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α-D-2′-Deoxyadenosine, an irradiation product of canonical DNA and a component of anomeric nucleic acids: crystal structure, packing and Hirshfeld surface analysis

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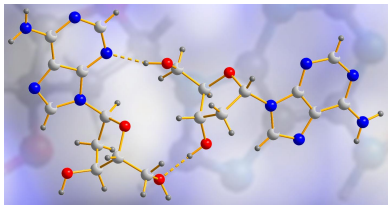
α-D-2′-Deoxyribonucleosides are products of the γ-irradiation of DNA under oxygen-free conditions and are constituents of anomeric DNA. They are not found as natural building blocks of canonical DNA. Reports on their conformational properties are limited. Herein, the single-crystal X-ray structure of α-D-2′-deoxyadenosine (α-dA), $C_{10}H_{13}N_5O_3$, and its conformational parameters were determined. In the crystalline state, α-dA forms two conformers in the asymmetric unit which are connected by hydrogen bonds. The sugar moiety of each conformer is arranged in a 'clamp'-like fashion with respect to the other conformer, forming hydrogen bonds to its nucleobase and sugar residue. For both conformers, a *syn* conformation of the nucleobase with respect to the sugar moiety was found. This is contrary to the *anti* conformation usually preferred by α-nucleosides. The sugar conformation of both conformers is C2′-*endo*, and the 5′-hydroxyl groups are in a *+sc* orientation, probably due to the hydrogen bonds formed by the conformers. The formation of the supramolecular assembly of α-dA is controlled by hydrogen bonding and stacking interactions, which was verified by a Hirshfeld and curvedness surface analysis. Chains of hydrogen-bonded nucleobases extend parallel to the *b* direction and are linked to equivalent chains by hydrogen bonds involving the sugar moieties to form a sheet. A comparison of the solid-state structures of the anomeric 2′-deoxyadenosines revealed significant differences of their conformational parameters.

1. Introduction

In canonical double-stranded DNA, all four canonical nucleosides display a β-D configuration; α-anomeric nucleosides are not found in native DNA. However, γ-irradiation of DNA under oxygen-free (anoxic) conditions can cause lesions that yield α-D nucleosides as single or multiple mutations (Amato & Wang, 2014). This is explained by the formation of C1′ radicals at the 2′-deoxyribose moiety formed during irradiation and the nonstereospecific recombination resulting in a mixture of anomers (β and α). Lesiak & Wheeler (1990) reported the formation of α-2′-deoxyadenosine (α-dA) (Fig. 1) as a major lesion product upon γ-irradiation of poly-dA–poly-dT duplexes and salmon testis DNA under a nitrogen atmosphere. These α-dA mutations can have a significant impact on DNA stability, which strongly depends on the nearest neighbours (Ide *et al.*, 1995; Johnson *et al.*, 2012). The NMR solution structure of a DNA duplex containing an α-dA modification revealed local helical changes at the modification site depending on the sequence context (Aramini *et al.*, 2004).



However, compared to other types of damage, this type of DNA damage perturbs the DNA helix only to a minor extent and, as a consequence, recognition by repair enzymes is very challenging (Johnson *et al.*, 2012). The enzymatic repair machinery for α-anomeric lesions is conserved in mammalian cells which shows the biological significance (Johnson *et al.*, 2012).

Our laboratory and others constructed oligonucleotides containing exclusively α-nucleosides (Morvan *et al.*, 1987*a*,*b*; Paoletti *et al.*, 1989; Chai *et al.*, 2020; Zhang *et al.*, 2022*a*). They were hybridized with complementary strands with all the nucleoside residues in a β-D conformation. These duplexes are as stable as those of canonical DNA with both strands in a β-D configuration. However, strands are in a parallel and not an antiparallel orientation as in natural DNA. Moreover, α-oligonucleotides were used as invader strands in DNA displacement reactions (Zhang *et al.*, 2022*b*) or implemented in the construction of α/β-heterochiral DNA duplexes containing silver-mediated base pairs (Chai *et al.*, 2020).

The chemical synthesis of nucleosides often produces α-D anomers as by-products during glycosylation. The outcome of the glycosylation reaction (α/β ratio) can be influenced by the structures of the starting materials and the experimental conditions. Various methods were established to synthesize α-D nucleosides by anomerization of β-D anomers or by stereoselective synthesis (Ni *et al.*, 2019). Thus, a number of α-D nucleosides were prepared, including those with a modified nucleobase or sugar moiety. Due to the difference in the configuration at C1′, monomeric α-D nucleosides show altered properties compared to their β-anomers (Ciuffreda *et al.*, 2007). According to the work of Sundaralingam (1971) and Latha & Yathindra (1992) on the solid-state conformations of α-nucleosides, the flexibility of the glycosylic bond, connecting the nucleobase and the sugar moiety, as well as the sugar conformation, seems to be more restricted compared to β-nucleosides. However, examples of α-nucleosides with properties outside the proposed favoured conformational range were reported recently (Seela *et al.*, 2002; Budow-Busse *et al.*, 2021).

A number of X-ray studies were performed to elucidate the solid-state structure of α-nucleosides, but to our surprise, from the four α-D-2′-deoxyribonucleosides with canonical nucleobases, only X-ray studies of the pyrimidine nucleosides α-2′-deoxythymidine (α-dT) (Görbitz *et al.*, 2005) and α-2′-deoxycytidine (α-dC) (Budow-Busse, *et al.*, 2021) have been reported. The crystal structure of the anomeric purine nucleoside α-2′-deoxyadenosine (α-dA, **1**) (Fig. 1) is still unknown. Only a preliminary X-ray analysis of a complex of human endonucleoase 1 (APE1) with an oligonucleotide containing α-dA, **1**, was published by Retailleau *et al.* (2010).

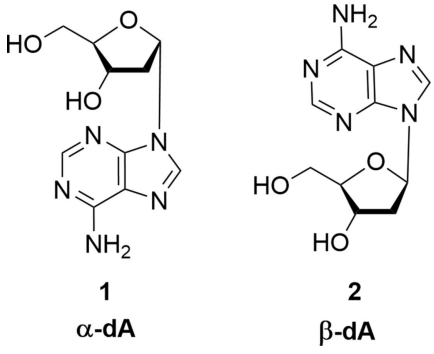


Figure 1
Structures of anomeric 2′-deoxyadenosines.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{13}N_5O_3$
M_r	251.25
Crystal system, space group	Triclinic, *P*1
Temperature (K)	100
a, *b*, *c* (Å)	5.2027 (2), 8.9738 (3), 12.3715 (4)
α, β, γ (°)	78.249 (1), 83.171 (1), 76.338 (1)
V (Å^3)	547.97 (3)
Z	2
Radiation type	Cu *Kα*
μ (mm^{-1})	0.98
Crystal size (mm)	0.19 × 0.08 × 0.05
Data collection	
Diffractometer	Bruker D8 Venture Photon III
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.84, 0.95
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17188, 3858, 3752
R_{int}	0.041
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.027, 0.065, 1.08
No. of reflections	3858
No. of parameters	357
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.17
Absolute structure	Flack *x* determined using 1744 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.01 (8)

Computer programs: *APEX4* (Bruker, 2021), *SAINT* (Bruker, 2019), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *DIAMOND* (Putz & Brandenburg, 2022).

To obtain more knowledge of crystal structures of α-D-2′-deoxyribonucleosides with a canonical nucleobase, we performed a single-crystal X-ray analysis of α-D-2′-deoxyadenosine (**1**). α-D-2′-Deoxyadenosine (**1**) had been synthesized previously by Ness and Fletcher in 1960 (Ness & Fletcher, 1960), and improved synthetic methods were reported by Robins (Robins & Robins, 1965) and Shinozuka (Shinozuka *et al.*, 1992).

The work described herein is the first study of the crystal structure of an α-anomeric canonical purine 2′-deoxyribonucleoside. The crystal structure of α-dA (**1**) revealed an unexpected *syn* conformation of the nucleobase. The solid-state conformational properties of **1** were studied in detail and compared to those of the corresponding β-D nucleoside (β-dA, **2**) (Fig. 1) (Sato, 1984). The interactions of the molecules within the crystalline network were analysed. Hirshfeld surface analyses were performed for both anomers (α-dA, **1**, and β-dA, **2**) to support the X-ray data.

Table 2
Selected geometric parameters of the anomeric 2′-deoxyadenosines α-**1a**, α-**1b** and β-dA (**2**).

	Conformer α-**1a**	Conformer α-**1b**	β-dA (**2**) (Sato, 1984)
Glycosylic bond length (N9—C1′) (Å)	1.473 (3)	1.474 (3)	1.474 (2)
Torsion angle χ (O4′—C1′—N9—C4) (°)	78.0 (3)	72.7 (3)	−165.0 (7)
Relative sugar/base orientation	*syn*	*syn*	*anti*
Pseudorotational phase angle *P* (°)	135.67	143.35	13.28
Maximum amplitude τ_m (°)	30.51	31.68	36.34
Sugar pucker	*S*-type, C2′-*endo*, $_1T^2$	*S*-type, C2′-*endo*, $_1T^2$	*N*-type, C3′-*endo*, $^3T_2$
Torsion angle γ (O5′—C5′—C4′—C3′) (°)	50.2 (3)	46.8 (3)	175.5 (1)
Relative orientation of exocyclic 5′-OH	+synclinal (*gauche*)	+synclinal (*gauche*)	+antiperiplanar (*trans*)

2. Experimental

2.1. Synthesis and crystallization of α-2′-deoxyadenosine (1)

α-2′-Deoxyadenosine (**1**) was synthesized following the glycosylation protocol reported by Ness (1968). *N*-Benzoyladenine and Hoffer's chlorosugar (Hoffer, 1960) were used as starting materials and, in our hands, a 1:1 anomeric mixture of the protected α-dA and β-dA was obtained. Deprotection in 0.2 *M* NaOMe (room temperature, overnight) afforded α-dA (**1**).

