $+sc$ orientation of the 5′-OH group according to the backbone torsion angle γ. The observation of significantly different sugar puckers in spite of closely related aglycones shows that no simple correlation exists between sugar conformation and character of the nucleoside but that a complex interplay of different effects is at work.[17,18] The structures reported in this work will hopefully contribute to a better understanding of this interplay.

1. Experimental

The preparation and characterization of compounds **1**, **2**, and **3** were described recently.[5]

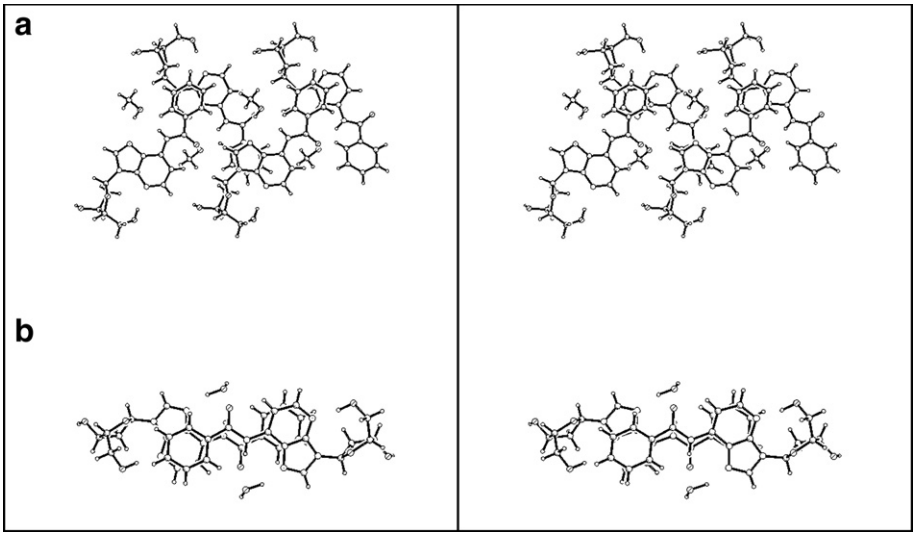

Figure 6. Stereo view of the π–π interactions observed in the crystal structures of (a) **4**·CH_3OH and (b) **4**·H_2O.

1.1. Preparations

1-Deaza-6-benzoylamino-2′-deoxynebularine **4** (=7-benzoylamino-3-(2′-deoxy-β-D-*erythro*-pentofuranosyl)-3*H*-imidazolo[4,5-*b*]pyridine) was synthesized according to a literature procedure.[19] Crystallization from MeOH gave solvate **4**·CH_3OH as colorless crystals. Subsequent crystallization of **4**·CH_3OH from water gave the corresponding hydrate **4**·H_2O. ^{1}H NMR (Me_2SO-d_6, 200 MHz): δ/ppm 10.42 (s, 1H, NH), 8.64 (s, 1H, H8), 8.32 (d, 1H, H2), 8.03 and 7.60 (m, 6H, H1 and Phe), 6.51 (dd, 1H, H1′), 5.34 (d, 1H, C3′-OH), 5.18 (t, 1H, C5′-OH), 4.45 (m, 1H, H3′), 3.91 (m, 1H, H4′), 3.59 (m, 2H, H5′ and H5″), 2.82 and 2.32 (m, 2H, H2′ and H2″); Anal. Calcd (%) for $C_{18}H_{18}N_4O_4$·H_2O: C, 58.1; H, 5.4; N, 15.0. Found: C, 57.8; H, 5.5; N, 14.9.

1.2. Instrumentation

Microanalyses were measured on a Leco CHNS 932 instrument.

1.3. X-ray crystallography

X-ray data collection for all compounds was carried out on an Enraf-Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).[20] Data reduction and cell refinement were performed by using the programs DENZO and SCALEPACK.[21] Reflections, which were partly measured on previous and following frames, were used to scale these frames to each other. Merging of redundant reflections in part eliminates absorption effects and also considers crystal decay if present. All structures were solved by direct methods[22] and refined by full-matrix least-squares methods based on F^2 by using the SHELXTL-PLUS[23] and SHELXL-97[24] programs. Table 2 summarizes the crystallographic data for all compounds. Table 1 lists structural parameters that define the conformations of the 2′-deoxy-β-D-ribonucleosides.