For crystallization, compound **1** was dissolved in methanol and was obtained as colourless plates by slow evaporation of the solvent (room temperature, 8 d). A plate-like specimen of **1** was used for the X-ray crystallographic analysis.

2.2. X-ray diffraction and refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All carbon-bound H atoms were placed in idealized positions and refined using a riding model, with C—H = 0.95 Å for aromatic CH groups, 0.99 Å for secondary CH_2 groups and 1.00 Å for tertiary CH groups, using $U_{iso}(H) = 1.2U_{eq}(C)$. The positions of the H atoms at N6*A*, N6*B*, O3′*A*, O3′*B*, O5′*A* and O5′*B* were located in a difference map and were refined freely.

3. Results and discussion

3.1. Molecular geometry and conformation of α-2′-deoxyadenosine (1)

The crystals of α-2′-deoxyadenosine (**1**) are triclinic with the space group *P*1 (Table 1). There are two molecules in the asymmetric unit, denoted as conformer α-**1a** and conformer α-**1b**, which are connected *via* hydrogen bonds. The three-dimensional (3D) structures of α-**1a** and α-**1b** are shown in Fig. 2 and indicate an α-orientation of the nucleobases. The anomeric centre at C1′ shows an *S*-configuration, confirming the α-D anomeric structure of **1** which, in addition, is supported by the Flack parameter. Throughout the article, purine numbering is used instead of systematic numbering for the molecules. Selected geometric parameters are summarized in Table 2.

The crystal structure of β-2′-deoxyadenosine monohydrate was reported in 1965 by Watson and co-workers (Watson *et al.*, 1965), while the crystal structure of anhydrous β-dA (**2**) was published 20 years later (Sato, 1984). The geometric parameters of β-dA (**2**) (Table 2) (Sato, 1984) were used as a comparison for the two conformers of α-dA (**1**) (α-**1a** and α-**1b**). For the remodelled 3D structure of β-dA (**2**), see Fig. S1 in the supporting information. Remodelling was carried out using the original structure data (CIF file) of **2** (Sato, 1984) downloaded from the Cambridge Structural Database (CCDC deposition code 1124124; Groom *et al.*, 2016).

The shape of nucleosides is characterized by four conformational parameters (Saenger, 1984): (i) the glycosylic torsion angle, (ii) the puckering of the furanose ring, (iii) the degree of deviation from planarity of the furanose ring and (iv) the orientation of the 5′-hydroxyl group. The geometric parameters (i)–(iv) of conformers α-**1a** and α-**1b** are discussed in the following.

(i) The positioning of the nucleobase with respect to the sugar moiety (*syn*/*anti*) is defined by the torsion angle χ (O4′—C1′—N9—C4) (IUPAC–IUB Joint Commission on Biochemical Nomenclature, 1983). In the *anti* conformation (180 to ±90°) of purine nucleosides, the six-membered pyrimidine ring is pointing away from the sugar moiety, and there is no particular hindrance of the nucleobase and the sugar residue. On the contrary, in the *syn* conformation (0 to ±90°), the pyrimidine ring is located above the sugar ring, giving rise to close interatomic contacts. A C2′-*endo* conformation of the sugar ring reduces the intramolecular strain, wherein the nucleobase and the C5′ atom are in an equatorial orientation and at a maximum distance (Saenger, 1984). Purine β-nucleosides are rather flexible and adopt *anti*, high-*anti* and even *syn* conformations, whereas α-nucleosides seem to prefer a rather narrow range of *anti* conformations (Sundaralingam, 1971; Latha & Yathindra, 1992). Therefore, we were very surprised to find χ torsion angles of 78.0 (3) and 72.7 (3)° for α-**1a** and α-**1b**, respectively, which are in the range of the *syn* conformation. To the best of our knowledge, this is the first report on α-nucleosides with the nucleobase in a *syn* conformation.

(ii) The five-membered 2′-deoxyribofuranosyl moiety is nonplanar, with one or two atoms twisted out of plane, referred to as sugar puckering and defined by the phase angle of pseudorotation *P* (Altona & Sundaralingam, 1972). In general, nucleosides prefer either of the two principal sugar puckering modes, named C3′-*endo* (*N*) or C2′-*endo* (*S*) (Fig. 3). They correspond to the major displacement of C3′ or C2′ from the median C1′/O4′/C4′ plane and place the more electronegative substituents of C2′ and C3′ in a preferred axial orientation (Saenger, 1984). β-2′-Deoxyribonucleosides

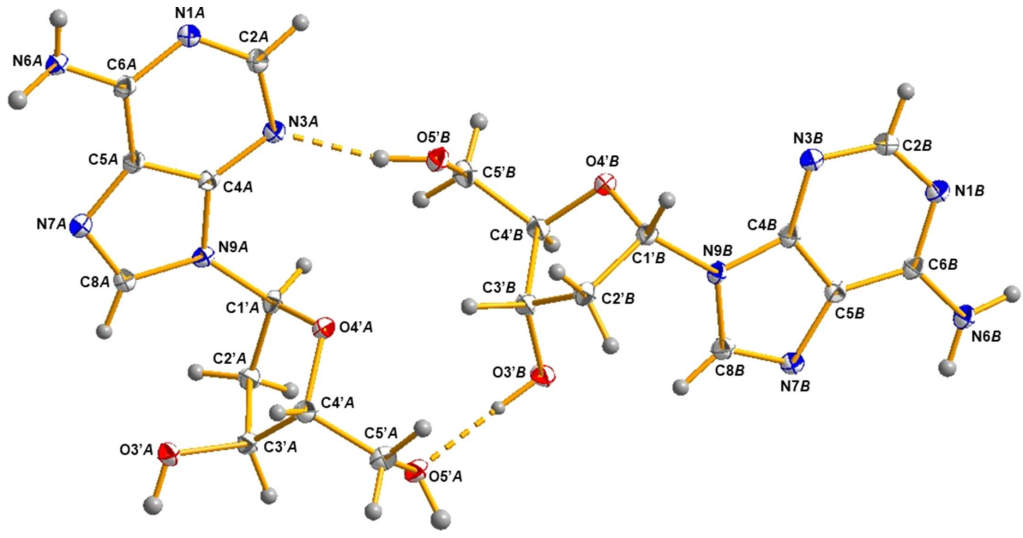


Figure 2
Perspective view and atomic numbering scheme of the two conformers of α-dA (α-**1a** and α-**1b**), being connected to each other by two hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary size.

favour C2′-*endo* conformations, while α-nucleosides show a preference for C2′-*exo*, C3′-*exo* and C4′-*endo* conformations (Sundaralingam, 1971; Latha & Yathindra, 1992). However, in the cases of α-**1a** and α-**1b**, phase angles of pseudorotation of P = 135.7° for α-**1a** and P = 143.4° for α-**1b** were found. They correspond to C2′-*endo* conformations (Table 2) and lie clearly outside the preferred conformational range. This is in line with studies on α-2′-deoxycytosine (Budow-Busse *et al.*, 2021), α-5-acetyl-2′-deoxyuridine (Hamor *et al.*, 1977) and α-5-aza-7-deaza-2′-deoxyguanosine (Seela *et al.*, 2002), also reporting C2′-*endo* conformations.

(iii) The second parameter used to characterize the geometry of the furanose ring is the maximum out-of-plane puckering amplitude τ_m. The puckering amplitude τ_m indicates the degree of deviation from planarity of the furanose ring and generally shows an average value of 39° for β-nucleosides, ranging from about 35 to 45° (Altona & Sundaralingam, 1972). The particular environment of the sugar moiety, *e.g.* hydrogen-bonding and stacking interactions, has an effect on the degree of sugar puckering (small or large τ_m) and, as a result, the puckering amplitude τ_m and the phase angle of pseudorotation P are independent parameters. For α-nucleosides, the range of τ_m is significantly broadened (28–50°), though the average τ_m value remains around 39°. The two conformers α-**1a** and α-**1b** support this finding and adopt τ_m values of 30.5 and 31.7°, respectively. These values correspond to a flattening of the 2′-deoxyribose moiety, probably a consequence of hydrogen-bonding and stacking interactions (see next section).

(iv) The conformation around the exocyclic C4′—C5′ bond relative to the sugar ring is determined by the torsion angle γ (O5′—C5′—C4′—C3′) (Saenger, 1984). The distribution of conformers around the C4′—C5′ bond depends on the nature of the nucleobase and the sugar pucker. However, the difference between the conformational preference about the C4′—C5′ bond of β- and α-nucleosides (Sundaralingam, 1971) seems to be neglectable. For conformers α-**1a** and α-**1b**, γ torsion angles of 50.2 (3) and 46.8 (3)° are found (Table 2), corresponding to a +synclinal (+*sc*) conformation. In β-nucleosides, a +synclinal conformation around the exocyclic C4′—C5′ bond, in combination with a *syn* orientation of the nucleobase, positions the nucleobase and atom O5′ above the ribosyl moiety (Saenger, 1984). For these β-nucleosides, interactions between atom O5′ and the nucleobase might pull the torsion angles γ in the +*sc* range. On the contrary, due to the α-anomeric orientation of the nucleobase, this combina-

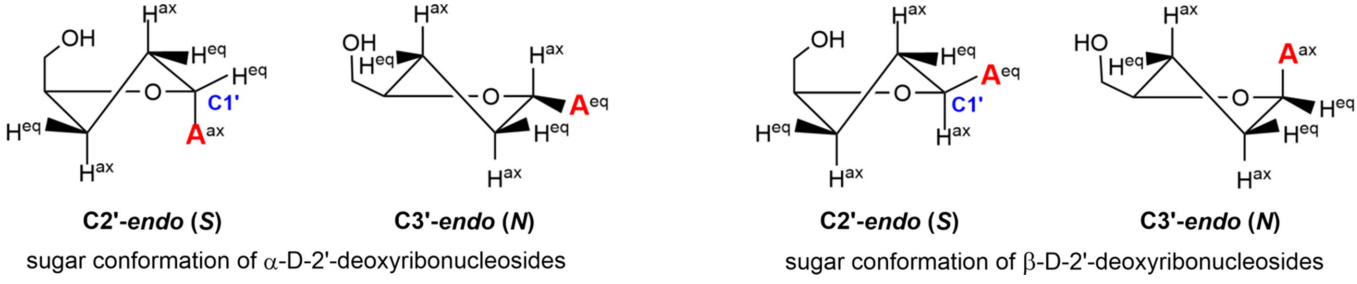


Figure 3
N and *S* conformations of α-D and β-D-2′-deoxyribonucleosides in solution. '**A**' corresponds to adenine, 'ax 'is axial and 'eq' is equatorial.

tion (+*sc* and *syn*) leads to an arrangement in α-nucleoside **1** in which atom O5′ is located 'above' the sugar residue, while the nucleobase is positioned on the other ('below') side of the sugar moiety. As can be clearly seen from Fig. 2, possible interactions between the 5′-hydroxyl group and the nucleobase as in β-nucleosides can be ruled out. Instead, the hydrogen bonds formed between conformers α-**1a** and α-**1b** might account for the +*sc* orientation of the 5′-hydroxyl groups.

Taken together, both conformers (α-**1a** and α-**1b**) show a high correlation in their overall structural shape (see geometric parameters given in Table 2). Moreover, it is surprising that although the α-anomeric conformers α-**1a** and α-**1b**, and the canonical β-dA (**2**) differ only in their configuration (α *versus* β), significant differences of the solid-state structures are apparent from their conformational parameters (Table 2) (for a perspective view of **2**, see Fig. S1 in the supporting information). This is particularly true for the torsion angle χ, the pseudorotational phase angle *P*, the maximum amplitude τ_m and the torsion angle γ.

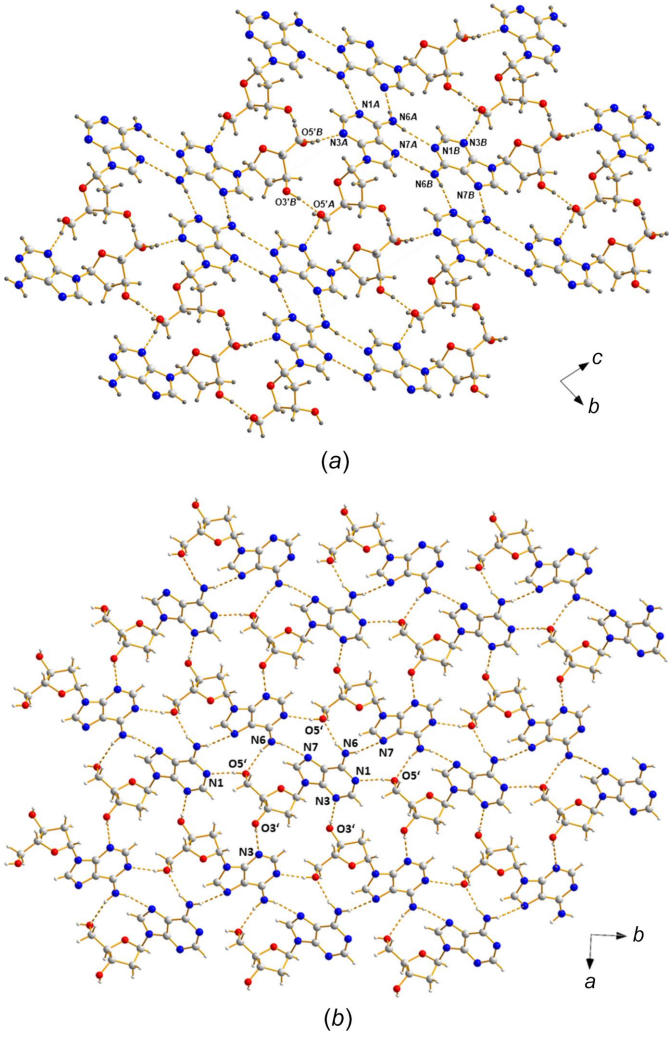


Figure 4
Detailed view of the hydrogen-bonding schemes (dashed lines) of (*a*) α-dA (**1**) (viewed in the *bc* plane) and (*b*) β-dA (**2**) (viewed in the *ab* plane).

Table 3
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6*B*—H01*B*···N1*A*^{i}	0.89 (4)	2.36 (4)	3.239 (3)	170 (1)
N6*B*—H02*B*···N7*A*^{ii}	0.86 (4)	2.14 (4)	2.998 (3)	173 (1)
O5′*B*—H5′*B*···N3*A*	0.90 (4)	1.91 (4)	2.787 (3)	163 (1)
O3′*B*—H3′*B*···O5′*A*	0.90 (4)	1.78 (4)	2.680 (3)	171 (1)
N6*A*—H01*A*···N1*B*^{iii}	0.92 (3)	2.33 (3)	3.243 (3)	172 (1)
N6*A*—H02*A*···N7*B*^{iv}	0.94 (4)	2.12 (4)	3.056 (3)	178 (1)
O5′*A*—H5′*A*···N3*B*^{v}	0.95 (5)	1.85 (5)	2.758 (3)	159 (1)
O3′*A*—H3′*A*···O5′*B*^{v}	0.92 (4)	1.80 (4)	2.691 (2)	163 (1)

Symmetry codes: (i) $x-2, y, z+1$; (ii) $x-2, y-1, z+1$; (iii) $x+2, y+1, z-1$; (iv) $x+2, y, z-1$; (v) $x, y+1, z$.

3.2. Crystal packing and hydrogen bonding

The asymmetric unit of α-2′-deoxyadenosine (**1**) contains two molecules (α-**1a** and α-**1b**) which show different conformational properties. Both molecules are connected *via* hydrogen bonds in an unsymmetrical fashion. From the representation of the extended crystalline network shown in Fig. 4(*a*), it is evident that the sugar moiety of each conformer is arranged in such a way that this moiety functions as a 'clamp' with respect to the other conformer, forming hydrogen bonds to its nucleobase and sugar residue. In detail, the exocyclic 5′-hydroxyl group forms a hydrogen bond to atom N3 of the nucleobase (O5′*B*—H5′*B*···N3*A* and O5′*A*—H5′*A*···N3*B*^{v}; for symmetry codes, see Table 3). The sugar-to-sugar contact is observed between the O3′-hydroxyl group as hydrogen donor and O5′ as hydrogen acceptor (O3′*A*—H3′*A*···O5′*B*^{v} and O3′*B*—H3′*B*···O5′*A*). In addition, bifurcated hydrogen bonds are formed by the amino groups, connecting two neighbouring molecules *via* N1 (N6*A*—H01*A*···N1*B*^{iii} and N6*B*—H01*B*···N1*A*^{i}) and N7 (N6*A*—H02*B*···N7*B*^{iv} and N6*B*—H02*B*···N7*A*^{ii}) of the nucleobase. Despite the fact that conformational differences exist for conformers α-**1a** and α-**1b**, both molecules form hydrogen bonds with an identical donor–acceptor pattern.

As it was of interest to figure out the differences between the anomers of 2′-deoxyadenosine in the solid state, images of the crystalline network of β-2′-deoxyadenosine (**2**) were generated, using the original CIF file of Sato (1984). As indicated by Fig. 4(*b*), the arrangement of the individual molecules of β-dA (**2**) is completely different compared to that of the α-anomer (**1**), resulting in another hydrogen-bonding scheme. In β-dA (**2**), the amino group is in a 'clamp'-like position with respect to the neighbouring molecule, forming a bifurcated hydrogen bond to N7 of the nucleobase and O5′ of the sugar moiety as acceptors. Nucleobase-to-sugar contacts use N1 and N3 as hydrogen acceptors and the exocyclic O3′- and O5′-hydroxyl groups as hydrogen donors. Contrary to the crystal structure of α-dA (**1**), sugar-to-sugar contacts do not exist in β-dA (**2**).