In all structures it was necessary to refrain from anisotropic refinement of some of the non-hydrogen atoms to save parameters and to attain a reflection-to-parameter ratio of at least 8:1, as required for non-centrosymmetric space groups and structures without heavy atoms. In all structures these isotropically refined atoms were exclusively part of the purine derivatives as they showed the smallest anisotropic displacement factors in trial refinements. An exception was made in compound **2**, where the refinement of the sugar moiety yielded large anisotropic displacement factors and therefore atoms C-2a, C-5b, O-5b, and O-3b were chosen to be refined isotropically only. Attempts to apply a disorder model were not successful and resulted in unreasonable interatomic distances and angles. In all compounds, hydrogen atoms were placed in geometrically calculated positions and

Table 2. Crystallographic data for compounds **1**, **2**, **3**, **4**·CH_3OH and **4**·H_2O

	1	**2**	**3**	**4**·CH_3OH	**4**·H_2O
Formula	$C_{12}H_{14}N_2O_3$	$C_{11}H_{13}N_3O_3$	$C_{11}H_{13}N_3O_3$	$C_{19}H_{22}N_4O_5$	$C_{18}H_{20}N_4O_5$
Formula weight	234.25	235.24	235.24	386.41	372.38
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1$ (No. 4)	$C222_1$ (No. 20)	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)
a (Å)	5.8146(5)	7.256(2)	7.164(1)	7.860(2)	6.9486(7)
b (Å)	7.893(1)	21.920(5)	14.921(3)	9.194(3)	9.027(1)
c (Å)	12.622(2)	13.741(4)	20.167(2)	13.385(3)	27.091(3)
α (°)	90	90	90	90	90
β (°)	94.019(8)	90	90	105.06(2)	90
γ (°)	90	90	90	90	90
V (Å^3)	577.9(1)	2186(1)	2155.7(6)	934.0(4)	1699.3(3)
Z	2	8	8	2	4
D_{calc} (g cm^{-3})	1.346	1.430	1.450	1.374	1.456
μ(Mo Kα) (mm^{-1})	0.098	0.106	0.108	0.101	0.108
F(000)	248	992	992	408	784
Crystal size (mm)	0.20 × 0.20 × 0.10	0.10 × 0.05 × 0.05	0.10 × 0.10 × 0.05	0.15 × 0.10 × 0.05	0.15 × 0.10 × 0.05
Temperature (K)	298(2)	298(2)	150(2)	298(2)	150(2)
Radiation (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
θ_{min}, θ_{max} (°)	3.1, 25.4	3.0, 25.4	3.0, 25.4	3.2, 25.4	3.0, 25.3
Dataset	0:7, 0:9, −15:15	0:8, 0:26, 0:16	0:8, 0:18, 0:24	0:9, 0:11, −16:15	0:8, 0:10, 0:32
Tot., uniq. data, R_{int}	4302, 1133, 0.021	12,172, 1141, 0.029	19,084, 2280, 0.057	10,519, 1797, 0.045	10,488, 1822, 0.035
Observed data [$I > 2\sigma(I)$]	873	404	949	670	868
N_{ref}, N_{par}	1133, 142	1141, 138	2280, 285	1797, 221	1822, 229
R, wR_2, S [$I > 2\sigma(I)$][a]	0.033, 0.071, 0.98	0.103, 0.271, 0.84	0.032, 0.050, 0.62	0.030, 0.045, 0.61	0.033, 0.046, 0.75
Max. and Av. shift/error	0.00 and 0.00	0.00 and 0.00	0.00 and 0.00	0.00 and 0.00	0.00 and 0.00
Min. and Max. resd. dens. (e Å^{-3})	0.19 and −0.10	0.75 and −0.27	0.17 and −0.19	0.13 and −0.15	0.19 and −0.16

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \left[\Sigma w\left(F_o^2 - F_c^2\right)^2/\Sigma w\left(F_o^2\right)^2\right]^{1/2}$.

refined either with a common isotropic displacement factor or with a value fixed at 1.2 or 1.3 times U_{eq} of the corresponding donor atom. Exceptions are the sugar OH groups O-3b and O-5b in compounds **1**, **3**, **4a**, and **4b**, where the coordinates of the hydrogen atoms were allowed to refine freely with a fixed U value, as well as the protons of the water molecule in **4b**, which were refined without any restraints.

Acknowledgments

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Supplementary data

The supplementary data contains tables with hydrogen bond geometries of all five structures. CCDC 650844–650848 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2007.11.007.

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