Another typical feature of the crystal structures of nucleosides are stacking interactions. Due to the aromatic nature of the heterocyclic nucleobase, this moiety is prone to form stacking interactions. Fig. 5 shows that also in the case of α-2′-deoxyadenosine (**1**) the nucleobases of the two conformers (α-**1a** and α-**1b**) are stacked. Always one type of

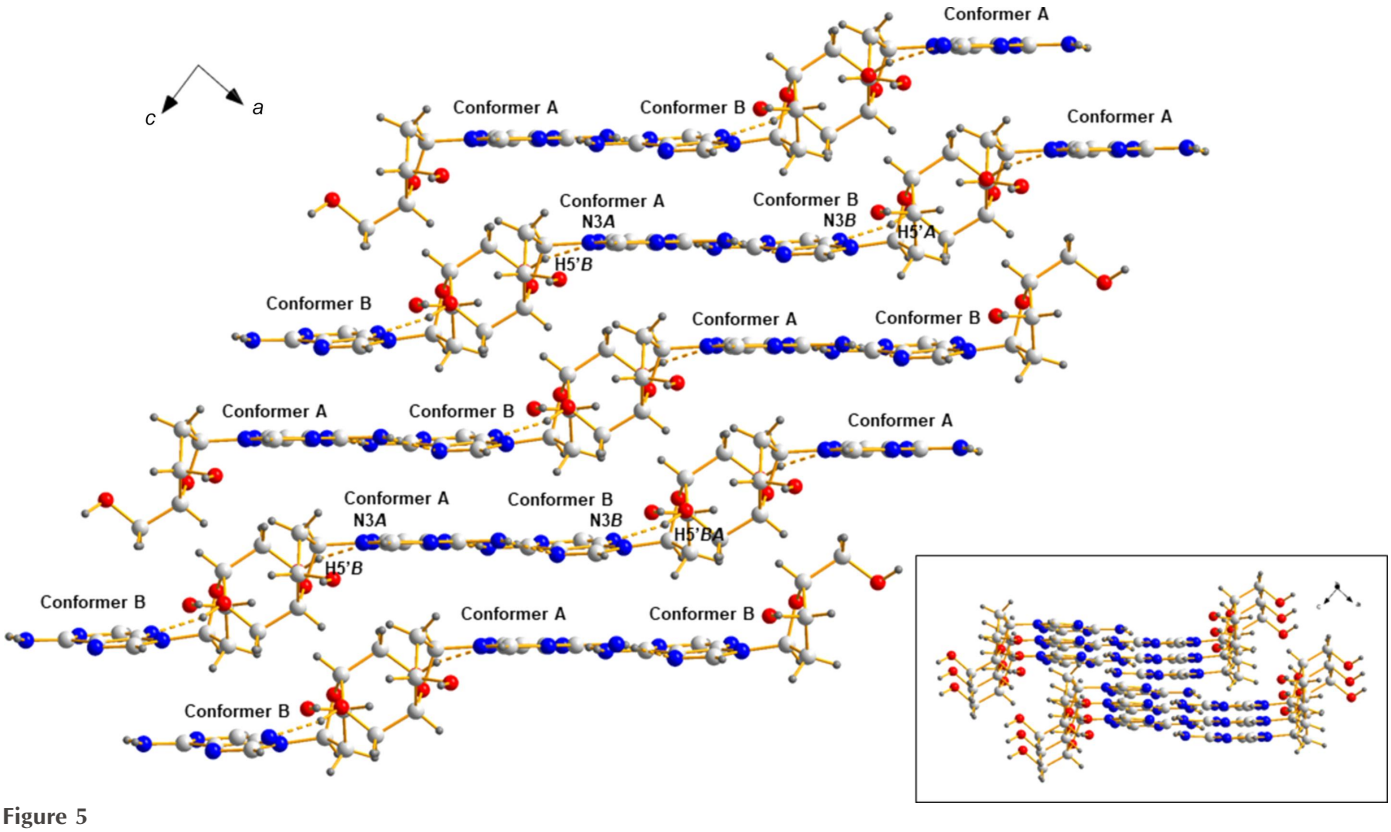


Figure 5
Staircase-like arrangement of conformers α-**1a** and α-**1b** within the extended crystalline network (viewed in the *ca* plane). Inset: stacking interactions of the conformers.

conformer forms piles of stacked molecules (see inset of Fig. 5). Moreover, the nucleobases of α-**1a** and α-**1b** are facing each other, forming a rather flat entity. Accordingly, the sugar moieties of α-**1a** and α-**1b** are also sited opposite each other. The pattern of alternating conformers is continued and the above and below pairs of neighbouring nucleobases are identically positioned (non-alternating), but shifted in such a way that the nucleobases of identical conformers form a staircase-like arrangement. As a result, the two conformers (α-**1a** and α-**1b**) form a highly-ordered packing arrangement.

In the earlier crystal study on β-dA (**2**) of Sato (1984), no relevant stacking interactions were reported. We inspected thoroughly the crystal data of **2** and performed a Hirshfeld surface analysis (for details, see the next section) and found large flat areas in the curvedness plots of **2** which indicate stacking interactions. Indeed, remodelling of the extended crystalline network of β-dA (**2**) proves the occurrence of stacking interactions of the aromatic nucleobases (see Figs. S3 and S4 in the supporting information).

3.3. Hirshfeld surface analyses of α-2′-deoxyadenosine (1) and β-2′-deoxyadenosine (2)

To obtain additional information on the role of crystal packing forces and to visualize the relative strengths of the intermolecular interactions, a Hirshfeld surface analysis of α-2′-deoxyadenosine (**1**) was carried out. For this purpose, the program *CrystalExplorer* (Version 17; Spackman & Jayatilaka, 2009; Turner *et al.*, 2017) was used. The Hirshfeld surfaces of the two conformers of α-dA (**1**) mapped over a d_{norm} range of −0.5 to 1.5 Å are represented, together with close-contact molecules of the central molecules inside the Hirshfeld surface [Fig. 6(*a*) and Fig. S5 in the supporting information]. Therein, the red surface areas denote strong interactions with distances shorter than the sum of the van der Waals radii and negative d_{norm}, white surface areas represent contacts with distances equal to the sum of the van der Waals radii and blue surfaces refer to weak contacts. Surfaces of the two conformers of **1** plotted over curvedness are shown in Figs. 6(*b*) and S7 (see supporting information). For shape-index plots, see Fig. S6 in the supporting information.

Inspection of the Hirshfeld surface of conformers α-**1a** and α-**1b** reveals a large unperturbed area [Fig. 6(*a*)], with the major red spots located on the top view area. These spots correspond to the short-range hydrogen bonds connecting the sugar moiety of one conformer to the nucleobase and sugar residue of the other conformer, as described in the previous section. Additional and less intense spots indicate the presence of weaker contacts formed by the amino groups. As a result, the Hirshfeld analyses are consistent with the hydrogen-bonding data (Table 3). Moreover, the curvedness plot of **1** [Fig. 6(*b*)] shows large flat areas due to the presence of the aromatic nucleobase and confirms the contribution of stacking interactions to the overall crystal packing.

Two-dimensional (2D) fingerprint plots (Fig. 7 and Fig. S11 in the supporting information) provide a visual summary of

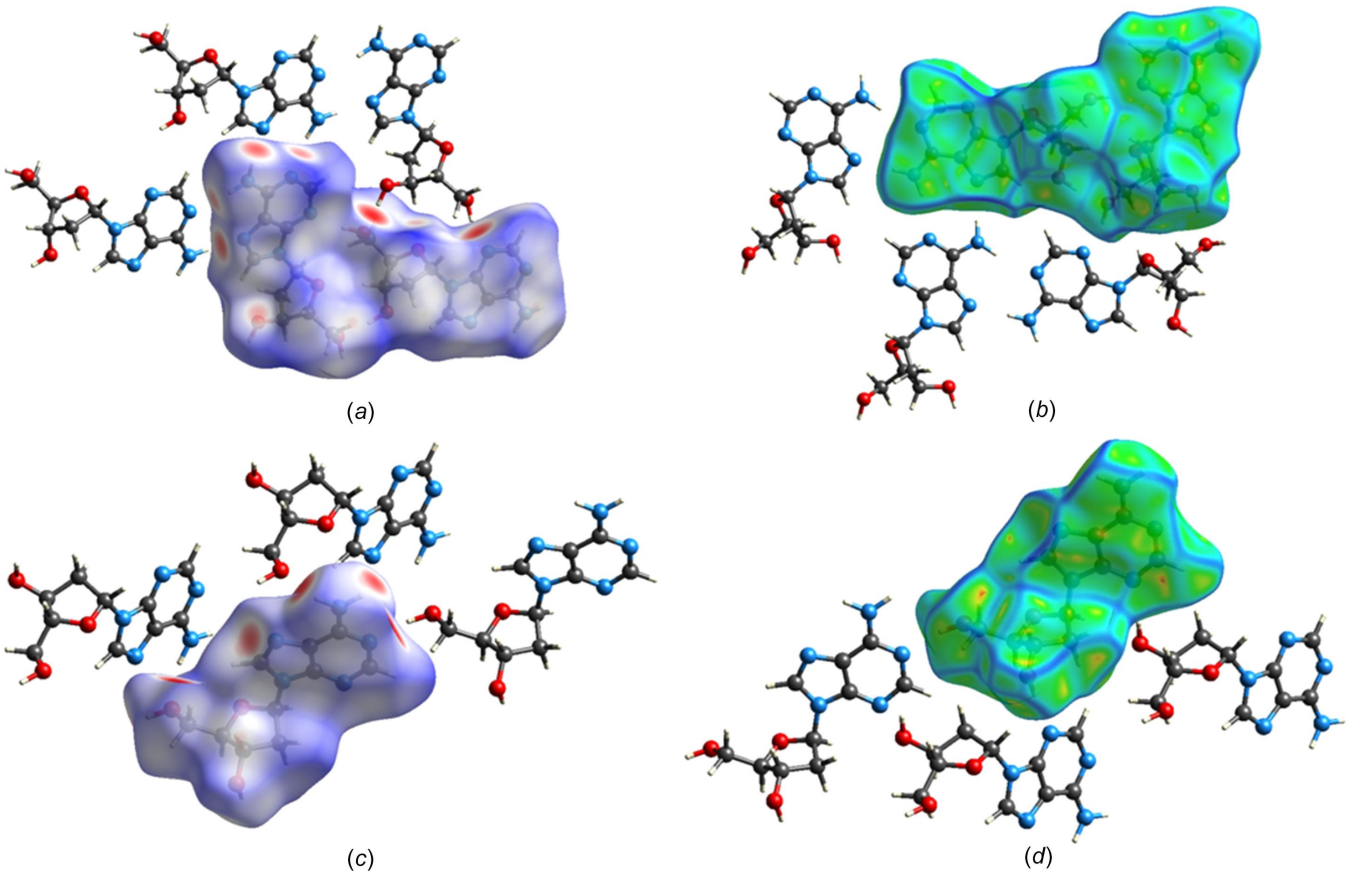


Figure 6
The Hirshfeld surfaces of α-dA (**1**) (upper part) and β-dA (**2**) (lower part) with close-contact molecules, (*a*)/(*c*) mapped over d_{norm} (−0.5 to 1.5 Å) and (*b*)/(*d*) mapped over the curvedness (−4.0 to 4.0 Å). Green areas represent flat regions and blue lines indicate edges.

the contribution of each contact type and their relative proportion to the Hirshfeld surface. The plots are resolved into N···H/H···N, O···H/H···O, C···H/H···C and H···H contacts [Figs. 7(*b*)–(*e*)]. The N···H/H···N (25.2%) and O···H/H···O (13.3%) contacts provide a significant contribution to the surface and form the two characteristic spikes. They represent the strong hydrogen bonds interconnecting conformers α-**1a** and α-**1b**. The wings of the plot are occupied by C···H/H···C interactions (13.6%), which include numerous weak hydrogen bonds. The nonspecific van der Waals H···H contacts (41.8%) occupy the major portion of the surface.

Due to the early publication date of the crystal structure of β-2′-deoxyadenosine (**2**) (Sato, 1984), to the best of our knowledge, a Hirshfeld surface analysis has not yet been performed for β-dA (**2**). Therefore, we also carried out a Hirshfeld surface analysis of **2** [Fig. 6(*c*) and Fig. S8 in the supporting information] using the crystal structure data (CCDC deposition number 1124124; Sato, 1984). For shape index and curvedness plots of **2**, see Fig. 6(*d*) and Figs. S9 and S10 in the supporting information. The Hirshfeld surface analysis of β-dA mapped over d_{norm} and curvedness supports the hydrogen-bonding (Sato, 1984) and stacking interactions of **2**. The calculated 2D fingerprint plots for **2** are shown in

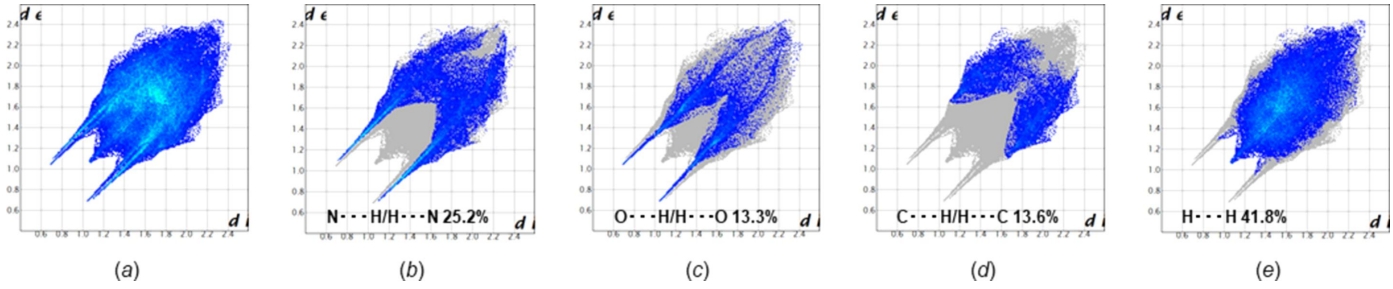


Figure 7
2D fingerprint plots showing the percentage contributions of the various interactions to the total Hirshfeld surface area of α-dA (**1**), showing (*a*) all interactions and resolved contacts of (*b*) N···H/H···N, (*c*) O···H/H···O, (*d*) C···H/H···C and (*e*) H···H.

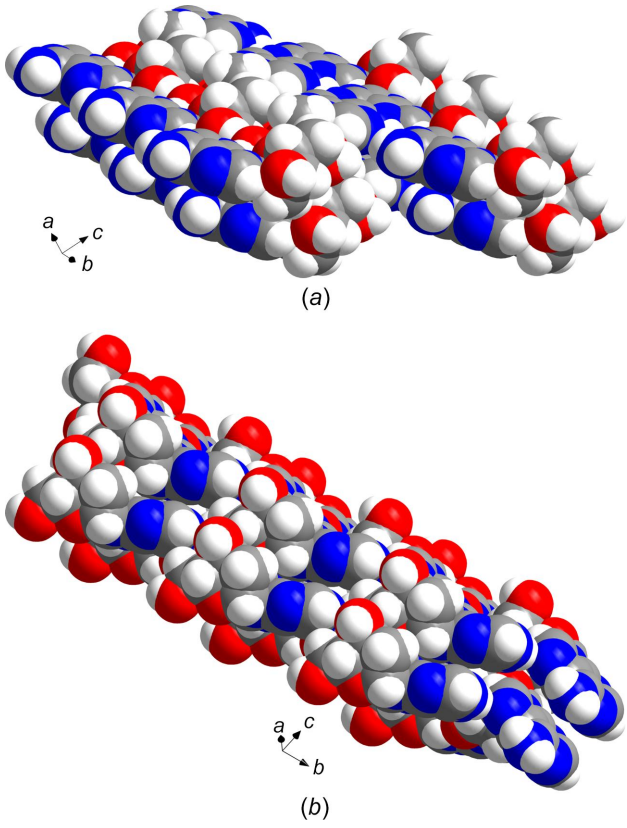


Figure 8
Space-filling models of (*a*) α-dA (**1**) and (*b*) β-dA (**2**).

Fig. S11 in the supporting information and confirm the significant contribution of the N···H/H···N (22.2%) and O···H/H···O (18.7%) contacts to the overall crystal packing forces.

4. Conclusion

The present work is the first report on a single-crystal X-ray analysis of an α-D-2′-deoxyribonucleoside carrying a canonical purine nucleobase. In the crystalline state, α-dA forms two conformers (α-**1a** and α-**1b**) in the asymmetric unit which are connected *via* hydrogen bonds. In contrast to the *anti* conformation commonly preferred by α-nucleosides, the nucleobase moiety of α-**1a** and α-**1b** adopts a *syn* conformation. For both conformers, the sugar conformation is C2′-*endo* and the 5′-hydroxyl group is in a +*sc* orientation.

Comparison of the solid-state structure of α-dA to canonical β-2′-deoxyadenosine (**2**) (Sato, 1984) revealed significant differences in the conformational parameters and in the packing of their supramolecular networks (see space-filling models in Fig. 8). In the supramolecular network of α-dA (**1**), the sugar moieties of each conformer act as clamps by forming hydrogen bonds to the nucleobases and sugar residues of the other conformer. The nucleobases form hydrogen-bonded chains which are linked to equivalent chains by hydrogen bonds involving the sugar moieties to form sheets. The nucleobases and the sugar moieties of alternating α-**1a** and α-**1b** conformers are organized face-to-face with respect to each other. A staircase-like arrangement is formed by the nucleobases of each conformer. In addition, piles of stacked molecules are formed by always one type of conformer. The hydrogen-bonding pattern is supported by a Hirshfeld surface analysis, and curvedness surfaces confirm the contribution of stacking interactions to the overall crystal packing.

α-D-2′-Deoxyadenosine (**1**) is not found in native DNA, but it is formed as a major lesion product upon γ-irradiation of DNA under anoxic conditions. Furthermore, it is a component of anomeric DNA formed by one strand in an α-D and the other in a β-D configuration. The latter is as stable as canonical DNA and shows similar base recognition. One of the recent developments in the realm of anomeric DNA is the construction of entirely new nucleic acid structures and the design of new recognition systems to expand the genetic code.

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supporting information

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α-D-2′-Deoxyadenosine, an irradiation product of canonical DNA and a component of anomeric nucleic acids: crystal structure, packing and Hirshfeld surface analysis

Peter Leonard, Aigui Zhang, Simone Budow-Busse, Constantin Daniliuc and Frank Seela

Computing details

α-D-2′-Deoxyadenosine

Crystal data

$C_{10}H_{13}N_5O_3$
$M_r = 251.25$
Triclinic, $P1$
$a = 5.2027$ (2) Å
$b = 8.9738$ (3) Å
$c = 12.3715$ (4) Å
$\alpha = 78.249$ (1)°
$\beta = 83.171$ (1)°
$\gamma = 76.338$ (1)°
$V = 547.97$ (3) Å^3
$Z = 2$
$F(000) = 264$
$D_x = 1.523$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 9907 reflections
$\theta = 3.7$–$68.5°$
$\mu = 0.98$ mm^{-1}
$T = 100$ K
Plate, colourless
0.19 × 0.08 × 0.05 mm

Data collection

Single crystal diffractometer
Radiation source: CuKα, micro focus tube
MX mirror monochromator
Detector resolution: 7.3910 pixels mm^{-1}
phi/ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.84$, $T_{max} = 0.95$
17188 measured reflections
3858 independent reflections
3752 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 68.3°$, $\theta_{min} = 3.7°$
$h = -6 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.065$
$S = 1.08$
3858 reflections
357 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.1416P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Absolute structure: Flack *x* determined using 1744 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.01 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement.
_reflns_Friedel_fraction is defined as the number of unique Friedel pairs measured divided by the number that would be possible theoretically, ignoring centric projections and systematic absences.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1B	−0.2612 (4)	−0.0771 (2)	0.91430 (16)	0.0156 (4)
N3B	0.1000 (4)	−0.0209 (2)	0.78214 (16)	0.0153 (4)
N9B	0.1791 (4)	0.2381 (2)	0.77689 (17)	0.0148 (4)
N7B	−0.1333 (4)	0.3158 (2)	0.90854 (16)	0.0159 (4)
N6B	−0.5149 (4)	0.1031 (3)	1.01668 (18)	0.0173 (5)
H01B	−0.565 (7)	0.201 (5)	1.028 (3)	0.033 (9)*
H02B	−0.614 (8)	0.036 (5)	1.038 (3)	0.040 (10)*
O4′B	0.2679 (4)	0.2614 (2)	0.58235 (14)	0.0180 (4)
O5′B	0.6105 (3)	0.3959 (2)	0.39970 (15)	0.0194 (4)
H5′B	0.666 (8)	0.455 (5)	0.337 (4)	0.049 (11)*
O3′B	0.1877 (3)	0.6054 (2)	0.65699 (15)	0.0206 (4)
H3′B	0.229 (6)	0.700 (4)	0.640 (3)	0.026 (8)*
C2B	−0.0621 (5)	−0.1102 (3)	0.8379 (2)	0.0168 (5)
H2B	−0.031478	−0.211828	0.820936	0.020000*
C4B	0.0495 (5)	0.1181 (3)	0.81508 (19)	0.0134 (5)
C5B	−0.1428 (5)	0.1674 (3)	0.89507 (19)	0.0142 (5)
C6B	−0.3109 (5)	0.0658 (3)	0.94379 (19)	0.0145 (5)
C8B	0.0599 (5)	0.3528 (3)	0.8369 (2)	0.0154 (5)
H8B	0.112205	0.449471	0.827461	0.018000*
C2′B	0.5353 (5)	0.3676 (3)	0.6706 (2)	0.0164 (5)
H200	0.716982	0.335757	0.636456	0.020000*
H201	0.546691	0.395337	0.743077	0.020000*
C3′B	0.3725 (5)	0.5039 (3)	0.5950 (2)	0.0166 (5)
H300	0.492005	0.563193	0.543473	0.020000*
C4′B	0.2276 (5)	0.4250 (3)	0.5301 (2)	0.0170 (5)
H400	0.033723	0.473554	0.535398	0.020000*
C1′B	0.3843 (5)	0.2381 (3)	0.6838 (2)	0.0158 (5)
H100	0.513258	0.135125	0.693995	0.019000*
C5′B	0.3270 (5)	0.4360 (3)	0.4093 (2)	0.0187 (5)
H501	0.256106	0.364234	0.375837	0.022000*
H502	0.263989	0.543512	0.369022	0.022000*
N1A	1.2440 (4)	0.4435 (2)	0.08135 (17)	0.0173 (5)
N3A	0.8746 (4)	0.5300 (2)	0.20877 (17)	0.0162 (4)
N9A	0.8311 (4)	0.8015 (2)	0.22604 (16)	0.0139 (4)
N7A	1.1731 (4)	0.8578 (2)	0.10746 (17)	0.0160 (4)

N6A	1.5141 (4)	0.6061 (3)	−0.01629 (18)	0.0189 (5)
H01A	1.564 (6)	0.700 (4)	−0.031 (3)	0.023 (8)*
H02A	1.621 (7)	0.517 (5)	−0.041 (3)	0.035 (9)*
O4′A	0.6986 (4)	0.74763 (19)	0.41755 (14)	0.0190 (4)
O5′A	0.3529 (3)	0.8734 (2)	0.59441 (15)	0.0179 (4)
H5′A	0.301 (9)	0.921 (6)	0.658 (4)	0.064 (13)*
O3′A	0.8166 (3)	1.1095 (2)	0.35321 (15)	0.0207 (4)
H3′A	0.777 (7)	1.204 (5)	0.375 (3)	0.039 (10)*
C2A	1.0339 (5)	0.4264 (3)	0.1534 (2)	0.0179 (5)
H2A	0.992823	0.326258	0.166822	0.021000*
C4A	0.9469 (5)	0.6684 (3)	0.1840 (2)	0.0146 (5)
C5A	1.1565 (5)	0.7041 (3)	0.11119 (19)	0.0145 (5)
C6A	1.3098 (5)	0.5850 (3)	0.05724 (19)	0.0150 (5)
C8A	0.9771 (5)	0.9092 (3)	0.1765 (2)	0.0159 (5)
H8A	0.939186	1.012478	0.190988	0.019000*
C2′A	0.4711 (5)	0.9828 (3)	0.3188 (2)	0.0170 (5)
H203	0.281089	0.990702	0.343694	0.020000*
H204	0.485722	1.052096	0.246080	0.020000*
C3′A	0.6181 (5)	1.0253 (3)	0.4036 (2)	0.0169 (5)
H301	0.489052	1.087611	0.452963	0.020000*
C4′A	0.7470 (5)	0.8669 (3)	0.4707 (2)	0.0170 (5)
H401	0.942486	0.858648	0.468554	0.020000*
C1′A	0.6087 (5)	0.8148 (3)	0.3116 (2)	0.0164 (5)
H101	0.475785	0.759094	0.296019	0.020000*
C5′A	0.6359 (5)	0.8410 (3)	0.5899 (2)	0.0187 (5)
H503	0.704050	0.731678	0.625585	0.022000*
H504	0.693462	0.910244	0.630574	0.022000*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1B	0.0186 (10)	0.0141 (11)	0.0144 (10)	−0.0046 (8)	0.0007 (8)	−0.0029 (8)
N3B	0.0164 (10)	0.0145 (10)	0.0151 (10)	−0.0045 (8)	0.0017 (8)	−0.0035 (8)
N9B	0.0160 (10)	0.0138 (10)	0.0140 (10)	−0.0049 (8)	0.0023 (8)	−0.0013 (8)
N7B	0.0178 (10)	0.0158 (11)	0.0136 (10)	−0.0043 (9)	0.0019 (8)	−0.0027 (8)
N6B	0.0180 (11)	0.0157 (12)	0.0179 (11)	−0.0058 (10)	0.0050 (8)	−0.0036 (9)
O4′B	0.0261 (9)	0.0161 (9)	0.0125 (8)	−0.0084 (7)	0.0025 (7)	−0.0019 (6)
O5′B	0.0200 (9)	0.0176 (9)	0.0187 (9)	−0.0054 (7)	0.0063 (7)	−0.0018 (7)
O3′B	0.0241 (10)	0.0131 (9)	0.0223 (10)	−0.0025 (7)	0.0072 (7)	−0.0049 (7)
C2B	0.0208 (13)	0.0165 (13)	0.0142 (12)	−0.0056 (10)	−0.0003 (10)	−0.0039 (9)
C4B	0.0143 (12)	0.0152 (12)	0.0111 (11)	−0.0051 (10)	−0.0005 (9)	−0.0011 (9)
C5B	0.0143 (11)	0.0150 (12)	0.0129 (12)	−0.0024 (10)	−0.0019 (9)	−0.0019 (9)
C6B	0.0161 (12)	0.0156 (12)	0.0111 (11)	−0.0026 (10)	−0.0026 (9)	−0.0007 (9)
C8B	0.0179 (12)	0.0136 (12)	0.0149 (12)	−0.0039 (10)	0.0007 (9)	−0.0041 (9)
C2′B	0.0146 (12)	0.0151 (12)	0.0190 (13)	−0.0034 (10)	0.0019 (10)	−0.0035 (9)
C3′B	0.0171 (12)	0.0139 (12)	0.0176 (12)	−0.0036 (9)	0.0039 (9)	−0.0028 (9)
C4′B	0.0166 (12)	0.0143 (12)	0.0186 (13)	−0.0036 (10)	0.0008 (10)	−0.0007 (9)
C1′B	0.0149 (12)	0.0162 (12)	0.0148 (12)	−0.0029 (10)	0.0040 (9)	−0.0026 (9)

C5′B	0.0198 (12)	0.0189 (13)	0.0166 (12)	−0.0050 (10)	−0.0012 (10)	−0.0003 (10)
N1A	0.0182 (11)	0.0169 (11)	0.0168 (11)	−0.0056 (9)	0.0024 (8)	−0.0033 (8)
N3A	0.0174 (10)	0.0152 (11)	0.0161 (10)	−0.0050 (8)	0.0014 (8)	−0.0029 (8)
N9A	0.0132 (10)	0.0142 (10)	0.0141 (10)	−0.0030 (8)	0.0029 (8)	−0.0046 (8)
N7A	0.0173 (10)	0.0156 (10)	0.0156 (10)	−0.0054 (8)	0.0013 (8)	−0.0032 (8)
N6A	0.0192 (11)	0.0176 (12)	0.0196 (12)	−0.0052 (9)	0.0065 (9)	−0.0057 (9)
O4′A	0.0285 (10)	0.0137 (9)	0.0138 (9)	−0.0057 (7)	0.0045 (7)	−0.0028 (6)
O5′A	0.0179 (9)	0.0190 (9)	0.0173 (9)	−0.0057 (7)	0.0043 (7)	−0.0057 (7)
O3′A	0.0209 (10)	0.0169 (10)	0.0261 (10)	−0.0092 (8)	0.0088 (7)	−0.0080 (8)
C2A	0.0213 (13)	0.0151 (13)	0.0173 (13)	−0.0055 (10)	0.0010 (10)	−0.0024 (10)
C4A	0.0153 (12)	0.0160 (12)	0.0128 (12)	−0.0032 (10)	−0.0022 (9)	−0.0027 (9)
C5A	0.0149 (12)	0.0163 (12)	0.0127 (12)	−0.0043 (10)	−0.0002 (9)	−0.0028 (10)
C6A	0.0147 (12)	0.0168 (12)	0.0130 (12)	−0.0029 (10)	−0.0018 (10)	−0.0018 (9)
C8A	0.0160 (12)	0.0147 (13)	0.0166 (12)	−0.0044 (10)	0.0008 (10)	−0.0018 (9)
C2′A	0.0146 (12)	0.0165 (12)	0.0187 (12)	−0.0034 (10)	0.0039 (9)	−0.0034 (9)
C3′A	0.0160 (12)	0.0155 (13)	0.0197 (13)	−0.0060 (10)	0.0048 (9)	−0.0051 (10)
C4′A	0.0159 (12)	0.0163 (12)	0.0197 (13)	−0.0041 (10)	0.0012 (10)	−0.0063 (10)
C1′A	0.0166 (12)	0.0193 (13)	0.0139 (12)	−0.0066 (10)	0.0029 (9)	−0.0037 (10)
C5′A	0.0173 (12)	0.0189 (13)	0.0195 (13)	−0.0025 (10)	−0.0003 (10)	−0.0049 (10)

Geometric parameters (Å, º)

N1B—C2B	1.338 (3)	N1A—C2A	1.343 (3)
N1B—C6B	1.362 (3)	N1A—C6A	1.358 (3)
N3B—C2B	1.336 (3)	N3A—C2A	1.334 (3)
N3B—C4B	1.349 (3)	N3A—C4A	1.348 (3)
N9B—C8B	1.377 (3)	N9A—C8A	1.372 (3)
N9B—C4B	1.377 (3)	N9A—C4A	1.377 (3)
N9B—C1′B	1.474 (3)	N9A—C1′A	1.473 (3)
N7B—C8B	1.316 (3)	N7A—C8A	1.309 (3)
N7B—C5B	1.389 (3)	N7A—C5A	1.393 (3)
N6B—C6B	1.334 (3)	N6A—C6A	1.337 (3)
N6B—H01B	0.89 (4)	N6A—H01A	0.92 (3)
N6B—H02B	0.86 (4)	N6A—H02A	0.94 (4)
O4′B—C1′B	1.414 (3)	O4′A—C1′A	1.411 (3)
O4′B—C4′B	1.455 (3)	O4′A—C4′A	1.447 (3)
O5′B—C5′B	1.430 (3)	O5′A—C5′A	1.428 (3)
O5′B—H5′B	0.90 (4)	O5′A—H5′A	0.95 (5)
O3′B—C3′B	1.428 (3)	O3′A—C3′A	1.431 (3)
O3′B—H3′B	0.90 (4)	O3′A—H3′A	0.92 (4)
C2B—H2B	0.9500	C2A—H2A	0.9500
C4B—C5B	1.382 (3)	C4A—C5A	1.385 (3)
C5B—C6B	1.410 (3)	C5A—C6A	1.409 (3)
C8B—H8B	0.9500	C8A—H8A	0.9500
C2′B—C1′B	1.523 (3)	C2′A—C1′A	1.524 (4)
C2′B—C3′B	1.524 (3)	C2′A—C3′A	1.525 (4)
C2′B—H200	0.9900	C2′A—H203	0.9900
C2′B—H201	0.9900	C2′A—H204	0.9900

C3′B—C4′B	1.530 (4)	C3′A—C4′A	1.537 (3)
C3′B—H300	1.0000	C3′A—H301	1.0000
C4′B—C5′B	1.513 (4)	C4′A—C5′A	1.511 (4)
C4′B—H400	1.0000	C4′A—H401	1.0000
C1′B—H100	1.0000	C1′A—H101	1.0000
C5′B—H501	0.9900	C5′A—H503	0.9900
C5′B—H502	0.9900	C5′A—H504	0.9900

C2B—N1B—C6B	118.0 (2)	C2A—N1A—C6A	118.1 (2)
C2B—N3B—C4B	111.1 (2)	C2A—N3A—C4A	111.2 (2)
C8B—N9B—C4B	105.42 (19)	C8A—N9A—C4A	105.31 (19)
C8B—N9B—C1′B	130.5 (2)	C8A—N9A—C1′A	129.4 (2)
C4B—N9B—C1′B	123.8 (2)	C4A—N9A—C1′A	125.2 (2)
C8B—N7B—C5B	104.2 (2)	C8A—N7A—C5A	103.84 (19)
C6B—N6B—H01B	119 (2)	C6A—N6A—H01A	120 (2)
C6B—N6B—H02B	117 (3)	C6A—N6A—H02A	117 (2)
H01B—N6B—H02B	122 (3)	H01A—N6A—H02A	122 (3)
C1′B—O4′B—C4′B	109.90 (19)	C1′A—O4′A—C4′A	109.97 (18)
C5′B—O5′B—H5′B	108 (3)	C5′A—O5′A—H5′A	103 (3)
C3′B—O3′B—H3′B	108 (2)	C3′A—O3′A—H3′A	108 (2)
N3B—C2B—N1B	129.3 (2)	N3A—C2A—N1A	129.3 (2)
N3B—C2B—H2B	115.3000	N3A—C2A—H2A	115.4000
N1B—C2B—H2B	115.3000	N1A—C2A—H2A	115.4000
N3B—C4B—N9B	127.2 (2)	N3A—C4A—N9A	127.5 (2)
N3B—C4B—C5B	126.3 (2)	N3A—C4A—C5A	126.3 (2)
N9B—C4B—C5B	106.5 (2)	N9A—C4A—C5A	106.3 (2)
C4B—C5B—N7B	110.2 (2)	C4A—C5A—N7A	110.3 (2)
C4B—C5B—C6B	117.1 (2)	C4A—C5A—C6A	117.3 (2)
N7B—C5B—C6B	132.6 (2)	N7A—C5A—C6A	132.4 (2)
N6B—C6B—N1B	118.9 (2)	N6A—C6A—N1A	119.3 (2)
N6B—C6B—C5B	123.2 (2)	N6A—C6A—C5A	122.8 (2)
N1B—C6B—C5B	117.9 (2)	N1A—C6A—C5A	117.9 (2)
N7B—C8B—N9B	113.6 (2)	N7A—C8A—N9A	114.3 (2)
N7B—C8B—H8B	123.2000	N7A—C8A—H8A	122.8000
N9B—C8B—H8B	123.2000	N9A—C8A—H8A	122.8000
C1′B—C2′B—C3′B	104.2 (2)	C1′A—C2′A—C3′A	104.4 (2)
C1′B—C2′B—H200	110.9000	C1′A—C2′A—H203	110.9000
C3′B—C2′B—H200	110.9000	C3′A—C2′A—H203	110.9000
C1′B—C2′B—H201	110.9000	C1′A—C2′A—H204	110.9000
C3′B—C2′B—H201	110.9000	C3′A—C2′A—H204	110.9000
H200—C2′B—H201	108.9000	H203—C2′A—H204	108.9000
O3′B—C3′B—C2′B	111.5 (2)	O3′A—C3′A—C2′A	112.6 (2)
O3′B—C3′B—C4′B	110.7 (2)	O3′A—C3′A—C4′A	110.4 (2)
C2′B—C3′B—C4′B	103.6 (2)	C2′A—C3′A—C4′A	103.9 (2)
O3′B—C3′B—H300	110.3000	O3′A—C3′A—H301	109.9000
C2′B—C3′B—H300	110.3000	C2′A—C3′A—H301	109.9000
C4′B—C3′B—H300	110.3000	C4′A—C3′A—H301	109.9000
O4′B—C4′B—C5′B	108.9 (2)	O4′A—C4′A—C5′A	108.83 (19)

O4′B—C4′B—C3′B	107.2 (2)	O4′A—C4′A—C3′A	107.12 (19)
C5′B—C4′B—C3′B	113.4 (2)	C5′A—C4′A—C3′A	113.3 (2)
O4′B—C4′B—H400	109.1000	O4′A—C4′A—H401	109.2000
C5′B—C4′B—H400	109.1000	C5′A—C4′A—H401	109.2000
C3′B—C4′B—H400	109.1000	C3′A—C4′A—H401	109.2000
O4′B—C1′B—N9B	110.40 (19)	O4′A—C1′A—N9A	110.6 (2)
O4′B—C1′B—C2′B	105.17 (19)	O4′A—C1′A—C2′A	105.50 (19)
N9B—C1′B—C2′B	114.2 (2)	N9A—C1′A—C2′A	113.5 (2)
O4′B—C1′B—H100	109.0000	O4′A—C1′A—H101	109.0000
N9B—C1′B—H100	109.0000	N9A—C1′A—H101	109.0000
C2′B—C1′B—H100	109.0000	C2′A—C1′A—H101	109.0000
O5′B—C5′B—C4′B	109.8 (2)	O5′A—C5′A—C4′A	109.8 (2)
O5′B—C5′B—H501	109.7000	O5′A—C5′A—H503	109.7000
C4′B—C5′B—H501	109.7000	C4′A—C5′A—H503	109.7000
O5′B—C5′B—H502	109.7000	O5′A—C5′A—H504	109.7000
C4′B—C5′B—H502	109.7000	C4′A—C5′A—H504	109.7000
H501—C5′B—H502	108.2000	H503—C5′A—H504	108.2000

C4B—N3B—C2B—N1B	2.7 (4)	C4A—N3A—C2A—N1A	0.4 (4)
C6B—N1B—C2B—N3B	−1.4 (4)	C6A—N1A—C2A—N3A	−1.1 (4)
C2B—N3B—C4B—N9B	179.1 (2)	C2A—N3A—C4A—N9A	−179.2 (2)
C2B—N3B—C4B—C5B	−0.3 (3)	C2A—N3A—C4A—C5A	0.2 (3)
C8B—N9B—C4B—N3B	−178.9 (2)	C8A—N9A—C4A—N3A	179.4 (2)
C1′B—N9B—C4B—N3B	5.9 (4)	C1′A—N9A—C4A—N3A	3.0 (4)
C8B—N9B—C4B—C5B	0.7 (2)	C8A—N9A—C4A—C5A	−0.1 (3)
C1′B—N9B—C4B—C5B	−174.6 (2)	C1′A—N9A—C4A—C5A	−176.5 (2)
N3B—C4B—C5B—N7B	178.8 (2)	N3A—C4A—C5A—N7A	−179.3 (2)
N9B—C4B—C5B—N7B	−0.8 (3)	N9A—C4A—C5A—N7A	0.1 (3)
N3B—C4B—C5B—C6B	−3.0 (4)	N3A—C4A—C5A—C6A	0.1 (3)
N9B—C4B—C5B—C6B	177.4 (2)	N9A—C4A—C5A—C6A	179.6 (2)
C8B—N7B—C5B—C4B	0.5 (3)	C8A—N7A—C5A—C4A	−0.1 (3)
C8B—N7B—C5B—C6B	−177.3 (3)	C8A—N7A—C5A—C6A	−179.4 (3)
C2B—N1B—C6B—N6B	177.5 (2)	C2A—N1A—C6A—N6A	−178.4 (2)
C2B—N1B—C6B—C5B	−2.4 (3)	C2A—N1A—C6A—C5A	1.3 (3)
C4B—C5B—C6B—N6B	−175.6 (2)	C4A—C5A—C6A—N6A	178.8 (2)
N7B—C5B—C6B—N6B	2.1 (4)	N7A—C5A—C6A—N6A	−1.9 (4)
C4B—C5B—C6B—N1B	4.3 (3)	C4A—C5A—C6A—N1A	−0.8 (3)
N7B—C5B—C6B—N1B	−178.0 (2)	N7A—C5A—C6A—N1A	178.4 (2)
C5B—N7B—C8B—N9B	0.0 (3)	C5A—N7A—C8A—N9A	0.1 (3)
C4B—N9B—C8B—N7B	−0.4 (3)	C4A—N9A—C8A—N7A	0.0 (3)
C1′B—N9B—C8B—N7B	174.4 (2)	C1′A—N9A—C8A—N7A	176.2 (2)
C1′B—C2′B—C3′B—O3′B	93.7 (2)	C1′A—C2′A—C3′A—O3′A	97.7 (2)
C1′B—C2′B—C3′B—C4′B	−25.4 (2)	C1′A—C2′A—C3′A—C4′A	−21.8 (2)
C1′B—O4′B—C4′B—C5′B	133.1 (2)	C1′A—O4′A—C4′A—C5′A	136.4 (2)
C1′B—O4′B—C4′B—C3′B	10.0 (3)	C1′A—O4′A—C4′A—C3′A	13.5 (2)
O3′B—C3′B—C4′B—O4′B	−109.2 (2)	O3′A—C3′A—C4′A—O4′A	−114.8 (2)
C2′B—C3′B—C4′B—O4′B	10.4 (2)	C2′A—C3′A—C4′A—O4′A	6.2 (2)
O3′B—C3′B—C4′B—C5′B	130.5 (2)	O3′A—C3′A—C4′A—C5′A	125.2 (2)

C2′B—C3′B—C4′B—C5′B	−109.8 (2)	C2′A—C3′A—C4′A—C5′A	−113.9 (2)
C4′B—O4′B—C1′B—N9B	97.2 (2)	C4′A—O4′A—C1′A—N9A	95.5 (2)
C4′B—O4′B—C1′B—C2′B	−26.4 (2)	C4′A—O4′A—C1′A—C2′A	−27.7 (2)
C8B—N9B—C1′B—O4′B	−101.2 (3)	C8A—N9A—C1′A—O4′A	−97.5 (3)
C4B—N9B—C1′B—O4′B	72.7 (3)	C4A—N9A—C1′A—O4′A	78.0 (3)
C8B—N9B—C1′B—C2′B	17.0 (4)	C8A—N9A—C1′A—C2′A	20.9 (3)
C4B—N9B—C1′B—C2′B	−169.0 (2)	C4A—N9A—C1′A—C2′A	−163.6 (2)
C3′B—C2′B—C1′B—O4′B	32.2 (2)	C3′A—C2′A—C1′A—O4′A	30.6 (2)
C3′B—C2′B—C1′B—N9B	−89.0 (2)	C3′A—C2′A—C1′A—N9A	−90.8 (2)
O4′B—C4′B—C5′B—O5′B	−72.4 (2)	O4′A—C4′A—C5′A—O5′A	−68.8 (3)
C3′B—C4′B—C5′B—O5′B	46.8 (3)	C3′A—C4′A—C5′A—O5′A	50.2 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6*B*—H01*B*···N1*A*^{i}	0.89 (4)	2.36 (4)	3.239 (3)	170 (1)
N6*B*—H02*B*···N7*A*^{ii}	0.86 (4)	2.14 (4)	2.998 (3)	173 (1)
O5′*B*—H5′*B*···N3*A*	0.90 (4)	1.91 (4)	2.787 (3)	163 (1)
O3′*B*—H3′*B*···O5′*A*	0.90 (4)	1.78 (4)	2.680 (3)	171 (1)
N6*A*—H01*A*···N1*B*^{iii}	0.92 (3)	2.33 (3)	3.243 (3)	172 (1)
N6*A*—H02*A*···N7*B*^{iv}	0.94 (4)	2.12 (4)	3.056 (3)	178 (1)
O5′*A*—H5′*A*···N3*B*^{v}	0.95 (5)	1.85 (5)	2.758 (3)	159 (1)
O3′*A*—H3′*A*···O5′*B*^{v}	0.92 (4)	1.80 (4)	2.691 (2)	163 (1)

Symmetry codes: (i) *x*−2, *y*, *z*+1; (ii) *x*−2, *y*−1, *z*+1; (iii) *x*+2, *y*+1, *z*−1; (iv) *x*+2, *y*, *z*−1; (v) *x*, *y*+1, *z*.